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STRUCTURAL STUDIES OF SOME
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CHAPTER I

INTRODUCTION

I.1. Synopsis

This thesis is a study of the structures and energetics of the metal complexes of dithizone, $C_6H_5.N:N.C(S).NH.NH.C_6H_5$, and thiocarbohydrazide, $H_2N.HN.C(S).NH.NH_2$.

Dithizone was first prepared and studied by E. Fisher as part of his classic work on phenylhydrazine. It is a weak acid capable of forming intensely coloured metal complexes with at least twentythree elements and, since the work of Walter² and H. Fischer³, has been used extensively for trace metal analysis, particularly in solvent extraction procedures.

The applications of dithizone in analytical chemistry have been covered in numerous review articles⁴⁻¹² and have also been the subject of a book¹³.

Thiocarbohydrazide can be considered as the parent compound of fully reduced dithizone, 1,5-diphenylthiocarbazide ($C_6H_5.HN.HN.C(S).NH.NH.C_6H_5$), and also as the next higher homologue in the series beginning with thiourea, $H_2N.C(S).NH_2$, and thiosemicarbazide, $H_2N.HN.C(S).NH_2$. Although the metal complexes of both of the precursors have been studied¹⁴⁻¹⁷ and the X-ray crystal structures of many of them published¹⁸⁻²² there has been virtually nothing published concerning the metal complexes of

thiocarbohydrazide. Duval and Loc²³ and Buu-Hof, Loc and Xuong²⁴ reported the formation of colours and precipitates of thiocarbohydrazide with some metal ions in aqueous solution and the oxygen analogue, carbohydrazide $\text{H}_2\text{N}.\text{HN}.\text{C}(\text{O}).\text{NH}.\text{NH}_2$, has been shown²⁵ to form metal complexes with $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ in dilute acid solution.

The reasons for selecting these systems for investigation are;

- (a) an interest in ligands with dual donor sites available for coordination to metal ions,
- (b) the different physical and chemical properties of the two structurally similar systems of complexes enables a range of physical methods of investigation to be used, and
- (c) the possibility of obtaining informative correlations of the physical properties of the large number of metal dithizonates.

1.2. The Chemistry of Dithizone

Dithizone is a violet-black solid, melting at 165° to 169°C , and soluble to some extent in most organic solvents giving green solutions. Its solubility in chloroform at room temperature is 2 gm. per 100 ml. and in carbon tetrachloride about 0.05 gm. per 100 ml. The weak acid property of dithizone ($\text{pK}_a \sim 5$) enables it to dissolve in alkaline media giving an orange-yellow solution and in strong acid to give a deep violet solution. In solution, dithizone is also potentially capable of tautomerism.

Methylation of dithizone has been shown^{26,27} to yield the S-methyl derivative $\text{C}_6\text{H}_5.\text{N}:\text{N}.\text{C}(\text{S}.\text{CH}_3):\text{N}.\text{NH}.\text{C}_6\text{H}_5$, which is a formazan.

S-methyldithizone dissolves in organic solvents giving a violet solution initially but there is a gradual colour change to yellow-brown. Similar observations have been made for a number of formazans and the change has been attributed to the presence of configurational isomerism²⁸.

Mild oxidation of dithizone yields an orange, crystalline dehydro derivative which has been shown²⁹ to be a tetrazolium thiobetaine. The structure was depicted as a series of resonance hybrids of the type shown below.

Dehydrodithizone readily adds on methyl iodide to give the yellow tetrazolium iodide.

I.3. Nomenclature

I.3.i. Dithizone.- The name dithizone is an abbreviated form of 1,5-diphenylthiocarbazone, which is the name for the thioketo tautomer $C_6H_5.N:N.C(S).NH.NH.C_6H_5$. The alternative formulation as the thioenolic tautomer 3-mercapto-1,5-diphenylformazan, $C_6H_5.N:N.C(S.H):N.NH.C_6H_5$, is also used. The procedure adopted for naming formazans is that of Beilstein's "Handbuch". S-Methyldithizone thus becomes 3-methylthio-1,5-diphenylformazan.

The symbol 'Dz' has been suggested by Hibbard³⁰ to represent dithizone, however 'H₂Dz' is normally preferred as it implies that dithizone is dibasic and it will be the symbol used throughout this work.

Dehydrodithizone is 5-mercapto-2,3-diphenyltetrazolium thiobetaine while the S-methyl derivative is 5-methylthio-2,3-diphenyltetrazolium iodide.

I.3.ii. Metal Complexes of Dithizone.- Two systems of metal complexes have been identified, with the stoichiometries $M^{n+}(HDz)_n$ and $M^{n+}(Dz)_{n/2}$. The former have been called 'primary' and 'keto' dithizonates and the latter 'secondary' and 'enol' dithizonates, however only the 'primary', 'secondary' notation will be retained when discussing the two classes as the alternative titles are misleading.

I.3.iii. Thiocarbohydrazide.- The name used is that given in the I.U.P.A.C. 1957 Rules. The symbol Htcz will be adopted to represent the uncharged ligand.

I.4. Abbreviations

The abbreviated forms of the compounds listed below will be used in the following chapters.

H ₂ Dz	=	dithizone
Htcaz	=	thiocarbohydrazide
Htscaz	=	thiosemicarbazide
Hcaz	=	carbohydrazide
tu	=	thiourea
py	=	pyridine
en	=	ethylenediamine
DMS	=	dimethylsulphoxide
THF	=	tetrahydrofuran
DMF	=	dimethylformamide
HAc	=	acetic acid

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CHAPTER II

EXPERIMENTAL

II.1. Analyses

The micro-analyses for carbon, hydrogen, nitrogen and sulphur were performed in the micro-analytical laboratory of Otago University. The micro-Dumas method used for nitrogen generally gave poor results and the carbon and hydrogen analyses for the mercury complexes were initially inaccurate although some improvement was later affected by using gold foil to remove the heavy metal.

Chloride ion was determined either volumetrically with standard silver nitrate solution or gravimetrically as silver chloride. Iron was determined volumetrically with potassium permanganate by first reducing the ferric ion to ferrous using a Jones reductor. Complexometric titrations with EDTA^{1,2} were used for cobalt, with murexide as the indicator, and for lead, zinc and cadmium using eriochrome black T as the indicator. Copper was determined volumetrically using the potassium iodide-thiosulphate method. Nickel and palladium were determined gravimetrically as their dimethylglyoxime derivatives and mercury as both HgS and $\text{Hg}[\text{Zn}(\text{NCS})_4]$. Silver was determined volumetrically with both standard ammonium thiocyanate and complexometrically with EDTA³. In the EDTA titration excess $\text{K}_2[\text{Ni}(\text{CN})_4]$ was added and the nickel ions released by the formation of the silver cyanide complex were then determined using murexide as the indicator.

The metal dithizonates were decomposed by digesting them with 70% perchloric acid in a large Kjeldahl flask. The procedure adopted was to weigh out approximately 0.1 to 0.2 gm. of the complex onto tissue paper thus enabling the sample to be readily transferred to the flask. Five ml. of perchloric acid were then added and after five min. of gentle heating the sample was heated strongly until all of the organic material had been removed. The total time required for complete decomposition being of the order of 10 to 15 min.

The decomposition of the thiocarbonylhydrazide complexes for the chloride ion analyses involved digesting 0.1 to 0.2 gm. samples in 20 ml. of dilute nitric acid for 30 min. Solutions for the analysis of the metal ion were obtained by decomposing the sample in 5 ml. of concentrated nitric acid which enabled the heating period to be shortened to 5 min. It was necessary to use a mixture of concentrated nitric and sulphuric acids in order to decompose the complex $\text{Hg}[\text{Co}(\text{tcz})_2\text{Cl}_2]$, with a digestion time of approximately one hour.

The majority of the metal dithizonates are isolated as amorphous powders which retain varying amounts of solvent. They are unstable since the ligand is oxidised to give dehydrodithizone (see Chapter I), the reaction proceeding particularly rapidly in solution.

The metal thiocarbonylhydrazides are, with the exception of the Ni(II) , Zn(II) and Cd(II) complexes, extremely insoluble. These properties make it difficult to obtain any of the complexes of either dithizone or thiocarbonylhydrazide in a reasonably pure form.

II.2. Solvents

The following solvents were used without further purification; 'AnalaR' grade chloroform, acetone, methanol, ethanol, n-butanol, n-propanol, glacial acetic acid, pyridine and benzene; reagent grade ethanalamine, triethanolamine, isoquinoline, carbon disulphide, n-hexane, cyclohexane and methylethylketone. 'B.D.H.' dimethylformamide and dimethylsulphoxide were dried with molecular sieve (grade 4a) before using.

Water.- Two methods of obtaining pure water were used. Ordinary distilled water containing 0.1% sodium hydroxide and 0.05% potassium permanganate was refluxed for one hour and then the pure distillate collected. Alternatively, the distilled water was passed through a column of 'biode-mineralit', a mixed cation, anion exchange resin.

Carbon Tetrachloride.- The solvent was first shaken with 'AnalaR' sulphuric acid for one hour and then refluxed over potassium hydroxide for approximately two hours. The fraction distilling over between 64.5 and 65.0°C was collected and the purity checked by measuring its ultraviolet absorption spectrum.

Tetrachloroethylene.- The fraction distilling over in the range 119.5 to 120.5°C was collected.

$$n_D^{20} \quad 1.5018, \text{ (lit.}^4 \text{ 1.50180)}.$$

Methylene Chloride.- We collected the fraction distilling over at 39.5°C.

$$n_D^{25} \quad 1.4272, \text{ (lit.}^4 \text{ 1.42721)}.$$

Tetrahydrofuran.- We collected the fraction distilling over in the range 65 to 66°C.

II.3. Preparations

1,5-Diphenylthiocarbazone (dithizone).- This compound was synthesised by the method of Cleland and Billman⁵ from phenylhydrazine and carbon disulphide. The resulting black solid was purified immediately before using by one of two methods⁶. The first involved diluting a filtered, saturated chloroform solution of dithizone by half with carbon tetrachloride. The black microcrystalline solid which slowly separated out was then filtered rapidly, washed with a little carbon tetrachloride and dried by pressing between filter paper. As rather large volumes of pure solvent were required for this method an alternative procedure was developed. This was to evaporate the chloroform solution of dithizone down under a stream of nitrogen at approximately 40°C until half to threequarters of the dithizone had separated out from the solution. The pure solid was then filtered, washed with a few ml. of carbon tetrachloride and dried as before.

5-Methylmercapto-2,3-diphenylformazan (S-methyldithizone).- The method of Irving and Bell⁷ was used whereby dimethylsulphate is added dropwise to a cold solution of dithizone in ammonium hydroxide. The resulting black precipitate was recrystallised from chloroform/carbon tetrachloride as deep violet needles with a metallic green lustre.

Anal. Calc. for $C_{14}H_{14}N_2S$: C, 62.2; H, 5.2; N, 20.7.

Found: C, 61.9; H, 5.4; N, 20.7.

5-Mercapto-2,3-diphenyltetrazolium thiobetaine.- Two methods of synthesising this compound were used. The first, which was similar to the method of Bamberger⁸, involved bubbling air through a solution of

dithizone in KOH/methanol for 24 hrs. After standing for two days orange-brown crystals were obtained. These were recrystallised from ethanol to yield orange-red needles.

The alternative method⁹ used was to add amylnitrite dropwise to a boiling solution of 3 gm. of dithizone in ether (700 ml.). At the first appearance of a green dyestuff the solution was cooled rapidly and filtered from undissolved dithizone. After approximately 15 min. an orange-yellow precipitate separated out which was recrystallised from ethanol, again yielding orange-red needles.

Anal. Calc. for $C_{15}H_{10}N_4S$: C, 61.4; H, 3.9; N, 22.0.

Found: C, 61.5; H, 4.2; N, 21.9.

5-Methylmercapto-2,3-diphenyltetrazolium Iodide.- The method of Ogilvie and Corwin¹⁰ was used to prepare this derivative. Yellow crystals were obtained from the reaction mixture.

M.p. 203° dec. (Lit. value 203-207 dec.).

Potassium Dithizonate.- An excess of dithizone was shaken with a solution of KOH/methanol for 10 min. and then any undissolved material was filtered off leaving a bright, orange-red methanol solution. The solvent was evaporated off under reduced pressure to yield a violet-brown solid. It was not possible to obtain the compound free from either KOH or dehydrodithizone impurity as any recrystallisation had to be carried out using polar solvents in which oxidation occurred.

Many of the metal dithizonates could be prepared by using one of the three methods outlined below. The relevant details for these complexes are given in Table II.1. together with references to any

previously published work. The more difficult preparations will be given in detail in the text.

Method A.- An aqueous solution of the metal ion was shaken with a chloroform solution of dithizone for 30 min., the pH of the aqueous phase being maintained at a constant value. The solid which separated out was filtered off and recrystallised from some suitable solvent.

Method B.- The same procedure as above was used but if the resulting complex was soluble in chloroform it was necessary to separate off the chloroform layer and then reduce the volume of the solvent by evaporation in a stream of nitrogen. The solid which separated out was filtered, washed with a little carbon tetrachloride and dried in vacuo over P_2O_5 .

Method C.- An aqueous solution of the metal ion was added slowly, with stirring, to a solution of dithizone in KOH/methanol. The resulting precipitate was filtered, washed with several portions of hot water and then dried in vacuo over P_2O_5 .

Antimony trichloride-dithizone.- Dithizone was added to a hot solution of $SbCl_3$ in hydrochloric acid until a saturated solution was obtained. On cooling, metallic green crystals were precipitated from the solution. These were filtered, washed with dilute hydrochloric acid and then with ethanol, and dried in vacuo over P_2O_5 .

Anal. Calc. for $C_{13}H_{12}N_4SCl_5Sb$: C, 32.3; H, 2.5; N, 11.6.

Found: C, 34.8; H, 2.8; N, 11.8.

TABLE II.1

Analytical Results for some Metal Dithizonates

Compound	Method of Preparation	pH for Extraction	Recryst. Media	Calc.		Found		Ref.
				C	H	C	H	
Zn(HDz) ₂	A	8	py/H ₂ O	54.2	3.9	55.8	4.1	11
Zn(HDz) ₂ ·THF	A	8	THF	55.6	4.7	55.4	4.5	
Cd(HDz) ₂	A	7	py/H ₂ O	50.1	3.6	49.7	4.3	12
Cd(HDz) ₂ ·2py	A	7	py	55.3	4.1	55.3	4.4	
Hg(HDz) ₂	A	2	py/H ₂ O	43.9	3.1	35.8	3.0	12,13
HgDz	C			34.3	2.2	15.5	2.0	
Hg(HDz) ₂ ·2py	A	5	CHCl ₃ /py	45.0	3.4	44.2	3.5	
Tl(HDz)	B	10	CHCl ₃	34.0	2.4	42.6	3.4	
Tl ₂ Dz	C			23.5	1.5	18.1	1.7	
Sn(HDz) ₂	B	7		49.6	3.5	36.3	3.6	
Pb(HDz) ₂	A	10	py/H ₂ O	43.5	3.1	41.4	3.3	14
Bi(HDz) ₃	B	8	CHCl ₃	48.0	3.4	47.9	3.6	
Co(HDz) ₂	B	8		54.8	3.9	53.2	4.3	15
Ni(HDz) ₂	A	8	CHCl ₃	54.9	3.9	55.6	4.6	
Ni(HDz) ₂ ·2py	A	8	py/H ₂ O	59.5	4.4	59.4	4.7	
Pd(HDz) ₂	B	6						
Pt(HDz) ₂	B	6		44.2	3.4	52.2	4.0	
Ag ₂ Dz	A	6	py/H ₂ O	33.2	2.1	28.7	2.6	
								45.8

Bis(dithizonato)manganese(II).- An aqueous solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added slowly with stirring to dithizone in KOH/methanol. The resulting mixture of violet-red $\text{Mn}(\text{HDz})_2$ and pink $\text{Mn}(\text{OH})_2$ was filtered off and washed with dilute hydrochloric acid. The $\text{Mn}(\text{HDz})_2$ was then extracted with warm chloroform and the solvent removed by evaporation in a stream of nitrogen. This yielded a metallic green micro-crystalline solid. Needle shaped crystals of the complex were also obtained from dry acetone solution. However, the complex is extremely unstable in either chloroform or acetone solution and the recrystallisation must be completed in as short a time as possible.

Anal. Calc. for $\text{C}_{26}\text{H}_{22}\text{N}_8\text{S}_2\text{Mn}$: C, 55.2; H, 3.9.

Found: C, 53.1; H, 4.4.

Bis(dithizonato)iron(II).- A ferrous cation exchange resin (Zeo-Karb 225) was prepared by soaking the resin, in the hydrogen form, in a concentrated aqueous solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. After stirring for 10 min. the aqueous solution was decanted off and a fresh solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added and the mixture stirred for a further 10 min. The resin was then collected, washed with water and ethanol and allowed to dry.

The ferrous resin was now added to a chloroform solution of dithizone and the mixture shaken for 30 min. The pH of the aqueous phase was maintained in the range 7 to 8 by the careful addition of dilute ammonium hydroxide. The violet chloroform solution was then separated from both the aqueous layer and the resin and the volume of solvent reduced by evaporation using a stream of nitrogen under

reduced pressure. The black solid which separated out was collected, washed with carbon tetrachloride and dried in vacuo over P_2O_5 .

Anal. Calc. for $C_{26}H_{22}N_8S_2Fe$: C, 55.1; H, 3.9; Fe, 9.9.

Found: C, 49.8; H, 4.0; Fe, 9.6.

Tris(dithizonato)cobalt(III).— A solution of Co(II) dithizonate in chloroform was shaken with an aqueous solution of $CoCl_2 \cdot 6H_2O$ for 24 hrs. The violet-brown chloroform layer was then separated off and the volume of solvent reduced by half by evaporating in a stream of nitrogen. The violet solid which separated out was collected, washed with carbon tetrachloride and dried in vacuo over P_2O_5 .

Anal. Calc. for $C_{39}H_{33}N_{12}S_3Co$: C, 56.8; H, 4.0.

Found: C, 49.1; H, 4.0.

Bis(dithizonato)copper(II)¹⁶.— Cation exchange resin in the Cu(II) form was prepared by a similar method to that described for Fe(II).

The Cu(II) resin was then added slowly to dithizone in chloroform and the mixture shaken until the solution turned a deep red-violet. The resin was filtered off, and after adding an equal volume of carbon tetrachloride, the volume of the solvent was reduced by evaporation in a stream of nitrogen to yield a red-brown solid. The solid was collected, washed with carbon tetrachloride until the filtrate was a violet colour and then dried in vacuo over P_2O_5 . The filtrate is initially coloured brown due to the presence of some of the secondary complex.

Anal. Calc. for $C_{26}H_{22}N_8S_2Cu$: C, 54.4; H, 3.9; Cu, 11.1.

Found: C, 54.3; H, 4.1; Cu, 10.9.

Secondary Cu(II) Dithizonate¹⁶. - An aqueous solution of $\text{Cu}(\text{NH}_3)_6^{2+}$ was shaken with a chloroform solution of $\text{Cu}(\text{HDz})_2$. The chloroform layer turned brown and was separated off and the volume of solvent reduced by evaporation in a stream of nitrogen. The black solid which separated out was collected, washed with carbon tetrachloride and dried in vacuo over P_2O_5 .

Anal. Calc. for $\text{C}_{13}\text{H}_{10}\text{N}_4\text{SCu}$: C, 49.1; H, 3.2; Cu, 20.0.

Found: C, 45.0; H, 3.2; Cu, 19.9.

Mono(dithizonato)copper(I). - An aqueous solution of CuCl_3^{2-} was prepared by adding 1 gm. $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ dissolved in 10 ml. of H_2O to a boiling solution of 2 gm. Na_2SO_3 and 2 gm. NaCl in 20 ml. of H_2O .

The aqueous solution of CuCl_3^{2-} was then shaken with a chloroform solution of dithizone for 10 min. The chloroform layer was separated off and the solvent removed by evaporation in a stream of nitrogen. This left a dark brown solid which was washed with a little carbon tetrachloride and dried in vacuo over P_2O_5 .

Tris(dithizonato)gold(III). - An aqueous solution of HAuCl_4 was shaken with a chloroform solution of dithizone. The chloroform layer turns orange-brown in colour but slowly changes back to green on standing as the complex is unstable in solution. The orange-brown chloroform layer was separated off and the solvent removed by evaporation in a stream of nitrogen. The solid was collected, washed with carbon tetrachloride and dried in vacuo over P_2O_5 .

Anal. Calc. for $\text{C}_{39}\text{H}_{33}\text{N}_{12}\text{S}_3\text{Au}$: C, 48.6; H, 3.4.

Found: C, 43.1; H, 3.3.

Mono(dithizonato)gold(1).- Excess of an aqueous solution of HAuCl_4 was shaken with a chloroform solution of dithizone. The green chloroform layer first turned orange-brown as the Au(III) complex was formed, then after further shaking a black solid slowly separated out which was sparingly soluble in chloroform giving an unstable violet solution. The solid was filtered off, washed with carbon tetrachloride and dried in vacuo over P_2O_5 .

Anal. Calc. for $\text{C}_{13}\text{H}_{11}\text{N}_4\text{SAu}$: C, 34.5; H, 2.5.

Found: C, 31.7; H, 2.6.

The only new complex described in this work is that of antimony which is apparently an adduct formed by dithizone with SbCl_3 . Sb(III) has previously been shown to form a dithizonate which is orange-red in molten naphthalene¹⁷ and strawberry-red in chloroform and carbon tetrachloride^{18,19} but no solid complex was isolated and characterised.

The metal complexes of thiocarbohydrazide are all reported here for the first time.

Thiocarbohydrazide.- The method of Audrieth and Kippur²⁰ was used to prepare this compound which was then recrystallised from water.

Anal. Calc. for $\text{CH}_6\text{N}_4\text{S}$: C, 11.3; H, 5.7; N, 52.8; S, 30.2.

Found: C, 11.6; H, 6.0; N, 51.7; S, 30.5.

Bis(thiocarbohydrazide)zinc(II) chloride.- A warm solution of ZnCl_2 in dimethylformamide/ H_2O (5:1) was added to a warm solution of thiocarbohydrazide in dimethylformamide in an approximately 1:2 mole ratio. Colourless crystals separated out from the solution on standing for one hr. These were filtered and washed with 0.1 M hydrochloric acid

and then dried in vacuo over P_2O_5 .

Anal. Calc. for $C_{24}H_{12}N_8S_2ZnCl_2$: C, 6.9; H, 3.5; Zn, 18.8; Cl, 20.3.

Found: C, 7.2; H, 3.7; Zn, 18.9; Cl, 20.6.

Bis(thiocarbohydrazide)cadmium(II) chloride.— Colourless crystals

were obtained by a similar method to that given above.

Anal. Calc. for $C_{24}H_{12}N_8S_2CdCl_2$: C, 6.1; H, 3.1; N, 28.3; Cd, 28.4; Cl, 17.9.

Found: C, 6.4; H, 3.4; N, 28.0; Cd, 28.4; Cl, 17.8.

Bis(thiocarbohydrazide)mercury(II) chloride.— Solutions of mercuric

chloride and thiocarbohydrazide in dimethylformamide were mixed in an approximately 1:2 mole ratio. A dense white precipitate separated immediately. After standing for 30 min. the compound was filtered, washed with a little 0.1 M hydrochloric acid and then dried in vacuo over P_2O_5 . It is important not to heat the mixed solutions as a black decomposition product is formed.

Anal. Calc. for $C_{24}H_{12}N_8S_2HgCl_2$: C, 5.0; H, 2.5; N, 23.1.

Found: C, 5.2; H, 2.7; N, 22.3.

Bis(isothiocyanato)bis(thiocarbohydrazide)iron(II).— A solution of

potassium thiocyanate (2.0 gm.) in water (10 ml.) was added slowly with stirring to a hot solution ($\sim 70^\circ$) of $FeSO_4 \cdot 7H_2O$ (2.8 gm.) and thiocarbohydrazide (2.0 gm.) in water (100 ml.). The pale green crystals which separated were filtered, washed with hot water and then dried in vacuo over P_2O_5 for two hours.

Anal. Calc. for $C_{44}H_{12}N_{10}S_4Fe$: C, 12.5; H, 3.2; Fe, 14.5.

Found: C, 12.5; H, 3.3; Fe, 14.9.

Dichlorobis(thiocarbohydrazide)cobalt(II).— Two isomers of this compound were isolated. A violet compound was prepared by adding a hot solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 gm.), dissolved in the minimum volume of water, to a hot solution of thiocarbohydrazide (2.0 gm.) in water (20 ml.) containing one ml. of 2 M hydrochloric acid. Violet crystals separated out immediately, and after decanting the solution, these were washed with several portions of ethanol and then collected and dried in vacuo over P_2O_5 .

Anal. Calc. for $\text{C}_2\text{H}_{12}\text{N}_8\text{S}_2\text{CoCl}_2$: C, 7.0; H, 3.5; Co, 17.2.

Found: C, 7.1; H, 3.7; Co, 16.7.

A brown isomer was prepared using the same reagents as above but in the absence of 2 M hydrochloric acid. The crystals which separated out were similarly treated.

Anal. Calc. for $\text{C}_2\text{H}_{12}\text{N}_8\text{S}_2\text{CoCl}_2$: C, 7.0; H, 3.5; Co, 17.2; Cl, 20.7.

Found: C, 6.9; H, 3.7; Co, 17.2; Cl, 20.8.

Tris(thiocarbohydrazide)nickel(II) chloride.— Thiocarbohydrazide (3.5 gm.) was added to a solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 gm.) in water (50 ml.). A few drops of 2 M hydrochloric acid were added and the mixture was shaken for one hr. The resulting blue solution was filtered and allowed to stand in a desiccator over concentrated sulphuric acid. Blue crystals of the tris hydrate were formed over a period of approximately ten days. The anhydrous complex was obtained by heating the hydrate at 110° for 24 hrs.

Anal. Calc. for $\text{C}_5\text{H}_{18}\text{N}_{12}\text{S}_3\text{NiCl}_2$: C, 8.0; H, 4.1; N, 37.5; Ni, 13.1; Cl, 15.8.

Found: C, 8.0; H, 4.3; N, 37.2; Ni, 12.8; Cl, 16.0.

Tris(thiocarbohydrazide)copper(II) chloride.- A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.7 gm.) in 2 M hydrochloric acid (5 ml.) was added to thiocarbohydrazide (3.5 gm.) in 2 M hydrochloric acid (25 ml.). The green precipitate which separated immediately was filtered, washed thoroughly with hot 0.1 M hydrochloric acid and then dried in vacuo over P_2O_5 .

Anal. Calc. for $\text{C}_3\text{H}_{18}\text{N}_{12}\text{S}_3\text{CuCl}_2$: C, 8.0; H, 4.0; Cu, 14.0; Cl, 15.7.
Found: C, 8.0; H, 3.9; Cu, 14.0; Cl, 15.5.

Bis(thiocarbohydrazide)palladium(II) chloride.- A solution of PdCl_2 (0.45 gm.) in 2 M hydrochloric acid was added to a solution of thiocarbohydrazide (0.55 gm.) in 2 M hydrochloric acid (20 ml.). A yellow precipitate separated from the solution. This was filtered, washed with 0.1 M hydrochloric acid and then dried in vacuo over P_2O_5 .
Anal. Calc. for $\text{C}_2\text{H}_{12}\text{N}_8\text{S}_2\text{PdCl}_2$: C, 6.2; H, 3.1; Pd, 27.3.
Found: C, 6.5; H, 3.0; Pd, 27.0.

Attempts to isolate complexes of the thioenolic tautomer of thiocarbohydrazide, analogous to the metal dithizonates, generally yielded amorphous black products. The exception was $\text{Hg}[\text{Co}(\text{tcz})_2\text{Cl}_2]$, the preparation of which is described below together with a summary of the other attempted preparations.

Mercury dichlorobis(thiocarbohydrazidato)cobalt(III).- A solution of thiocarbohydrazide (2.2 gm.) dissolved in 2 N hydrochloric acid (50 ml.) was slowly added to $\text{Na}_2[\text{Co}(\text{CO}_3)_3]$ (3 gm.) (prepared by the method of Gauer and Drinkland²¹). An aqueous solution of mercuric chloride was

then added to the red-brown solution and a salmon pink precipitate separated out. The product was collected, washed with hot water and dried in vacuo over P_2O_5 .

Anal. Calc. for $C_{20}H_{10}N_8S_2Cl_2HgCo$: C, 4.4; H, 2.0; Co, 10.9.

Found: C, 3.0; H, 1.4; Co, 11.0.

Fe(II).— A green precipitate was formed on the addition of an aqueous solution of cyanide ions to an aqueous solution of $Fe(Htcz)_2^{2+}$. The compound turned black on exposure to air and the resulting black solid was similar in appearance to that formed when either hydroxide or nitrite ions were added to an aqueous solution containing $Fe(Htcz)_2^{2+}$. The pale green crystalline complex $[Fe(Htcz)_2NCS_2]$, described earlier, also decomposes over a period of days giving a black product of unknown composition. Analysis of the product involving cyanide ion gave the following results for which no simple formula could be assigned.

C, 19.2; H, 3.5; N, 18.9; Fe, 24.2.

Ni(II).— An orange-brown crystalline complex was formed in an alkaline solution of thiocarbonylhydrazide and nickel(II) ions. However, on exposure to air the compound darkened to give a black amorphous solid.

Hg(II), Ag(I).— The addition of $Hg(II)$ or $Ag(I)$ ions to an aqueous solution of thiocarbonylhydrazide yielded an initial white precipitate which turned black. The reaction being rapid for $Ag(I)$ but slower in the case of $Hg(II)$.

Co(III).- A slightly acidic solution of thiocarbohydrazide and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ gradually changed colour on standing to give a red-brown solution from which a brown solid separated out. No solvent suitable for recrystallising this solid was found.

Pt(II).- The addition of an aqueous solution of K_2PtCl_6 to an aqueous solution of thiocarbohydrazide caused the slow formation of a black precipitate which was later found to be a mixture of two compounds. The major product was soluble in both dimethylformamide and acetone to give a bright green solution while a second compound dissolved in water and in ethanol to give a blue-violet solution. Analytical results for the former compound were: C, 15.1; H, 3.1; N, 23.8.

Carbohydrazide.- This compound was prepared by the method of Mohr, Brezinski and Audrieth²² from diethyl carbonate and hydrazine hydrate.

Tris(carbohydrazide)nickel(II) chloride.- Blue crystals were obtained by a similar method to that used to prepare the corresponding complex of thiocarbohydrazide.

The Ni(II) and Ag(I) complexes of thiosemicarbazide, $\text{Ni}(\text{Htscaz})_3\text{Cl}_2$ and $\text{Ag}(\text{Htscaz})\text{Cl}$, were prepared by mixing aqueous solutions of the free ligand and the metal ion. The solution was then evaporated over a water bath until crystals began to form and on standing colourless crystals of the Ag(I) complex and blue crystals of the Ni(II) complex were obtained.

Bis(thiosemicarbazidato)nickel(II)..- Red-brown crystals were obtained on heating a mixture of thiosemicarbazide and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in dimethylsulphoxide. These were collected, washed with ethanol and then dried in vacuo over P_2O_5 .

The following 'B.D.H.' compounds were used without further purification; reagent-grade sym-diphenylcarbazone (Krumholz²³ has shown that this compound is a 1:1 mixture of the "azide" and "azone"), oxamide, dithiooxamide, urea, thiourea, methylthiourea, phenylthiourea, sym-diphenylurea and sym-diphenylthiourea; 'AnalaR' grade sym-diphenylcarbazide and thiosemicarbazide.

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CHAPTER III

X-RAY CRYSTALLOGRAPHIC STUDIES

III.1. Introduction

In any structural investigation the ultimate requirements are the spacial dimensions or cartesian coordinates of the atoms which constitute the molecule under study. For this reason it was considered that a necessary part of this project should be an X-ray crystallographic study of the metal dithizonates.

The following structural problems require solving in the dithizone system,

- (a) the structure of dithizone, which is potentially capable of both tautomerism and geometrical isomerism,
- (b) the structures of the primary dithizone complexes, with particular regard as to whether coordination occurs through both sulphur and nitrogen donor atoms or only through nitrogen donors and
- (c) the structures of the secondary dithizonates.

For each tautomer of dithizone there are four possible configurational isomers (see structures I-VIII) and it is important that the species which exist in solution and in the solid state be identified. A knowledge of the structure in the solid state should help to identify the important species in solution.

I

II

III

IV

V

VI

VII

VIII

Harding¹ has completed an X-ray crystallographic study of dithizone in which the molecule was found to exist as the thioketo tautomer with the trans-anti configuration (I) shown in Figure III.1a. Harding was unable to locate the N-H groups by detecting differences in the bond lengths as both -N-N-C systems were the same, within the expected error. The planarity of the -N-N-C(S)-N-N- skeleton (see Figure III.1b) again prevented identification of either the azo group or the N-H groups. Harding was able to conclude that there was no evidence for an S-H group in dithizone in the solid state.

The only complete three-dimensional structural study of a metal complex of dithizone was also by Harding who investigated $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}^2$. The mercury(II) ion was found to be coordinated by the thioenolate through the mercapto and azo groups which formed a distorted tetrahedron about the metal as shown by structure IX ($\text{M} = \text{Hg}(\text{II})$).

IX

A two dimensional X-ray crystallographic study of $\text{Cu}(\text{HDz})_2^3$ showed that the copper(II) ion was also coordinated through sulphur and nitrogen with what appeared to be a square planar arrangement of the ligand donor atoms (IX, $\text{M} = \text{Cu}(\text{II})$).

Limited structural information has been obtained from surface film measurements of dithizone and some of the metal chelates^{4,5}.

The present work involves a study of the X-ray powder diffraction spectra of a number of the metal complexes, primarily to investigate the possibility of their being isomorphous, and a two-dimensional X-ray crystallographic study of $\text{Zn}(\text{HDz})_2$ to learn whether coordination occurs through nitrogen donors only or whether the structure is similar to that of the dithizonates of mercury(II) and copper(II).

III.2. Experimental

III.2.i. Powder Studies.- X-ray powder diffraction patterns were obtained using a Phillips Geiger Counter Diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation.

Powder patterns were obtained for the primary dithizonates of $\text{Cu}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Hg}(\text{II})$ and $\text{Ni}(\text{II})$ and also for the secondary dithizonate of $\text{Cu}(\text{II})$.

Unit cell parameters for the $\text{Cd}(\text{II})$ and $\text{Ni}(\text{II})$ dithizonates were obtained by Ito's procedure⁶ which is briefly outlined below.

III.2.ii. Ito's Procedure for Indexing Powder Diffraction Data.- The basis of Ito's method is that any unit cell can be represented as a triclinic cell corresponding to three non-coplanar vectors in reciprocal space. Each line of a powder pattern is related to a vector in reciprocal space so that a selection of six suitable vectors or lines will define the edges and interfacial angles of the reciprocal cell. Ito's method is concerned with the technique of selecting these six lines.

The calculations are based on the reciprocal cell relationship

$$Q_{hkl} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* \\ + 2hla^*c^* \cos \beta^* + 2klb^*c^* \cos \alpha^*$$

where a^* , b^* , c^* , α^* , β^* and γ^* are the six parameters necessary to define the reciprocal lattice and $Q_{hkl} = 1/d_{hkl}^2$.

Initially, three lines are assigned as Q_{100} , Q_{010} and Q_{001} and a search is then made for pairs of lines which are evenly spaced about the sums $Q_{100} + Q_{010}$, $Q_{100} + Q_{001}$ and $Q_{010} + Q_{001}$. These are then assigned as Q_{110} and $Q_{1\bar{1}0}$, Q_{101} and $Q_{10\bar{1}}$, and Q_{011} and $Q_{01\bar{1}}$ respectively. Although a reciprocal cell is defined by these nine lines or vectors there are usually a number of possible internally consistent sets of nine Q values which will lead to a reciprocal cell. This is particularly true of monoclinic and triclinic unit cells.

A computer programme devised by Haendler and Cooney⁷ has been used in this work to obtain the various possible sets of Q values. Only those vector-sets which gave correct $\{III\}$ Q values were retained and these were tested further to see whether the observed powder pattern could be completely indexed. Direct cell parameters were obtained from the reciprocal cell parameters for the vector set enabling the powder pattern to be indexed and finally, the reduced cell was obtained and tested to see whether it could be transformed into a cell of higher symmetry using the Delaunay method⁸.

III.2.iii. Single Crystal Studies.- Single crystals of zinc(II) dithizonate were grown from tetrahydrofuran solution. The scarlet crystals have a metallic green lustre and are solvated. Analysis of the

crystals after several weeks indicated that there was one molecule of tetrahydrofuran for each molecule of complex.

Single crystals of cadmium(II) dithizonate were grown from py/H₂O solution as orange-red plates containing two molecules of pyridine.

Other single crystals that were obtained but not studied include Mn(HDz)₂ from acetone solution, Bi(HDz)₃ from chloroform solution and HgHDz from py/H₂O.

Unit cell parameters for zinc(II) and cadmium(II) dithizonate were obtained from precession photographs.

Densities were measured by flotation in aqueous potassium iodide at 20°C.

Two-dimensional X-ray crystallographic data was obtained for zinc(II) dithizonate from equi-inclination Weissenberg photographs of the b-projection. A multiple film technique was used with the intensities of the spots being estimated visually with the aid of a calibration strip. Observed intensities were corrected for Lorentz-polarisation factors but no absorption corrections were applied.

III.3. Results

III.3.1. X-ray Powder Diffraction Data.— The X-ray powder diffraction spectrum for Cu(HDz)₂ could be indexed in terms of the single crystal unit cell parameters obtained by Bryan and Knopf. The observed and calculated Q_{hkl} values for the principal faces are given in Table III.1. The complete powder pattern for Cu(HDz)₂ is given in Appendix I together with the powder patterns for Zn(HDz)₂, Cd(HDz)₂, Hg(HDz)₂, Ni(HDz)₂ and CuDz.

TABLE III.1

Calculated and Observed Q_{hkl} Values for $\text{Cu}(\text{HDz})_2$

hkl	Q_{hkl} (calc.)	Q_{hkl} (obs.)
100	0.0057	0.0055
010	0.0084	0.0082
001	0.0552	0.0556
110	0.0143	0.0141
$\bar{1}10$	0.0140	0.0134
200	0.0226	0.0222
020	0.0334	0.0312
300	0.0509	0.0501
101	0.0573	0.0567
$\bar{1}01$	0.0608	0.0614
011	0.0603	0.0595
111	0.0625	0.0620
030	0.0752	0.0754
002	0.2207	0.2200
222	0.2500	0.2525

The X-ray powder patterns for the dithizonates of zinc(II), cadmium(II) and mercury(II), that were initially isolated from solution as powders, could not be indexed in terms of the unit cell parameters obtained from the measurements on the single crystals of each compound. The patterns were all similar to that of $\text{Cu}(\text{HDz})_2$ having intense lines at approximately the same 2θ values, but it was noticeable that the d spacings for the three principal vectors increased by an amount approximately equal to the increase in radius of the central metal ion. By applying Ito's procedure to the data for the powder modification of $\text{Cd}(\text{HDz})_2$, a triclinic unit cell was obtained. If we compare the cell dimensions for $\text{Cd}(\text{HDz})_2$ with those previously obtained for $\text{Cu}(\text{HDz})_2$, the trend suggested by the powder patterns is confirmed in the case of these two complexes.

$a = 13.36 \text{ \AA}$

$b = 10.97 \text{ \AA}$

$c = 4.29 \text{ \AA}$

$\alpha = 85^\circ 44'$

$\beta = 84^\circ 25'$

$\gamma = 90^\circ 48'$

$a = 15.17 \text{ \AA}$

$b = 11.53 \text{ \AA}$

$c = 4.56 \text{ \AA}$

$\alpha = 89^\circ 45'$

$\beta = 98^\circ 30'$

$\gamma = 106^\circ 45'$

The X-ray powder pattern for crushed single crystals of cadmium(II) dithizonate can be indexed in terms of the single crystal unit cell parameters given in the next section. A list of the calculated and observed Q_{hkl} values is given in Table III.2.

TABLE III.2

Calculated and Observed Q_{hkl} Values for Crushed
Single Crystals of $\text{Cd}(\text{HDz})_2$

hkl	Q_{hkl} (calc.)	Q_{hkl} (obs.)
100	0.0042	
010	0.0071	
001	0.0032	
111	0.0116	0.0112
002	0.0126	0.0125
200	0.0167	0.0172
$\bar{1}11$	0.0173	0.0172
020	0.0285	0.0291
220	0.0293	0.0291
$\bar{2}01$	0.0313	0.0308
300	0.0376	0.0389
022	0.0410	0.0405
$\bar{1}03$	0.0496	0.0505
030	0.0640	0.0657
$\bar{2}02$	0.0700	0.0700
$\bar{2}22$	0.0806	0.0806
$\bar{3}03$	0.1173	0.1169

This result suggests that the existence of two modifications of the dithizonates of zinc(II), cadmium(II) and mercury(II) is not due to a phase change when the single crystals are crushed.

Ito's procedure was also applied to the powder diffraction data for $\text{Ni}(\text{HDz})_2$ and an orthorhombic unit was obtained with,

$$a = 12.51 \text{ \AA} \quad b = 10.98 \text{ \AA} \quad c = 4.12 \text{ \AA}$$

The observed and calculated Q_{hkl} values are listed in Table III.3.

TABLE III.3

Calculated and Observed Q_{hkl} Values for $\text{Ni}(\text{HDz})_2$

hkl	Q_{hkl} (calc.)	Q_{hkl} (obs.)
100	0.0064	0.0064
010	0.0083	0.0083
110	0.0146	0.0147
020	0.0351	0.0332
120	0.0395	0.0396
001	0.0589	0.0589
220	0.0610	0.0588
101	0.0646	0.0653
011	0.0653	0.0672
002	0.2356	0.2350

The X-ray powder pattern for CuDz shows three intense lines followed by a very broad line with a maximum at a d spacing of approximately $4.3 \text{ \AA}$, which corresponds with the 001 reflection of $\text{Cu}(\text{HDz})_2$.

III.3.11. Single Crystal Studies.— The systematic absences for both zinc(II) and cadmium(II) dithizonate are,

$$\begin{array}{ll} hkl & h + k \neq 2n \\ h0l & l \neq 2n \quad (h \neq 2n) \end{array}$$

so that the space group is either Cc or $C2/c$. The monoclinic cell dimensions are;

$Zn(HDz)_2$	$Cd(HDz)_2 \cdot 2py$
$a = 20.4 \text{ \AA}$	$a = 16.82 \text{ \AA}$
$b = 8.9 \text{ \AA}$	$b = 11.86 \text{ \AA}$
$c = 22.2 \text{ \AA}$	$c = 19.40 \text{ \AA}$
$\beta = 97^\circ 20'$	$\beta = 113^\circ 10'$
$U = 3997 \text{ \AA}^3$	$U = 3558 \text{ \AA}^3$

The calculated densities for four molecules per unit cell are;

$Zn(HDz)_2 \cdot 2THF$	, $D_c = 1.198 \text{ gm./c.c.}$
$Zn(HDz)_2 \cdot THF$	, $D_c = 1.077$ "
$Zn(HDz)_2$	, $D_c = 0.957$ "
$Cd(HDz)_2 \cdot 2py$	, $D_c = 1.457$ "
$Cd(HDz)_2$	, $D_c = 1.162$ "

The observed density for single crystals of zinc(II) dithizonate that were some months old = 1.11 gm./c.c. and for single crystals of cadmium(II) dithizonate = 1.42 gm./c.c.

III.3.iii. A Two-dimensional Crystallographic Study of $Zn(HDz)_2$.

Zinc(II) dithizonate crystallises with four molecules per unit cell in the monoclinic system. The systematic absences indicate the space group $C2/c$ or Cc . In the former, the molecule must possess either a twofold axis or a centre of symmetry whereas in the latter there are no demands on molecular symmetry. A centre of symmetry would seem to be unlikely as coordination about the zinc atom is probably tetrahedral, but the molecule could possess a twofold axis through the zinc atom.

Figure III.2.- Intensity distribution curve for zinc(II) dithizonate, compared with the theoretical curves for centrosymmetry ($\bar{1}$) and no centrosymmetry (1).

The method of Howells, Phillips and Rogers⁹ for distinguishing between centrosymmetric and non-centrosymmetric crystals was applied to the intensity data for zinc(II) dithizonate. The calculated intensity distribution is given together with the theoretical curves for the two cases in Figure III.2. The resulting curve is intermediate between the two possibilities leaving the question of the presence of centrosymmetry unanswered. This result may be due to the zinc atoms possessing too large a fraction of the total scattering power¹⁰.

A Patterson summation (equation (1)) was then computed for the b-projection.

$$P(U,W) = \frac{1}{A_b} \left\{ F^2(000) + \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} [F(h0l)_{\text{obs.}}]^2 \cos 2\pi(hU + lW) \right\} \quad \dots(1)$$

A_b is the area of the b-projection and U, W are fractional coordinates measured along the a and c axes. The area considered was one eighth of the unit cell.

No peaks were of sufficient intensity to be assigned as arising from the Zn-Zn vector which suggested that the zinc atoms lie either on a twofold axis or on a centre of symmetry.

We assumed that the coordinates of the zinc atom in b-projection were (0,0,0) and that most of the signs would therefore be positive. Based on this assumption, a two-dimensional Fourier analysis (equation (2)) was computed.

$$\rho(X,Z)_{\text{obs.}} = \frac{1}{A_b} \left\{ F(000) + \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} F(h0l)_{\text{obs.}} \cos 2\pi(hX + lZ) \right\} \quad \dots(2)$$

The two-dimensional electron density projection along the b axis for one eighth of the unit cell is shown in Figure III.3. Approximate atom positions are also shown for an equivalent portion of the unit cell.

Figure III.3. Fourier electron density projection for bis(dithizonato)zinc (II) along the b axis.

III.4. Discussion

The most noticeable feature of the X-ray powder diffraction data was that only the pattern for $\text{Cu}(\text{HDz})_2$ could be indexed in terms of the unit cell parameters for the single crystals. The dithizonates of zinc(II), cadmium(II) and mercury(II) are evidently polymorphous and it appears that the modification of each compound obtained in the powder form has a lattice with only one molecule per unit cell, as found for the triclinic crystals of $\text{Cu}(\text{HDz})_2$. The single crystal modifications of the zinc(II), cadmium(II) and mercury(II) dithizonates are obtained as solvates and it is apparent that the solvent molecule plays an important part in the crystal growth of these compounds.

Harding² observed that the pyridine of solvation in $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}$ was hydrogen bonded to the N.H proton of each coordinated dithizone molecule. These columns of pyridine molecules in the interstices of the crystal lattice are removed fairly readily leaving empty channels. The same phenomenon presumably occurs in zinc(II) dithizonate single crystals since the observed density suggested the presence of one molecule of tetrahydrofuran in crystals that were several weeks old. Initially therefore there may have been two molecules of solvent, as in $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}$. No solvent molecules were found in the two-dimensional electron density map and attempts to obtain three-dimensional data with the same crystals some months after the original photographs were taken only yielded powder photographs. The crystal lattice is evidently slowly destroyed after the loss of the solvent molecules.

The powder pattern obtained for CuDz , having a very broad line with a maximum corresponding approximately to the d spacing of the 001 plane of $\text{Cu}(\text{HDz})_2$, suggests some form of disorder along the c axis.

The electron density map of the b-projection of $\text{Zn}(\text{HDz})_2$ is reasonable evidence for bonding by sulphur and nitrogen donors, as found for both the $\text{Cu}(\text{II})$ and $\text{Hg}(\text{II})$ dithizonates. Attempts to obtain three-dimensional crystallographic data were curtailed by the decomposition of the original crystals and the unsuccessful attempts to prepare new ones.

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CHAPTER IV

INFRARED SPECTROSCOPY

IV.1. Introduction

From a study of the molecular vibrations of a system of metal complexes we can obtain information about their structures and the distribution of electron density within each molecule. There are alternative methods of obtaining this information. One method involves a qualitative study of the ligand vibrations by a comparison with the infrared spectra of related molecules and by considering the band shifts caused by isotopic substitution and solvent effects. The assignments made for the ligand are then taken as the basis for interpreting the infrared spectra of the metal complexes. An alternative method, which is also a more quantitative approach, is to obtain the frequencies and normal modes of vibration of each molecule by carrying out a normal coordinate analysis.

There has been very little infrared work reported for the metal dithizonates, and none concerning thiocarbohydrazide and its metal complexes.

Dyfveman¹ has published band frequencies for a number of the metal dithizonates in which differences between the infrared absorption spectra of the primary dithizonates of Ni(II), Pd(II), Pt(II) and Co on the one hand and the primary dithizonates of Au(III), Ag(I), Hg(II), Tl(I), Cu(II), Zn(II), Cd(II), In(III), Pb(II) and Bi(III) on the other were

interpreted as indicating that the two groups have different structures.

Duncan and Thomas² studied the N.H stretching frequencies of dithizone, the primary dithizonates of Cu(II), Hg(II) and Co(III) and the secondary dithizonate of Cu(II) in carbon tetrachloride solution.

It was concluded that the primary dithizonates all have structure I with the strength of the intramolecular hydrogen bond decreasing in the order $\text{Cu}(\text{HDz})_2 > \text{Co}(\text{HDz})_3 > \text{Hg}(\text{HDz})_2$. In the case of the secondary complex, CuDz , no N.H stretching vibration was detected.

I

The infrared spectra of $\text{Zn}(\text{HDz})_2$ and $\text{Cd}(\text{HDz})_2$ have been compared with the spectrum of $\text{Hg}(\text{HDz})_2$ ³. The similarity of the skeletal vibrations from $1,000 \text{ cm}^{-1}$ to $1,300 \text{ cm}^{-1}$ were interpreted as meaning that the $\text{Zn}(\text{II})$, $\text{Cd}(\text{II})$ and $\text{Hg}(\text{II})$ complexes are isostructural in the solid state.

The difficulty in interpreting the infrared spectra of the metal complexes of thioamides and thiohydrazides is because of the similarity of atomic masses and force constants. Extensive coupling occurs and this means, for example, that no one band in the infrared spectrum can be assigned as the C:S stretching vibration as it will contribute to a number of normal modes. Ideally then, only the second of the two methods of study mentioned earlier is practicable. However, as dithizone

has very little symmetry (probably C_1) all 84 fundamental modes of vibration are likely to be infrared active and the secular equation resulting from the normal coordinate analysis was considered to be too unwieldy to warrant further study. For this reason the dithizone system has been studied by the first method while the more manageable thiocarbohydrazide system has been investigated by carrying out a normal coordinate analysis of the free ligand. The similarity of the two ligand molecules should enable the results obtained for thiocarbohydrazide to be used to interpret some of the features of the dithizone system.

A brief synopsis of the theory necessary for an understanding of molecular vibrations is now given.

IV.2. The Study of Molecular Vibrations

We begin by assuming the Born-Oppenheimer theorem⁴ which states that we may separate the problems of electronic and nuclear motions. If, for a system of n mass points, we express the nuclear kinetic energy in terms of suitable coordinates, the wave equation for nuclear motion can be approximately separated into equations for translation, rotation and vibration.

To solve the vibrational problem we choose a coordinate system in terms of which we can express the kinetic and potential energy and then determine the transformation from our working coordinates to normal coordinates in which the vibrational wave equation is separable.

Normally our working coordinates are selected as a set of internal coordinates. These describe the internal configuration of the

molecule only and satisfy the Eckart⁵ and Sayvetz⁶ conditions for the removal of translation and rotation. A set of internal coordinates involving bond stretching, valence-angle bending, out-of-plane bending and torsion have been defined by Wilson⁷ and by Decius⁸. Decius⁹ has shown that this set of internal coordinates is sufficient to describe the most general vibrational displacement of any molecule and has outlined a procedure for defining a kinematically complete set of such coordinates for both cyclic and acyclic molecules.

Having defined a set of internal coordinates, R_i , we can now write the total potential energy of the molecule as a function of the coordinates, $V(R_i)$, which may be expanded in Taylor's series about the equilibrium configuration.

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial R_i} \right)_0 R_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_0 R_i R_j + \text{terms of order } R^3 \text{ and higher.}$$

V_0 defines the arbitrary zero, while the coefficients of R_i in the second term are all zero since the derivatives are to be taken in the equilibrium configuration for which by definition V is a minimum with respect to all R_i and hence $\left(\frac{\partial V}{\partial R_i} \right)_0 = 0$.

The coefficients of the third term are known as the harmonic force constants and can be written

$$\left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right)_0 = \left(\frac{\partial^2 V}{\partial R_j \partial R_i} \right)_0 = F_{ij}$$

The coefficients of higher terms are the anharmonic force constants which are generally ignored for polyatomic molecules involving small

amplitudes of vibration. Therefore

$$V = \frac{1}{2} \sum_i \sum_j F_{ij} R_i R_j$$

or in matrix notation

$$2V = R' F R$$

To solve the equations of motion for any system in either classical or quantum mechanics we require expressions for both the kinetic and potential energies in terms of some suitable set of equivalent coordinates. Fortunately it is possible to write the kinetic energy in terms of the coordinates R_i as

$$2T = \sum_{ij} M_{ij} \dot{R}_i \dot{R}_j$$

or in matrix notation

$$2T = \dot{R}' M \dot{R}$$

The coefficients M_{ij} are functions of the atomic mass and the equilibrium geometry of the molecule.

The vibrational wave equation for a molecule, in terms of the matrices F and M , can be separated by finding the transformation from the working coordinates R to normal coordinates, Q , in which all of the cross terms in the kinetic and potential energy expressions are eliminated. We require the normal coordinate transformation, L , which simultaneously diagonalises both F and M . The matrix L is defined as

$$R = L Q$$

with the conditions for the existence of L being given by matrix theory¹⁰.

The resulting vibrational secular equation

$$(F - \lambda M)L = 0,$$

where the λ 's are the eigen values, is usually expressed in terms of the reciprocal kinetic energy matrix, G , to give

$$(GF - \lambda E)L = 0$$

This equation will have $3n-6$ eigenvalues λ_i and an associated vector L_i which is a column of the L matrix.

The problem is therefore to set up the G and F matrices in internal coordinates and solve the resulting secular determinant. Standard methods have been given for evaluating G and tables of G matrix elements for the various coordinates are in the literature^{8,11,12}.

The more difficult problem is to evaluate the F matrix elements or force constants. Other than for small molecules it is usually impracticable to use a general harmonic force field and it becomes necessary to make some approximations and assume that certain force constants can be neglected. Urey and Bradley¹³ proposed the use of a function which is basically of the valence force type but which allows certain non-bonded interactions which may be likened to the van de Waals forces between such atoms. The potential energy in Urey-Bradley form requires the valence force constants K (stretching), H (angle bending) and the non-bonded interaction constants F and F' .

The order of the G and F matrices will be defined by the number of internal coordinates used to describe the internal configuration of the molecule. Sometimes, it is necessary to define more internal coordinates than there are normal modes of vibration. This means that not all of the internal coordinates are independent, certain combinations

of them being redundant. The resulting secular equation will have a zero root corresponding to each redundancy which thus provides a check on the calculation. However, it is usually more valuable to reduce the order of the secular equation by factoring it into blocks according to symmetry class. This also enables the redundant coordinates to be removed. To do this we use symmetry coordinates, S_i , obtained by a linear transformation of the internal coordinates R_i , using the orthogonal U matrix defined by

$$S = U R$$

After transforming G and F to give

$$\mathcal{G} = U G U'$$

$$\text{and } \mathcal{F} = U F U'$$

we are left with the factored secular equation

$$\mathcal{G} \mathcal{L} = \mathcal{L} \Lambda$$

where Λ is a diagonal matrix of the eigenvalues and $\mathcal{L}$ is the eigenvector matrix. For each root λ_i there is an associated column of the $\mathcal{L}$ matrix which gives the relative amplitudes of vibration in each symmetry coordinate. A more meaningful picture is, however, provided by the potential energy distribution among the symmetry coordinates, obtained from the relation

$$\lambda_i = \sum_{jk} \mathcal{L}_{ji} \mathcal{L}_{ki} \mathcal{F}_{jk}$$

The fractional contribution to each λ_i from the various $\mathcal{F}$ matrix elements is then given to a first approximation by

$$\mathcal{L}_{ji}^2 \mathcal{F}_{jj} / \lambda_i$$

IV.3. Experimental

Infrared spectra were recorded on a double-beam Perkin-Elmer Model 221 spectrophotometer. NaCl optics were used from 4000 cm.^{-1} to 650 cm.^{-1} , KBr optics from 750 cm.^{-1} to 400 cm.^{-1} and CsBr optics from 650 cm.^{-1} to 270 cm.^{-1} .

Wavelength calibration was carried out using polystyrene film, indene and water vapour.

The spectra of solid samples were determined either in the form of KBr discs or as mujol or hexachlorobutadiene mulls. Solution spectra were obtained using NaCl cells supplied by Perkin-Elmer.

Deuteration of water soluble compounds was carried out by dissolving the solid in D_2O (99.5% Merck reagent) and then removing the solvent under vacuum. This procedure was repeated and then the solid was stored over P_2O_5 . Water insoluble compounds were first dissolved in chloroform and then shaken with D_2O . The aqueous phase was decanted off and the chloroform solution shaken with a second aliquot of D_2O . The solvent was then removed under vacuum and the solid stored over P_2O_5 .

Relative band intensities are described in the tables as
s = strong, m = medium, w = weak, sh = shoulder and br = broad.

IV.4. The Thiocarbonylhydrazide System

IV.4.1. A Normal Coordinate Analysis of Htc₂az and Htc₂az-d₆-

Thiocarbonylhydrazide is a 12 atom molecule having 30 fundamental modes of vibration. To simplify the calculation of these modes we have assumed that the molecule is planar and have calculated only the in-plane modes.

1. The Symmetry of Htc₂az.- A planar thiocarbonylhydrazide molecule would have the following elements of symmetry, E, C₂, $\sigma_v(xz)$ and $\sigma_v(yz)$ and the molecule would belong to the C_{2v} point group. The 30 fundamental vibrations can be broken down according to their symmetry class using the C_{2v} character table.

C _{2v}	E	C ₂	$\sigma_v(xz)$	$\sigma_v(yz)$
A ₁	1	1	1	1
A ₂	1	1	-1	-1
B ₁	1	-1	1	-1
B ₂	1	-1	-1	1

In terms of cartesian coordinates the irreducible representation inclusive of the translations and rotations is

$$\Gamma = 12A_1 + 5A_2 + 12B_1 + 7B_2$$

On removing the symmetry species corresponding to the rotational and translational motion we are left with

$$\Gamma = 11A_1 + 4A_2 + 10B_1 + 5B_2$$

We shall consider the planar vibrations

$$11A_1 + 10B_1$$

If instead of cartesian coordinates we define the internal configuration by the 26 internal coordinates shown in Figure IV.1 then we obtain the irreducible representation

$$\Gamma = 13A_1 + 13B_1$$

Bond Lengths ($\text{\AA}$)

$r(\text{CS})$	$= 1.71$
$r(\text{CN})$	$= 1.33$
$r(\text{NN})$	$= 1.43$
$r(\text{NH})$	$= 1.00$

Atomic Masses (a.m.u.)⁻¹

μ_{C}	$= 0.0833$
μ_{H}	$= 0.9920$
μ_{D}	$= 0.4963$
μ_{N}	$= 0.0714$
μ_{S}	$= 0.0312$

Bond Angles

All assumed to be 120°

Figure IV.1.- The assumed molecular structure for thiocarbonylhydrazide showing the planar internal coordinates.

Thus we have five redundant coordinates, two in A_1 and 3 in B_1 , which correspond to the five sets of internal changes in bond angle

$$\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_2' = 0$$

$$\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 = 0$$

$$\Delta\beta_1' + \Delta\beta_2' + \Delta\beta_3' = 0$$

$$\Delta\gamma_1 + \Delta\gamma_2 + \Delta\gamma_3 = 0$$

$$\Delta\gamma_1' + \Delta\gamma_2' + \Delta\gamma_3' = 0$$

In setting up the secular equation to solve for the 21 planar vibrational modes, all 26 internal coordinates are retained.

2. G Matrix.— General expressions for the G matrix elements are calculated using the Wilson s-vector technique¹⁶. Numerical values can then be obtained by substituting in the bond lengths, bond angles and atomic masses. However, as no X-ray crystallographic study of thiocarbonylhydrazide has been reported it was necessary to use data obtained for other similar molecules. Truter has completed X-ray studies of thiourea¹⁷, thioacetamide¹⁸ and trimethylenethiourea¹⁹ which together with the X-ray data obtained for ethylenethiourea²⁰ and dithizone (see p. 29) enable reasonable estimates to be made for the C.N and C:S bond lengths. These are the same within the experimental error for all of the above compounds. The structural parameters which have been used are given in Figure IV.1 and the G matrix elements are tabulated in Appendix II.

3. F Matrix.- The advantage of using the Urey-Bradley force field is not only that it reduces the number of independent force constants but also that the constants are transferable among similar molecules. Based on the force constants obtained from studies of the normal vibrations of thioamides^{21,22}, hydrazine²³ and other similar molecules²⁴⁻³¹ using the Urey-Bradley force field, five sets of Urey-Bradley force constants were selected and are given in Table IV.1. These were then used to set up F matrices for thiocarbohydrazide.

4. Symmetry Coordinates.- The construction of symmetry coordinates is discussed in detail by Wilson, Decius and Cross¹² and by Slansky³². Symmetry coordinates for thiocarbohydrazide, excluding the redundant set, are listed in Table IV.2. The ξ and ζ matrices for the A_1 and B_1 symmetry species of thiocarbohydrazide and thiocarbohydrazide- d_6 are given in Tables IV.3-6.

5. Solving the Secular Equation.- The product matrix $\xi\zeta$ is non-symmetric and consequently more tedious to diagonalise than a symmetric matrix. A procedure has, however, been given^{12,33} whereby a symmetric matrix can be obtained and it is this method which we have used to solve the five secular equations for both thiocarbohydrazide and its deuterio analogue.

The calculated frequencies obtained for each of the five force fields are listed in Tables IV.7 and IV.8 together with observed band frequencies. The potential energy distribution among the symmetry coordinates for the five sets of normal modes for thiocarbohydrazide are given in Tables IV.9-13.

TABLE IV.1

Urey-Bradley Force Constants
(m. dyne/Å)

	<u>Set 1</u>	<u>Set 2</u>	<u>Set 3</u>	<u>Set 4</u>	<u>Set 5</u>
K_{CS}	3.50	3.50	3.50	3.70	3.30
K_{CN}	5.50	6.00	6.00	6.00	5.50
K_{NN}	3.30	3.60	3.60	3.60	3.60
K_{NH}	5.50	5.55	5.55	5.55	5.55
H_{SCN}	0.24	0.24	0.20	0.20	0.20
H_{CNH}	0.21	0.21	0.30	0.30	0.30
H_{CNN}	0.30	0.30	0.25	0.25	0.25
H_{NCN}	0.57	0.57	0.57	0.57	0.57
H_{NNN}	0.20	0.42	0.36	0.36	0.36
H_{HNH}	0.39	0.43	0.42	0.42	0.42
$F_{S\cdots N}$	1.06	1.06	1.06	1.06	1.06
$F_{N\cdots N}$	0.60	0.60	0.60	0.60	0.60
$F_{C\cdots H}$	0.50	0.50	0.50	0.50	0.50
$F_{C\cdots N}$	0.50	0.50	0.50	0.50	0.50
$F_{N\cdots H}$	0.49	0.49	0.49	0.49	0.49
$F_{H\cdots H}$	0.06	0.06	0.06	0.06	0.06

Note: $F' = -0.1 F$.

This additional simplification is made through the application of a two-body potential function of the Lennard-Jones type¹⁴. Devlin¹⁵ considers the assumption unwarranted although he agrees that the contribution of F' to the vibrational potential energy is probably small compared with that of F .

TABLE IV.2

Symmetry Coordinates

	Symmetry Coordinate	Vibrational Mode ^a
A ₁ Species	$S_1 = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_1')$	ν_{CN}
	$S_2 = \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r_2')$	ν_{NN}
	$S_3 = \frac{1}{\sqrt{2}}(\Delta r_3 + \Delta r_3')$	ν_{NH}
	$S_4 = \frac{1}{2}(\Delta r_4 + \Delta r_4' + \Delta r_5 + \Delta r_5')$	ν_{NH_2}
	$S_5 = \frac{1}{2}(\Delta r_4 + \Delta r_4' - \Delta r_5 - \Delta r_5')$	ν_{NH_2}
	$S_6 = \Delta R$	ν_{CS}
	$S_7 = \frac{1}{\sqrt{6}}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_2')$	δ_{NCN}
	$S_8 = \frac{1}{\sqrt{12}}(2\Delta\beta_1 + 2\Delta\beta_1' - \Delta\beta_2 - \Delta\beta_2' - \Delta\beta_3 - \Delta\beta_3')$	δ_{CNN}
	$S_9 = \frac{1}{2}(\Delta\beta_2 + \Delta\beta_2' - \Delta\beta_3 - \Delta\beta_3')$	β_{NH}
	$S_{10} = \frac{1}{\sqrt{12}}(2\Delta\gamma_2 + 2\Delta\gamma_2' - \Delta\gamma_1 - \Delta\gamma_1' - \Delta\gamma_3 - \Delta\gamma_3')$	β_{NH_2}
	$S_{11} = \frac{1}{2}(\Delta\gamma_1 + \Delta\gamma_1' - \Delta\gamma_3 - \Delta\gamma_3')$	γ_{NH_2}
B ₁ Species	$S_1 = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_1')$	ν_{CN}
	$S_2 = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_2')$	ν_{NN}
	$S_3 = \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r_3')$	ν_{NH}
	$S_4 = \frac{1}{2}(\Delta r_4 - \Delta r_4' + \Delta r_5 - \Delta r_5')$	ν_{NH_2}
	$S_5 = \frac{1}{2}(\Delta r_4 - \Delta r_4' - \Delta r_5 + \Delta r_5')$	ν_{NH_2}
	$S_6 = \frac{1}{\sqrt{2}}(\Delta\alpha_2 - \Delta\alpha_2')$	δ_{NCS}
	$S_7 = \frac{1}{\sqrt{12}}(2\Delta\beta_1 - 2\Delta\beta_1' - \Delta\beta_2 + \Delta\beta_2' - \Delta\beta_3 + \Delta\beta_3')$	δ_{CNN}
	$S_8 = \frac{1}{2}(\Delta\beta_2 - \Delta\beta_2' - \Delta\beta_3 + \Delta\beta_3')$	β_{NH}
	$S_9 = \frac{1}{\sqrt{12}}(2\Delta\gamma_2 - 2\Delta\gamma_2' - \Delta\gamma_1 + \Delta\gamma_1' - \Delta\gamma_3 + \Delta\gamma_3')$	β_{NH_2}
	$S_{10} = \frac{1}{2}(\Delta\gamma_1 - \Delta\gamma_1' - \Delta\gamma_3 + \Delta\gamma_3')$	γ_{NH_2}

^a ν , β , γ and δ denote stretching, bending, rocking and deformation modes respectively.

Matrices for Htcz

[illegible][illegible]

TABLE IV.4

2. Matrices for Htcaz-d₆

[illegible]

55.

[illegible]

TABLE IV.5

7 Matrices for Htcz and Htcz-d₆

A₁ Species

	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	s_{10}	s_{11}
s_1	1) 7.224 2) 7.724 3) 7.724 4) 7.724 5) 7.224	0.386	0.385	0	0	0.816	0.035	0.115	-0.171	0	0
s_2	1) 4.865 2) 5.165 3) " 4) " 5) "		0.372	0.526	0	0	0	0.125	0.173	-0.199	0
s_3			1) 6.127 2) 6.177 3) " 4) " 5) "	0	0	0	0	-0.161	-0.004	0	0
s_4				1) 5.900 2) 5.945 3) " 4) " 5) "	0	0	0	0	0	-0.085	0
s_5					1) 5.801 2) 5.851 3) " 4) " 5) "	0	0	0	0	0	-0.194
s_6						1) 5.180 2) 5.180 3) 5.175 4) 5.375 5) 4.975	-0.539	0	0	0	0
s_7							1) 1.111 2) 1.111 3) 1.084 4) " 5) "	0	0	0	0
s_8								1) 0.624 2) 0.676 3) 0.619 4) " 5) "	0	0	0
s_9									1) 0.397 2) 0.554 3) 0.571 4) " 5) "	0	0
s_{10}										1) 0.401 2) 0.533 3) 0.498 4) " 5) "	0
s_{11}											1) 0.402 2) 0.716 3) 0.631 4) " 5) "

	s_1	s_2	s_3	s_4	s_5	s_6	s_7	s_8	s_9	s_{10}
s_1	1) 6.292 2) 6.792 3) 6.792 4) 6.792 5) 6.292	0.386	0.385	0	0	0.564	0.115	-0.171	0	0
s_2	1) 4.865 2) 5.165 3) " 4) " 5) "		0.372	0.526	0	0	0.125	0.173	-0.199	0
s_3		1) 6.127 2) 6.177 3) " 4) " 5) "		0	0	0	-0.161	-0.004	0	0
s_4			1) 5.900 2) 5.945 3) " 4) " 5) "		0	0	0	0	-0.085	0
s_5				1) 5.801 2) 5.851 3) " 4) " 5) "		0	0	0	0	-0.194
s_6					1) 0.945 2) 0.864 3) " 4) " 5) "		0	0	0	0
s_7						1) 0.624 2) 0.676 3) 0.619 4) " 5) "		0	0	0
s_8							1) 0.397 2) 0.554 3) 0.571 4) " 5) "		0	0
s_9								1) 0.401 2) 0.533 3) 0.498 4) " 5) "		0
s_{10}										1) 0.402 2) 0.716 3) 0.631 4) " 5) "

TABLE IV.7

The Observed and Calculated Frequencies
of the Normal Vibrations of Thiocarbonylhydrazide

Obs. (cm. ⁻¹)	Calc. (cm. ⁻¹)				
	1	2	3	4	5
3300	3311	3326	3326	3326	3326
3300	3311	3324	3324	3324	3324
3270	3279	3294	3294	3294	3294
3270	3279	3294	3294	3294	3294
3205	3207	3220	3220	3220	3220
3205	3207	3220	3220	3220	3220
1642	1496	1712	1658	1658	1656
1622	1483	1710	1654	1654	1652
1530	1409	1519	1539	1539	1529
1495	1328	1495	1448	1448	1415
1453	1221	1436	1497	1497	1478
1287	1183	1245	1243	1251	1213
1080	1036	1066	1063	1065	1061
-	1026	1055	1049	1049	1047
1142	919	1230	1154	1154	1154
1142	919	1230	1154	1154	1154
930	851	874	865	873	852
588	541	559	536	536	535
469	466	468	464	464	462
326	336	348	337	337	335
-	183	185	178	178	178

TABLE IV.8

The Observed and Calculated Frequencies
of the Normal Vibrations of Thiocarbonylhydrazide-d₆

Obs. (cm. ⁻¹)	Calc. (cm. ⁻¹)				
	1	2	3	4	5
2456	2415	2426	2425	2425	2425
2456	2415	2428	2426	2426	2426
2470	2423	2437	2437	2437	2437
2470	2423	2437	2437	2437	2437
2325	2311	2321	2321	2321	2321
2325	2311	2321	2321	2321	2321
1235	1143	1295	1263	1263	1263
1205	1143	1292	1258	1258	1256
1400	1428	1376	1380	1380	1350
1525	1290	1495	1488	1488	1433
1060	884	1092	1098	1098	1097
1137	1055	1119	1117	1128	1102
971	915	970	967	967	967
960	972	971	964	964	963
878	707	945	887	887	887
878	707	945	887	887	887
803	735	791	784	788	775
586	528	547	524	524	524
449	447	450	446	448	442
320	302	313	304	305	303
-	61	62	60	60	60

TABLE IV.9

The Potential Energy Distribution Among the Symmetry
Coordinates of Thiocarbonylhydrazide with U-B Force Field 1

[illegible][illegible]

[illegible][illegible]

TABLE IV.11

The Potential Energy Distribution Among the Symmetry
Coordinates of Thiocarbonylhydrazide with U-B Force Field 3

[illegible][illegible]

[illegible][illegible]

TABLE IV.13

The Potential Energy Distribution Among the Symmetry
Coordinates of Thiocarbonylhydrazide with U-B Force Field 5

[illegible][illegible]

Figure IV.2.- Infrared absorption spectra of thiocarbonylhydrazide (solid curve) and thioacetamide (dashed curve) measured as nujol mulls.

The infrared absorption spectra of thiocarbonyldiazide and thiocarbonyldiazide- d_6 are shown in Figure IV.2. The bands observed from $4,000\text{ cm.}^{-1}$ to 280 cm.^{-1} are listed in Tables IV.14 and IV.15 together with band assignments made using the normal coordinates obtained for the second and third Urey-Bradley force fields. Included in this table are the absorption bands for thiosemicarbazide and the hydrochloride derivative of thiocarbonyldiazide. Mashima³⁴ has made qualitative assignments for some of the absorption bands of the former compound in the region $4000\text{--}650\text{ cm.}^{-1}$ and these are in reasonable agreement with the present results. We have been able to interpret the spectrum of Htcz.2HCl in terms of the assignments for the free amine which suggests that the molecular vibrations of thiocarbonyldiazide are reasonably well understood.

IV.4.ii. Infrared Spectra of the Metal Complexes of Thiocarbonyldiazide.-

The infrared spectra and structures of the thiocarbonyldiazide complexes have been interpreted in terms of the normal coordinates of the free ligand by comparing band shifts with those observed in the infrared spectrum of thiosemicarbazide when metal complexes of known structure are formed.

Bands observed in the infrared spectra of thiocarbonyldiazide and the metal complexes from $4000\text{--}280\text{ cm.}^{-1}$ are given in Tables IV.16 and IV.18. Similar bands observed in the infrared spectra of thiosemicarbazide, $\text{Ni(Htcz)}_3\text{Cl}_2$, Ni(tscz)_2 and Ag(Htcz)Cl are included in Tables IV.17 and IV.19.

TABLE IV.14

Infrared Absorption Bands of Htc₂az, Htc₂az.2HCl and
and Htscaz from 4000-700 cm.⁻¹

Assignment	Htc ₂ az	Htc ₂ az.2HCl	Htscaz
ν_{NH}	3300 m	3320 m	3360 m
$\nu_{\text{NH}_2} (\nu_{\text{NH}_3^+})$	3270 s	3190 s	3254 s
$\nu_{\text{NH}_2} (\nu_{\text{NH}_3^+})$	3205 s	3070 s.br.	3170 s
	2960 m	2625 s.br.	2960 m
$\beta_{\text{NH}_2} (\beta_{\text{NH}_3^+})$	1642 s	1567 m	1643 s
$\beta_{\text{NH}_2} (\beta_{\text{NH}_3^+})$	1622 s	1552 m	1620 s
$\beta_{\text{NH}} \& \nu_{\text{CN}}$	1530 s	1530 w	1530 s
$\nu_{\text{CN}} \& \beta_{\text{NH}}$	1495 s	(1501 m 1494 m 1482 m)	1480 m
	1453 w	1446 m	
a	1348 w	1408 sh	1315 w
$\nu_{\text{CN}} \& \nu_{\text{CS}}$	1287 s	(1341 s 1263 m 1220 m)	1282 s
$\gamma_{\text{NH}_2} (\gamma_{\text{NH}_3^+})$	1142 s	(1197 sh 1181 m 1152 m 1094 s)	1160 s
b	1081 m	1080 sh	
	1012 s	1058 sh	1001 s
	930 s	(965 m.br 909 m.br)	798 s
a	755 s	752 w	

TABLE IV. 15
Infrared Absorption Bands of Htcz and
Htsz from 700-280 cm^{-1}

Assignment	Htcz	Htsz
	680 s	641 m
δ CNN & δ NCS	588 s	597 s.br
	553 sh	566 s.br
δ NCN	469 m	503 m
	437 m.br	408 m
	420 w	400 m
c	371 m.br	357 m.br
δ CNN	326 w	327 s
	304 w	305 w
	293 w	289 w.br
	284 w	279 w.br

Footnote to Tables IV.14 and IV.15:

- ^a These bands are considered to be out-of-plane vibrations of the hydrazine group.
- ^b This band may be assigned as a coupled mode consisting of δ NN & δ CS on the basis of the N.C analysis, although the high intensity suggests that it is more reasonably assigned as an out-of-plane vibration.
- ^c This band corresponds to the torsional mode of hydrazine²³.

TABLE IV.16

Some Infrared Absorption Bands of Metal Thiocarbonylhydrazide Complexes from 4000-700 cm^{-1}

Assignment	Htc az	Zn(II)	Cd(II)	Hg(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Pd(II)
ν_{NH}	3300 m	3280 sh	3300 m	3275 s	3320 m	3285 s		3250 s	3312 m
ν_{NH_2}	3270 s	3200 s	3200 s	3140 sh	3280 s	3238 s	3250 s	3150 s	3140 s
ν_{NH_2}	3205 s	3255 s	3235 s	3180 s	3215 s	3255 s	3155 s	3210 s	3075 s
β_{NH_2}	1642 s	3096 s	3110 s	3090 s	3165 s	3190 s	3100 s	3110 sh	2975
β_{NH_2}	1622 s	1644 s	1640 s	1642 s	1631 sh	1643 s	1625 s	1644 s	1645 s
$\beta_{\text{NH}} \text{ \& } \nu_{\text{CN}}$	1530 s	1619 s	1613 s	1615 s	1624 s	1615 s	1608 s	1623 s	1620 s
$\nu_{\text{CN}} \text{ \& } \beta_{\text{NH}}$	1495 m	1564 m	1564 m	1564 sh	1537 m	1568 s	1549 m	1573 s	1565 m
$\nu_{\text{CN}} \text{ \& } \nu_{\text{CS}}$	1287 s	1550 sh	1553 m	1555 m	1497 m	1504 s	1532 m	1510 s	1550 m
γ_{NH_2}	1142 s	1501 m	1501 s	1501 m	1300 m	1311 m	1312 m	1343 m	1316 m
		1160 s	1150 s	1140 s	1275 sh	1156 s	1164 s	1205 s	1295 w
$\nu_{\text{CS}} \text{ \& } \delta_{\text{CN}} \text{ \& } \nu_{\text{CN}}$		1130 m	1118 m	1093 s	1112 w	1113 m	1128 sh	1144 m	1186 s
		930 s	977 s	971 s	935 s	974 s	951 s	1010 s	1156 s
									1113 m
									960 s
									913 s

TABLE IV.17

Some Infrared Absorption Bands of Metal Thiosemicarbazide
Complexes from 4000-700 cm^{-1}

Assignment	Htscsz	Ni(Htscsz) ₃ Cl ₂	Ni(tscsz) ₂	Ag(Htscsz)Cl
ν_{NH}	3360 m	3360 m		3340 m
ν_{NH_2}	3254 s	3260 s	3438 s	3310 m
			3175 s	3250 s
ν_{NH_2}	3170 s	3150 s	3270 s	
			3112 s	3155 s
β_{NH_2}	1643 s	1621 s	1643 s	
			1630 s	1635 s
β_{NH_2}	1620 s	1600 s	1616 s	
			1590 s	1612 s
$\beta_{\text{NH}} \& \nu_{\text{CN}}$	1530 s	1548 sh		
		1532 m		1540 m
$\nu_{\text{CN}} \& \beta_{\text{NH}}$	1480 m		1521 s	1480 m
$\nu_{\text{CN}} \& \nu_{\text{CS}}$	1282 s	1325 m	1320 m	1292 m
		1285 sh	1284 sh	1275 w
τ_{NH_2}	1160 s	1205 s	1227 s	
		1117 m	1136 m	1149 s
$\nu_{\text{CS}} \& \nu_{\text{CN}}$	798 s	798 s	678 s	806 s
				782 s

TABLE IV.18

Infrared Absorption Bands for Metal Thiocarbonylhydrazide Complexes
From 700 - 280 cm^{-1}

Zn(II)	Cd(II)	Hg(II)	Fe(II)	Ni(II)	Cu(II)	Pd(II)
		681 m		662 m	671 m	
633 m	617 s	615 s	648 w			645 m
581 m	581 s	594 m	620 w	580 s	581 s	608 s
550 s	526 s	504 w	550 s.br			567 sh
			485 m			
468 w	468 w	466 m	477 m	477 w	478 w	478 m
			470 m		442 m	435 s
		420 w	417 w	397 w	418 w	420 sh
391 w		393 m	379 s.br	375 w	390 m	362 s.br
351 w	351 w	373 s	351 m.br	351 w	341 s	340 w
316 m	326 w	326 w	317 m	325 w	326 sh	319 w
304 m	304 m	301 m	304 m	304 m	304 m	

TABLE IV.19

Infrared Absorption Bands for $\text{Ni}(\text{Htscz})_3\text{Cl}_2$ and $\text{Ni}(\text{tscz})_2$
From 700-280 cm^{-1}

$\text{Ni}(\text{Htscz})_3\text{Cl}_2$	$\text{Ni}(\text{tscz})_2$
641 w	
597 m.br	597 m
562 m.br	529 s
326 w	440 s
304 w	420 w
	388 m
	347 m

The similarity between the infrared spectra of $\text{Zn}(\text{Htcaz})_2\text{Cl}_2$, $\text{Cd}(\text{Htcaz})_2\text{Cl}_2$, $\text{Hg}(\text{Htcaz})_2\text{Cl}_2$, isomeric $[\text{Co}(\text{Htcaz})_2\text{Cl}_2]$ and $\text{Ni}(\text{Htcaz})_3\text{Cl}_2$ would suggest that they have similar structures.

Of the possible structures illustrated below, X-ray crystallographic studies have shown that II exists in $\text{Ni}(\text{Htscaz})_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ³⁵ and $\text{Zn}(\text{Htscaz})\text{Cl}_2$ ³⁶, III in $\text{Ni}(\text{tscaz})_2$ ³⁷ and VI in $\text{Ag}(\text{Htscaz})\text{Cl}$ ³⁸, where $\text{R} = \text{H}$ in each case.

In the infrared spectrum of $\text{Ni}(\text{Htscaz})_3\text{Cl}_2$, which is considered to have structure II ($\text{R} = \text{H}$)^{39,40}, bands which have been assigned as ν_{NH_2} and γ_{NH_2} in the free ligand are split, giving one band with a lower and one with a higher frequency. Similar splitting is observed in the spectra of the metal thiocarbonylhydrazides mentioned above, from which it can be concluded that structures II and IV ($\text{R} = \text{NH}_2$) are possible but that structure V in which both of the NH_2 groups are coordinated is unlikely.

Bands at 1530 cm.^{-1} and 1495 cm.^{-1} in thiocarbohydrazide have been assigned as coupled modes consisting principally of βNH and νCN . The band of higher frequency, which is predominantly βNH , is split and raised in the complexes while the band at 1495 cm.^{-1} is raised only slightly. These shifts can be explained by structure II whereas structure IV involving a coordinated NH group would require a lowering of one of the split βNH bands.

Of the corresponding bands in thiosemicarbazide at 1530 cm.^{-1} and 1480 cm.^{-1} , that of higher frequency is absent in the infrared spectrum of $\text{Ni}(\text{tscaz})_2$ while the low frequency band is raised to 1521 cm.^{-1} with increased intensity, due to the large increase in the C.N bond order. Both changes substantiate the assignments made for these bands.

The C:S stretching vibration contributes to two bands in thiocarbohydrazide. However, both contain contributions from other vibrations, in particular νCN . These bands, at 1287 cm.^{-1} and 930 cm.^{-1} are raised in the metal complexes implying that for structure II the increase in the C.N bond order nullifies any lowering of νCS due to coordination. The raising of these bands to higher frequencies could also be explained by structure IV. The evidence against this interpretation is that the comparable bands in thiosemicarbazide undergo a negligible shift in $\text{Ni}(\text{Htscaz})_3\text{Cl}_2$. Only for the thioenolic structure as in $\text{Ni}(\text{tscaz})_2$, is any significant shift observed, the band at 798 cm.^{-1} being lowered by approximately 100 cm.^{-1} .

These results suggest that the thiocarbonylhydrazide complexes of Zn(II), Cd(II), Hg(II), Co(II) and Ni(II) have structure II ($R = NH_2$) in which changes in the C:S bond order are negligible by comparison with the changes in the C.N bond order.

Large shifts to higher frequencies are observed in the infrared spectrum of $Cu(Htcz)_3Cl_2$ for all bands, due partly to ν_{CN} . Among the first row transition metals Cu(II) displays the strongest Arhland, Chatt and Davies B-type character⁴¹ so that of the thiocarbonylhydrazide complexes of these metals (providing they all have structure II), $Cu(Htcz)_3Cl_2$ should have the strongest metal to sulphur bond. According to the above explanation this would result in a high C.N bond order, which is observed, and which therefore favours the assignment of structure II ($R = NH_2$) for $Cu(Htcz)_3Cl_2$.

In $Pd(Htcz)_2Cl_2$, the stretching vibrations assigned to the free NH_2 group in the other complexes appear to be absent. The bands at 1142 cm^{-1} and 930 cm^{-1} in the free ligand are split into three bands and two bands respectively. The splitting of the latter band is similar to the splitting observed in the hydrochloride and in the 798 cm^{-1} band of thiosemicarbazide in $Ag(Htscz)Cl$. The Ag(I) complex was shown to contain sulphur atoms in two different environments, coordinated to two and three silver atoms respectively. The sulphur atoms in $Pd(Htcz)_2Cl_2$ may likewise be involved in two different environments. However, this would not explain the changes in ν_{NH_2} and γ_{NH_2} and it is necessary to invoke either structure IV in which

Pd(II) is coordinated by four nitrogen donors or a polymeric structure similar to II but with the free NH_2 groups linking the monomer units.

The small shifts observed for the ligand absorption bands in the infrared spectrum of $[\text{Fe}(\text{Htcz})_2\text{NCS}_2]$, suggest that thiocarbohydrazide is only weakly coordinated through the thioketo group and the hydrazinic nitrogen atom. The remaining octahedral lattice sites are presumably filled by the thiocyanate groups for which two bands are observed at 2088 cm.^{-1} and 470 cm.^{-1} . The first is assigned as the C:N stretching frequency while the latter is assigned as the NCS deformation mode. It has been shown^{42,43} that in N-thiocyanato complexes the deformation mode is similar to that for potassium thiocyanate, occurring at approximately 470 cm.^{-1} while in S-thiocyanato complexes it is lowered and split. The C:N stretching frequency is less characteristic, however Mitchell and Williams⁴⁴ have observed that the frequency is usually lower for N-thiocyanato than for S-thiocyanato groups. Hence the observed bands suggest the presence of N-thiocyanato groups in $[\text{Fe}(\text{Htcz})_2\text{NCS}_2]$.

IV.4.iii. Thiocarbohydrazidato Metal Complexes.- It was shown in Chapter II that attempts to isolate complexes of the charged ligand tcz^- , analogous to $\text{Ni}(\text{tscz})_2$, generally led to amorphous black products of indefinite composition. The intense colours of the solutions of these products suggests the presence of a chromophore other than C:N, already present for example in $\text{Ni}(\text{tscz})_2$. Their infrared absorption spectra have been investigated (Table IV.20) in the hope that some light would be thrown on their composition.

The complex $\text{Hg}[\text{Co}(\text{tc}az)_2\text{Cl}_2]$ is the least strongly coloured and may be the only one involving the anion $\text{tc}az^-$. The NH_2 deformation modes are lowered, with the shorter wavelength asymmetric and symmetric bending modes being replaced by a single broad band at 1595 cm^{-1} and the rocking mode now occurring at 1125 cm^{-1} . The absence of splitting in this latter mode, assigned as ΓNH_2 in the free ligand, may be due to the mercury ions acting as bridging groups linking the free NH_2 groups of III ($\text{R} = \text{NH}_2$). The coupled mode at 1287 cm^{-1} in the free ligand is replaced by one band at 1290 cm^{-1} and another at 1204 cm^{-1} which is tentatively assigned as a coupled mode involving νCS . The weak band at 826 cm^{-1} is assigned as νCS , being lowered some 100 cm^{-1} from its position in thiocarbonylhydrazide which is similar to the lowering of νCS for thiosemicarbazide on forming $\text{Ni}(\text{tsc}az)_2$.

The infrared spectra of the amorphous black products isolated for $\text{Ag}(\text{I})$, $\text{Ni}(\text{II})$, and $\text{Fe}(\text{II})$ generally show broad unresolved bands. The cyanide derivative of the $\text{Fe}(\text{II})$ compound has two strong absorption bands, at 2045 cm^{-1} and 1405 cm^{-1} . The first is the $\text{C}\equiv\text{N}$ stretching mode and the longer wavelength band is assigned as an azo stretching vibration as it occurs in the region expected for such a mode⁵⁷⁻⁶⁰ and the presence of an azo group would explain the intense colour of the compound. The $\text{Ni}(\text{II})$ compound has a band at 2080 cm^{-1} as have also the brown cobalt and the water soluble, 'blue-violet' $\text{Pt}(\text{II})$ compounds. Such a band suggests the presence of a $\text{C}\equiv\text{N}$ group which can only have resulted from structural changes in the ligand. No

TABLE IV.20

Infrared Absorption Bands of Some Metal Thiocarbonyhydrazidato
Complexes and Their Oxidation Products from 4000-700 cm^{-1} a

Hg[Co(tcay) ₂ Cl ₂]	Co(III)	Fe(II)CN	Ni(II)	Pt(II)	
				'green'	'blue-violet'
		3360 s.br		3342 s	3335 m
3295 sh				3250 m	
3250 sh	3264 m	3165 s.br			
3140 s.br	3180 s	3125 s.br	3125 w.br	3140 sh	3135 sh
3080 s.br		3010 sh		3105 s	3110 s
2925 m	2980 m				
	2050 m	2045 s			2058 s
					1725 m
1595 s	1613 s	1605 m	1585 m.br	1616 m.br	1610 s.br
				1600 sh	
				1550 w	1550 w
				1516 m	1514 m
1494 w	1504 s				1502 s
1479 m			1465 w	1485 w	
	1420 m	1405 s	1425 w		
1355 w.br					
1290 m.br	1278 m			1276 sh	1275 s
				1255 s	1249 sh
1204 m	1227 s		1216 w.br	1220 m	1230 m
	1192 sh	1192 sh		1165 w	1140 m
1128 s	1111 m	1124 m			1073
	1083 sh	1032 m			997
950 m.br	1000 s	980 m			877
826 w	853 s		875 w.br	885 m	851
	765 s			784 w	763

corresponding band is observed for the 'green' Pt(II) compound. Bands are also observed for these four compounds in the regions $1350-1425\text{ cm}^{-1}$ and $850-900\text{ cm}^{-1}$ which can be attributed to N:N and C:S stretching modes.

It is evident that the deprotonated form of thiocarbohydrazide is an unstable entity, undergoing oxidation to give products which may contain N:N or C:N groups. The apparent stability of the tcaz^- ion in the complex $\text{Hg}[\text{Co}(\text{tcaz})_2\text{Cl}_2]$ can be attributed to the bridging mercury ions coordinated to the free N.H_2 groups preventing oxidation of .NH.NH_2 to .N:NH .

IV.4. iv. Far Infrared Absorption Spectra of the Metal Thiocarbohydrazides.-

Assignments for certain ligand absorption bands below 700 cm^{-1} have been made on the basis of the normal coordinate analysis, although the assumption that the molecule is planar should result in larger discrepancies for these skeletal modes. The bands of most interest in the infrared spectra of the metal thiocarbohydrazide complexes in this region are those due to metal to ligand vibrations. However, the changes in the ligand absorption bands on coordination are complex and as there may be some doubt about the initial assignments for the bands, it was considered that an empirical identification of bands due to metal to ligand vibrations was not warranted.

IV.5. The Dithizone System

IV.5.i. Infrared Spectrum of Dithizone.- First we have investigated the infrared absorption spectra of simple compounds structurally similar to dithizone. A number of these are given in Tables IV.21 and IV.22. Both

TABLE IV.21

Infrared Absorption Bands of Some Amides and Carbo-
hydrazides (cm.^{-1})

Assignment	Urea ^a	s-Diphenylurea	Hcaz	s-Diphenyl Hcaz
		3435 sh	3355 s	3440 s
		3325 s	3323 m	3340 m
		3280 s	3300 s	3280 s
		3195 m		3240 s
		3140 m	3195 s	3185 sh
			1722 sh	
ν_{CO}	1686 s	1645 s	1705 sh	1667 s.br
	1629 s		1640 s.br	
β_{NH_2} Ph ²	1603 s		1628 s.br	
		1594 s		1596 s
				1575 m
β_{NH}		1547 s	1530 m.br	1535 m
		1493 s		
Ph		1444 s		1490 m
			1443 sh	1455 sh
$\nu_{\text{CN}} \& \beta_{\text{NH}}$	1464 m	1438 s	1428 w	1425 sh
		1347 w	1348 w.br	1415 sh
		1310 s	1323 w	1310 m
		1292 s		1297 sh
		1267 w		
γ_{NH_2}	1150 s	1230 s	1213 s	1255 s
				1175 m
		1152 w	1142 m	1150 w
		1073 w		1073 m
Ph		1024 m		1025 m
	1050 br	1049 m	1043 m	970 m.br
ν_{CN}	1000 s	911 w	1020 m	912 sh
		893 m	912 m	900 sh
				884 m
				878 m
	785 s			800 sh
				767
	719 s			757 sh
Ph		752 s		750 s
Ph		694 s		686 s

^a Data from reference (24).

TABLE IV.22

Infrared Absorption Bands of Some Thioamides and Thiohydrazides

	Thiourea	Methyl thiourea	s-Diphenyl- thiourea	Htcas	s-Diphenylthio- carbazine
ν NH	3420 s	3300 sh	3440 m	3300 m	3300 s
ν NH	3265 s	3240 s	3205 s	3270 s	3270 m
ν NH	3165 s	3150 s	3125 s	3205 s	3230 m 3150 s
					2925 s
Ph			1601 m 1592 m		1597 s
β NH ₂	1625 s 1610 s	1634 s		1642 s 1622 s	
β NH		1550 s	1546 m	1530 s	1547 m, br 1523 w
Ph			1494 s		1488 m
ν CN & β NH	1470 s	1490 m	1450 m	1495 m	1470 m
ν CN & β NH	1417 m			1453 w	1434 m
			1343 m	1348 m	1348 s
			1310 m		1305 m
ν CN & ν CS	1083 s	1296 s 1257 m	1293 s 1240 m	1287 s	1285 m 1222 m
Ph					1255 m
γ NH ₂				1142 s	
Ph					1155 m, br
Ph			1070 w		1075 w
				1081 m	1065 s
Ph			1022 w 1002 w		1023 m
			972 m		998 w
		972 m	932 m	1012 s	
ν CS & δ CNN & ν CN	730 s	774 m	765 m	930 s	946 s, br 887 m 855 s 825 m
		718 s		755 s	764 m 750 s 686 s
Ph			756 s 695 s		

thiourea and urea have been studied by a number of workers⁴⁵⁻⁴⁸ and Yamaguchi and co-workers have carried out normal coordinate analyses of the planar vibrations of both molecules^{24,49}. Detailed band assignments have also been published for isomeric hydroxyureas⁵⁰, oxamide ($\text{H}_2\text{N.C(O).C(O).NH}_2$) and dithiooxamide⁵¹, ethyleneurea⁵² and ethylenethiourea⁵³, diacetamide²⁶, diketopiperazine²⁵, thioformamide, thioacetamide and their N-methyl derivatives²² and various substituted hydrazines^{34,54,55}. Using these results in conjunction with those recorded in Tables IV.21 and IV.22 band assignments have been made for diphenylthiocarbazide ($\text{Ph.HN.HN.C(S).NH.NH.Ph}$) which on oxidation becomes the dithizone molecule. Thus we are indirectly provided with a means of interpreting the infrared spectrum of dithizone.

Information of a direct nature is obtained by studying the band shifts on exchanging the labile N.H protons with deuterium atoms to give dithizone- d_2 . The infrared spectra of dithizone and dithizone- d_2 as mulls and in chloroform solution are given in Figures IV.3 and IV.4 while the frequencies are tabulated in Table IV.23.

Dithizone has been shown to exist in the solid state as the thioketo tautomer with the trans- anti configuration (see p.29), so that we would expect to observe two N.H stretching vibrations in the solid state spectrum. In solution it is conceivable that one or more of the eight possible monomeric species exists and the nature of the solvent would be expected to be important in determining the predominant species.

Figure IV.3.- Infrared absorption spectra of dithione (solid curve) and dithione-d₂ (dashed curve) measured as nulls.

Figure IV.4.- Infrared absorption spectra of dithione (solid curve) and dithione-d₂ (dashed curve) measured in chloroform solution.

TABLE IV.23

Infrared Absorption Bands of Dithizone and Dithizone-d₂
from 4000-280 cm.⁻¹

Dithizone		Dithizone-d ₂	
2960 m	834 w	2960 m	973 w
1592 m	779 m	2230 m	902 w
1512 sh	761 s	1592 w	891 s
1495 s	751 s	1514 w	864 w
1483 s	714 s	1494 s	828 w
1475 sh	679 s	1453 s	798 w
1460 m	668 sh	1436 m	773 sh
1455 m	603 m	1420 m	762 s
1439 s	573 s	1389 s	747 s
1421 m	541 w	1346 w	709 m
1390-1405 m	520 m	1322 w	677 s
1339 s	505 m	1279 sh	631 s
1260 m	495 s	1254 s	597 m
1220 s	440 m	1220 s	577 s
1180 m	420 w	1188 w	545 m
1150 s	398 w	1172 w	516 s
1108 sh	386 w	1157 w	500 s
1080 m	376 w	1140 w	454 w
980 w	351 w	1096 w	314 w
908 w	326 w	1070 m	
897 s	304 s	1038 m	
802 sh		1020 sh	

No sharp N.H stretching vibration is detectable in the spectrum of dithizone in either the solid state or in solution in chloroform. This suggests that the N.H groups are participating in some form of hydrogen bonding. On deuteration a band which can be assigned as ν_{ND} appears in the solid state spectrum and in the spectrum of the chloroform solution at 2230 cm.^{-1} .

Other bands of interest in the spectrum of dithizone are coupled modes corresponding to those at 1470 , 1434 , 1285 , 1222 and 946 cm.^{-1} in the spectrum of diphenylthiocarbazide (see Table IV.22). Bands at 1483 and 1437 cm.^{-1} are shifted on deuteration and can be tentatively assigned as coupled modes consisting of ν_{CN} and β_{NH} . Bands at 1220 and 897 cm.^{-1} are apparently unchanged on deuteration and can be assigned as coupled modes involving at least ν_{CS} and ν_{CN} while bands at 1180 and 1150 cm.^{-1} which are shifted are possibly NH deformation modes.

Bellamy and Rogasch⁵⁶ have outlined a method for identifying bands due to the C:S group by solvent studies. When the thiocarbonyl group is the only major polar group present it should give rise to the only bands which are at all solvent sensitive. However, the presence of polar imino groups in dithizone will result in a more complicated dependence on the solvent. The other limiting factor will be the extent to which C:S stretching and N.H deformation modes are coupled, as this will also complicate the solvent dependence of the spectrum.

Bands observed in the vicinity of 1200 cm.^{-1} for dithizone in a range of solvents are given in Table IV.24. The band at 1220 cm.^{-1} and that at 1150 cm.^{-1} are shifted to lower frequencies in polar or

basic solvents which is in agreement with their being assigned as coupled modes involving ν_{CS} and NH deformation respectively.

TABLE IV.24

Solvent Shifts of Some Infrared Absorption Bands
of Dithizone

Solvent	cm. ⁻¹			
CHCl ₃	1250	1217	1175	1145
CH ₂ Cl ₂	1243	1217	1175	1143
Cl ₂ C:OCl ₂	1250	1217	1175	{ 1150 1132
CH ₃ CN	1248	1215	1175	1138
CS ₂	1244	1214	1175	1130
CH ₃ I	-	1212	1175	1135
THF	1244	1209	-	1129
py	1253	1205	1175	1129

The absence of any detectable shift in the band at 1175 cm.⁻¹ suggests that it is not due to a vibration of a polar group and is therefore unlikely to be an N.H deformation mode.

The solvent dependence of the band at 897 cm.⁻¹ could not be studied as the solvents tried absorb too strongly in this region.

Although no sharp N.H stretching bands are observed analogous to those of diphenylthiocarbazine it is possible to detect a weak and rather broad absorption at 3220 cm.⁻¹ in carbon disulphide, 3210 cm.⁻¹ in chloroform and 3160 cm.⁻¹ in carbon tetrachloride. These bands are assigned as the N.H stretching vibrations broadened by some form of hydrogen bonding.

The absence of a detectable S.H stretching vibration from the spectrum in all of the solvents that were tried would suggest that dithizone exists as the thioketo tautomer in solution as well as in the solid state. These results do not, however, preclude the existence of the thioenolic tautomer they merely suggest that the thioketo form predominates.

The stretching frequency of the azo group has been studied by Le Fèvre and co-workers^{57,58}, Ueno⁵⁹ and more recently by Bassignana and Cogrossi⁶⁰ who assigned the $\nu_{N:N}$ mode to the region $1410 \pm 30 \text{ cm.}^{-1}$. In the spectrum of dithizone there are two bands which could be attributed to $\nu_{N:N}$, these are at 1412 cm.^{-1} and $1390\text{--}1405 \text{ cm.}^{-1}$. The latter band has a slightly higher wavenumber when measured using the KBr disc technique.

Apart from the bands due to the monosubstituted benzene ring at $1592, 1512, 1495, 1455, 1108, 1080, 908, 751$ and 679 cm.^{-1} it has been possible to make certain other assignments which are summarised in Table IV.25. It should now be possible to interpret the infrared spectra of derivatives of dithizone and obtain confirmation or otherwise of the validity of these assignments.

IV.5.ii. Potassium Dithizonate.— Bands observed in the infrared spectra of the potassium salt of dithizone together with those of the other derivatives to be discussed are given in Table IV.26.

No ν_{NH} vibration was detected for KHDz but this may have been because of the presence of a broad ν_{OH} band due to hydroxide impurities. The coupled ν_{CN} and β_{NH} modes at 1483 and 1439 cm.^{-1} are apparently

TABLE IV.25

Infrared Band Assignments for Dithizone

Band (cm.^{-1})	Assignment
1483	νCN & βNH
1439	νCN & βNH
1421 or 1390-1405	$\nu\text{N:N}$
1260	νCN & ?
1220	νCN & νCS
1180	νCN & ?
1150	NH deformation
897	νCS

raised to 1512 and 1461 cm.^{-1} respectively while bands at 1260 and 1220 cm.^{-1} are respectively raised to 1284 cm.^{-1} and lowered to 1212 cm.^{-1} . The changes in the first three bands can be explained by an increase in the CN bond order while the lowering of the band at 1220 cm.^{-1} can be ascribed to the lower CS bond order. The shift of the band at 897 cm.^{-1} to 690 cm.^{-1} is also explained by the lower CS bond order. The band at 1372 cm.^{-1} in KHDz is tentatively assigned as $\nu\text{N:N}$.

IV.5.iii. S-Methyldithizone.- The compound, 3-methylthio-1,5-diphenylformazan, is known to exist in solution as two configurational isomers (see p. 3). In the infrared spectrum of the solid we were unable to detect any N.H stretching vibration. However, in chloroform, carbon disulphide and carbon tetrachloride solution bands occur at 3,334 cm.^{-1} , 3,326 cm.^{-1} and 3,338 cm.^{-1} respectively which can be assigned as νNH . A subsidiary band occurs in each solvent at 3,240 cm.^{-1} , 3,236 cm.^{-1} and

TABLE IV.26

Infrared Absorption Bands of Potassium dithizonate,
S-Methyldithizone and Dehydrodithizone

KHDz	S-Methyl HDz	Dehydro Dz
		3055 w
		3012 w
2920 w	2920 w	2935 w
1600 s	1603 s	1585 w
1512 s	1525 s	1484 s
1504 sh	1503 s	
1461 sh		
1453 s	1453 m	1457 m
	1433 m	
	1422 m	1395 w
1372 m	1377 s	1375 w
	1318 sh	1328 s
1310 w	1306 m	1300 sh
1284 m	1258 s	1257 m
1212 s	1212 m	
1172 sh	1180 w	1183 w
1160 w	1165 w	1170 w
	1153 w	
1130 s	1142 m	1120 m
	1101 s	
	1090 sh	
1080 m	1070 m	1078 m
	1020 w	1025 w
	1000 w	984 s
	970 m	979 sh
	960 sh	930 w
	917 w	917 m
	891 s	
	882 sh	
	866 m	
	834 m	833 m
770 sh	790 w	772 s
760 w	767 s	762 s
746 s	749 s	
690 m	686 s	685 s
685 m	677 s	678 s
	665 m

Figure IV.5.- Infrared absorption spectrum of 3-methyldithizone
 in : A, CHCl_3 after 1, 5 min., 2, 20 min.,
 3, 10 hr; B, CS_2 after 1, 2 min., 2, 12 hr;
 C, CCl_4 .

and $3,248\text{ cm}^{-1}$, which increases in intensity with time while the shorter wavelength band decreases (see Figure IV.5). The positions of both bands in chloroform solution were observed to be independent of the solute concentration in the range 0.01 M to 0.2 M.

The solutions, which are initially violet, turn yellow-brown due to a change of configuration. The lowering of the N.H stretching vibration and the concentration independence of the N.H bands suggests that the configurational change involves the formation of an intramolecular hydrogen bond.

In the solid state spectrum, the coupled mode at 1483 cm^{-1} is raised to 1525 cm^{-1} due to the increased CN bond order. The most interesting change, however, occurs in the band at 1220 cm^{-1} which is lowered to 1212 cm^{-1} . In carbon disulphide this band is initially at 1218 cm^{-1} but is gradually replaced by a second band at 1195 cm^{-1} . This shift is presumably caused by the formation of the intramolecular hydrogen bond and suggests that the mode involves either the Ph.N.H group or the azo group. There is apparently no shift in the band at 897 cm^{-1} attributed in part to ν_{CS} , although a new band does appear at 686 cm^{-1} which can be reasonably assigned as ν_{CS} for the S-methyl derivative.

IV.5.iv. Dehydrodithizone.- Dehydrodithizone can be formulated as a tetrazolium thiobetaine (see p. 3) so that its infrared absorption spectrum should be similar to those observed for related tetrazoles.

The characteristic infrared absorption bands of the tetrazole ring and of 5-mercaptotetrazoles have been studied by Lieber and

co-workers^{61,62}. A band was observed at approximately 1300 cm^{-1} and attributed to the cyclic N.N:N group, three skeletal modes were observed between 1090 cm^{-1} and 980 cm^{-1} and a vibration due to the C.S.C group was observed in the vicinity of 680 cm^{-1} .

Bands observed at 1328 cm^{-1} and 984 cm^{-1} for dehydrodithizone can be assigned as those due to the cyclic N.N:N group and to a skeletal vibration of the tetrazole ring. Both of the coupled modes involving the NH group, at 1483 and 1439 cm^{-1} , are absent as are the three strong bands at 1220 , 1180 and 1150 cm^{-1} and the ν_{CS} absorption at 897 cm^{-1} . These observations substantiate the assignments made for dithizone since there are no N.H groups in dehydrodithizone and the CS bond order should have decreased. Apart from the two bands mentioned above there are bands of medium intensity at 1257 cm^{-1} and 1120 cm^{-1} which may involve both ν_{CN} and ν_{CS} and another at 685 cm^{-1} which we can assign as ν_{CS} . In the S-methyl iodide derivative of dehydrodithizone, the bands at 1257 , 1120 and 984 cm^{-1} are replaced by bands of comparable intensity at 1187 , 1157 and 1003 cm^{-1} respectively.

IV.5.v. Infrared Spectra of the Metal Dithizonates.-

1. The Primary Dithizonates.- The infrared absorption spectra of the primary dithizonates have been measured in the solid state as mulls and as KBr discs. Bands for which reasonable assignments can be made are given in Table IV.27. The infrared absorption spectra of $\text{Zn}(\text{HDz})_2$ and its deuterio analogue are shown in Figure IV.6. The spectrum of $\text{Zn}(\text{HDz})_2$ is in reasonable agreement with previously published spectra¹⁻³ as are those of the other metal dithizonates.

Figure IV. b.-

Infrared absorption spectra of zinc dithizonate (solid curve) and zinc dithizonate- d_2 (dashed curve).

Spectra have also been measured in chloroform solution but the only differences observed were small shifts in bands due to N.H stretching.

The N.H stretching vibration for each of the metal complexes has approximately the same frequency as the shoulder observed for dithizone in solution in chloroform, carbon disulphide and carbon tetrachloride.

The band at approximately 1520 cm.^{-1} can be assigned as the 1483 cm.^{-1} band of dithizone shifted to higher wavenumbers due to the increased CN bond order. This behaviour is analogous to that observed for both potassium dithizonate and S-methyldithizone.

Bands at 1260 cm.^{-1} and 1220 cm.^{-1} in dithizone are shifted to higher and to lower wavenumbers respectively in all of the complexes except those of Ni(II) , Pd(II) and Au(III) . The shorter wavelength band is partly due to NCN and is raised in the metal complexes for the same reason as the band at 1483 cm.^{-1} is raised. The longer wavelength band due in part to NCS is lowered by the decrease in the C.S bond order.

The differences observed for the dithizone complexes of the nd^8 metal ions have previously been explained (see p.108) as being due to a difference in structure, with the metal ion coordinating to four nitrogen donor atoms rather than to two nitrogen and two sulphur donors. This would explain the shift to higher frequencies of the 1220 cm.^{-1} band of dithizone if the band were mainly NCS . We prefer to explain the experimental observations in terms of a greater increase in the CN bond order for the dithizonates of the nd^8 metal ions due to a difference in configuration rather than structure. If the 1220 cm.^{-1} band involves both NCS and NCN then the large increase in the CN bond order may

	ν_{NH}	$\nu_{\text{CN}} \text{ \& } \beta_{\text{NH}}$	ν_{CN}	$\nu_{\text{CS}} \text{ \& } \nu_{\text{CN}}$	ν_{CS}
Zn(II)	3213 m	1523 s	1274 s	1204 s	715 m
"	(2372 m)	(1495 s)	(1275 sh)	(1197 s)	(712 m)
					727 m
Cd(II)	3214 m	1523 s	1280 m	1205 s	709 w
					731 w
Hg(II)	3230 m	1525 s	1275 s	1191 s	720 w
					731 sh
Hg(I)	3230 br.w	1525 s	1259 s	1187 s	703 w
					730 m
Cu(II)	3225 m	1520 s	1283 m	1215 s	710 m
Cu(I)	3160 sh	1510 s	1260 br	1190 s	707 sh
Ag(I)	3190 w	1520 br	1260 br	1195 m	720 sh
Tl(I)	3172 m	1512 m	1267 br	1203 s	708 w
	3285 m				
Sn(II)	3211 m	1524 s	1280 sh	1209 s	708 w
Pb(II)	3215 m	1524 s	1280 s	1208 s	707 w
					708 sh
Sb(III)	3175	1520 br	1254 sh	1204 s	725 sh
	3245 sh				
Bi(III)	3221 m	1510 s	1271 s	1200 s	730 sh
Mn(II)	3180 w	1512 s	1268 sh	1197 m, br	709 w
				1205 sh	
Fe(II)	3188 m	1508 s	1280 s	1190 s	710 sh
	3230 w				
Co(II)	3190 w	1524	1289 m	1204 s	709 m
					720 sh
Co(III)		1517 br	1245 sh	1185 s	705 sh
					732 m
Ni(II)	3250	1528 s	1287 m	1236 s	712 m
"		(1515 m)	(1273 m)	(1200 s)	
					731 sh
Pd(II)	3224 b	1527 s	1300 m	1236 s	712 sh
					729 sh
Pt(II)	3240 m	1520 s	1273 m	1215 s	711 m
				1220 sh	730 sh
Au(III)	3234 w	1532 s	1287 m	1229 s	712 m

^b This value is for a chloroform solution of $\text{Pd}(\text{HDz})_2$.

nullify any lowering due to a decrease in the C.S bond order, as has already been observed for the 930 cm.^{-1} band of thiocarbohydrazide. This can also explain the larger shifts to higher frequencies for other bands involving νCN , at 1484 cm.^{-1} and 1260 cm.^{-1} .

The 897 cm.^{-1} band of dithizone is absent from the spectra of the metal complexes and either one or two new bands appear in the region from 700 cm.^{-1} to 730 cm.^{-1} which may be attributed to νCS .

Infrared spectra of the deuterated complexes Ni(DDz)_2 and Zn(DDz)_2 were measured in the solid state. The band at approximately 1520 cm.^{-1} is shifted to lower frequencies in both complexes and confirms the assignment of this band as a coupled mode involving mainly νCN with some βNH . Bands at 1236 cm.^{-1} in Ni(HDz)_2 and 1204 cm.^{-1} in Zn(HDz)_2 are lowered by 36 cm.^{-1} and 7 cm.^{-1} respectively, indicating that they probably involve some contribution from an N.H deformation vibration.

In conclusion it appears that the primary dithizonates retain their solid state configuration in solution and that this involves coordination through the thioenolic sulphur atom as has been shown for the Hg(II) , Cu(II) and Zn(II) complexes from X-ray crystallographic studies.

2.. The Secondary Dithizonates.— The infrared spectra of the secondary dithizonates of Cu(II) , Hg(II) , Au(III) , Tl(I) and Ag(I) were measured in the solid state as both mulls and as KBr discs. Broad, poorly resolved bands were observed indicating that the complexes are either polymers or strongly conjugated monomers. No νNH vibration nor any band in the vicinity of 1520 cm.^{-1} was detected confirming previous observations for

$\text{CuDz}^{1,2}$ and suggesting that the complexes involve the doubly charged dithizonate anion formed by the removal of the second N.H proton.

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CHAPTER V

A PROTON MAGNETIC RESONANCE STUDY
OF THE DITHIZONE SYSTEMV.1. Introduction

It has been shown that there are four possible configurational isomers for each of the tautomers of dithizone (see structures I-VIII on p. 28). One possible way to distinguish between the syn and anti isomers is to use the fact that only the syn isomer should be capable of intramolecular hydrogen bonding.

Harding has shown¹ that the trans-anti form of the thioketo tautomer exists in the solid state and has found no evidence for the presence of the thioenolic tautomer. The infrared spectrum of dithizone in the solid state (p. 84) confirms this and also suggests the presence of strong hydrogen bonding. However, it is not possible to tell whether this is inter or intramolecular hydrogen bonding. Again, there is no infrared evidence for the presence of the thioenolic tautomer in solution, but there are indications of strong hydrogen bonding.

The trans-anti configuration adopted by dithizone in the solid state is more likely to be involved in intermolecular hydrogen bonding, but in solution either one or both types of hydrogen bonding would be feasible. It was hoped that a study of the proton magnetic resonance spectrum of dithizone would show which type of hydrogen bonding was present in solution and thus indicate which of the isomeric species was present.

Derivatives of dithizone and of a number of related amides and thicamides have been studied so that chemical shifts could be correctly interpreted.

The proton n.m.r. spectra of the metal dithizonates have also been investigated.

There were three difficulties in this work. The first was that we were unable to find an inert solvent that was common to all of the compounds investigated. However, in some cases a particular compound could be studied in more than one solvent, thus giving an indication of those bands which were solvent sensitive. The second difficulty was the instability of most of the compounds in solution, which together with the use of a high resolution instrument operating at maximum gain, meant that caution was required before making proton assignments. Finally, the proton magnetic resonance spectra of hydrazine and its alkyl derivatives have been shown to give broad N.H signals² similar to those obtained in this investigation. This broadening, attributed to coupling between the proton and nitrogen quadrupoles, makes the detection of the N.H proton more difficult.

V.2. Experimental

Measurements were made using a Varian Associates, D.P.60 spectrometer. Chemical shifts were measured in c.p.s. from tetramethylsilane as the internal reference, using the side-band technique. Measurements can be made to ± 0.1 c.p.s. at 60 Mc./sec. The temperature of the probe, unless stated otherwise, was 20°C.

Deutero solvents were obtained from E. Merck while the remainder were 'B.D.H.' solvents distilled immediately before use.

Labile protons were deuterated by adding a drop of D_2O to the solution and then shaking for a few minutes.

V.3. Results and Discussion

V.3.i. Dithizone.— The chemical shifts observed for dithizone and some related amides and thioamides are given in Table V.1.

In compounds with a phenyl group, bands which occur at approximately 450 c.p.s. are attributable to phenyl protons³. The remaining bands are therefore due to protons bonded to either nitrogen or sulphur, or to both. This is confirmed by their disappearance on the addition of D_2O , since it is just such protons which are known to be labile⁴.

In dithizone the problem is to decide the exact nature of these protons since, ignoring geometrical isomerism and hydrogen bonding, the following three environments are possible,

I

II

III

A total of ten different solvents were tried with dithizone but only in those given in Table V.1 was it sufficiently soluble to observe meaningful spectra. In carbon disulphide, carbon tetrachloride, methylene chloride, acetone and pyridine it was either too insoluble or decomposed too rapidly.

TABLE V.1

Chemical Shifts for Dithizone and Related
Amides and Thioamides

Compound	Solvent	Chemical Shift (c.p.s.)	
Thiourea	acetone-d ₆	420*	
s-Diphenylurea	"	500*	471-464-451-443-438-431
s-Diphenylthiourea	"	560*	467-460-452-444-440-428
Carbohydrazide	DMS	457*	294*
Thiocarbohydrazide [†]	"	540*	280*
s-Diphenylcarbazine	acetone-d ₆	480*	438-428-417-412 345*
s-Diphenylthiocarbazine	"	555*	435-417-411
s-Diphenylcarbazone	"	586*	478-463-423 358*
Dithizone	CDCl ₃	760*	462-445
"	THF	765*	462-445
"	DMS		466-444-411
"	Sulpholane		457-444-410

* Bands which disappear on deuteration.

[†] The N.H and N.H₂ bands were very broad in this spectrum, having half-band widths of approximately 140 and 70 c.p.s. respectively. The corresponding values for carbohydrazide were 30 and 25 c.p.s.

First we will consider the n.m.r. spectra of the compounds listed in Table V.1 which are related to dithizone.

Diphenylcarbazine (Ph.HN.HN.C(O).NH.NH.Ph) has two bands, at 345 and 480 c.p.s., which can be assigned as the Ph.N.H and C(O).N.H protons respectively. These assignments are based on the spectrum observed for carbohydrazide (H₂N.HN.C(O).NH.NH₂) together with the shifts observed for the amide protons of urea and thiourea on forming their s-diphenyl derivatives.

Figure V.1.- Proton n.m.r. spectra of A, thiourea and B, s-diphenylthiourea in deuterioacetone.

Figure V.2.- Proton n.m.r. spectra of A, thiocarbohydrazide and B, s-diphenylthiocarbazine in deuterioacetone.

Figure V.3.- Proton n.m.r. spectrum of dithizone in deuteriochloroform.

The N.H proton of phenylhydrazine is observed as a band at 340 c.p.s. in the pure liquid, in agreement with our assignment for the Ph.N.H proton of *s*-diphenylcarbazide.

Diphenylcarbazone ($\text{Ph.HN.HN.C(O).N:N.Ph}$) has a broad band at 358 c.p.s. but none at 480 c.p.s., although a new band appears at 586 c.p.s. This new band could be either the O.H proton of the enolic tautomer or a hydrogen bonded N.H proton.

Figures V.1-3 show the n.m.r. spectra of thiourea, *s*-diphenylthiourea, thiocarbonylhydrazide, *s*-diphenylthiocarbazide and dithizone.

In the spectrum of thiocarbonylhydrazide the band at 540 c.p.s. is assigned as the C(S).N.H proton, as the intensity is approximately half that of the N.H_2 band at 280 c.p.s. In *s*-diphenylthiocarbazide the C(S).N.H band is at 555 c.p.s. but no Ph.N.H band is observed. This may be explained if we consider a shift comparable to the 140 c.p.s. shift found with thiourea and *s*-diphenylthiourea. This would lower the broad band at 280 c.p.s. in thiocarbonylhydrazide to approximately 420 c.p.s. in *s*-diphenylthiocarbazide, where it would be masked by the bands due to the phenyl protons.

The spectrum of dithizone in deuteriochloroform (see Figure V.3) shows a broad band at 760 c.p.s. but no band corresponding to either the C(S).N.H band of *s*-diphenylthiocarbazide or to the Ph.N.H band of *s*-diphenylcarbazone. The large shift for the observed band indicates that some form of intra or intermolecular interaction is taking place. A similar band is observed at 765 c.p.s. in tetrahydrofuran which suggests that the band is not due to solute-solvent interaction. The spectrum in

deuteriochloroform was found to be independent of the temperature for the range 20° - 60°C and also independent of the concentration of solute in the range 0.025 M to 0.13 M. The absence of any measurable shift of the band with increasing solute concentration would be expected for intramolecular interaction but not for intermolecular interaction⁵.

These results can be explained by the formation of an intramolecular hydrogen bond, as shown (IV), between the Ph.N.H proton and

IV

the azo group. Although the structure shown is that of the thioketo tautomer there is no reason to suppose that the thioenol tautomer is absent. We have been unable to distinguish between environments II and III, as no second N.H band was detected nor was a band observed in the region expected for an S.H proton^{6,7} from 100-200 c.p.s.

V.3.ii. S-Methyldithizone.- The compound 3-methylthio-1,5-diphenylformazan was investigated in some detail as it is sufficiently soluble in a wide range of solvents and can also be isolated as a pure crystalline solid more readily than the parent compound dithizone.

It is observed to undergo a slow colour change from violet to yellow-brown on dissolving in non-polar solvents which are unlikely to be

involved in strong hydrogen bonding, and a more rapid colour change in polar solvents capable of hydrogen bonding.

In Table V.2, the chemical shifts observed for S-methyldithizone in a number of different solvents are given.

TABLE V.2

Chemical Shifts for S-Methyldithizone

Solvent	Chemical Shift (c.p.s.)				
CDCl_3	617*	570*	474-444-436	148	139
CH_2Cl_2 $\neq$			444-434-426		139
C_2Cl_4	630*		474-444-434	148	
THF	643*	589*	474-440-432	148	139
DMS $\neq$	696*	640*	474-440-430		
CF_3COOH $\neq$			474-440-430	148	

* Bands which disappear on deuteration.

$\neq$ Solvent bands prevented the identification of some of the bands for the solute.

The spectrum of S-methyldithizone in deuterochloroform shows two sharp singlets for both the methyl and the N.H groups rather than the expected single peak for each (see Figure V.4.). The integral of this spectrum gave the relative intensities of the three distinct regions of absorption as 1.0 : 10.1 : 3.0 (± 0.2). This agrees with the two singlets at 617 and 570 c.p.s. being assigned to the N.H proton with the ten phenyl protons at 474-436 c.p.s. and the methyl protons at 148 and 139 c.p.s.

Figure V.4.- Proton n.m.r. spectrum of S-methyldithizone in deuteriochloroform.

The relative intensities of the two singlets at 148 and 139 c.p.s. in deuteriochloroform slowly changed with time, the low field singlet increasing while the high field singlet decreased. A similar change occurred with the two singlets at 570 and 617 c.p.s., the low field singlet becoming more intense.

On the addition of a drop of CF_3COOH to the deuteriochloroform solution a rapid change occurred and the high field methyl singlet disappeared completely. Apparently, there is a change from one form to another occurring in solution, with the conversion being catalysed by hydrogen bonding solvents.

Kuhn has reported⁸ four geometrical isomers for triphenylformazan (V). The trans-syn and cis-syn isomers, which are red, and the yellow trans-anti and cis-anti forms.

The conversion from the 'red' to the 'yellow' isomers occurring in the presence of visible light.

The results for S-methyldithizone can be explained in terms of a similar change, the violet trans-anti form VI being converted to the yellow-brown trans-syn form VII in solution.

The molecule is evidently stabilised in the solid state by intermolecular hydrogen bonding whereas in solution, as the monomer, it is converted to the trans-syn form which is the more stable because of intramolecular hydrogen bonding. This is analogous to the hydrogen bond formed by dithizone in solution in deuteriochloroform and in tetrahydrofuran.

That portion of the spectrum due to the phenyl protons is observed to broaden as more of the trans-syn isomer is formed (see Figure V.4), due to the increased ability of the two aromatic ring systems to couple.

No shifts were observed in the spectrum in deuteriochloroform when either the concentration of the solute was increased from 0.02 M to 0.2 M or when the temperature was raised from 20° to 60°. This eliminates the possibility of intermolecular hydrogen bonding.

An n.m.r. study of some N,N-disubstituted acetamides⁹ showed that the bulkier substituent on nitrogen is trans to the acetyl methyl group in the preferred isomer. Le Fèvre¹⁰ has confirmed this with some dipole moment measurements. The similarity of the acetamide skeleton (VIII, IX) to S-methyldithizone suggests that the violet

trans-anti isomer (VI) would be preferred, as is found in the solid state. The ability of the monomer, in solution, to form the trans-syn isomer (VII) being due to the additional stability gained through hydrogen bonding.

VIII

IX

Evidence that this interpretation is reasonable is also obtained from the observed separation of the two methyl singlets in VI and VII. The value of 11 c.p.s. being close to the values of the order of 10 c.p.s. reported for VIII and IX.

V.3.iii. The Metal Dithizonates.— In Table V.3, the chemical shifts observed for the protons in potassium dithizonate and each of the metal dithizonates investigated are given together with the solvent used.

The n.m.r. spectra of the metal dithizonates can be grouped into five classes.

Class 1.— Potassium dithizonate and the diamagnetic, primary dithizonates of Zn(II), Cd(II), Hg(II), Sn(II), Pb(II), Bi(III), Cu(I), Ag(I) and Hg(I) all have a band in the region 500–700 c.p.s. See for example the spectrum of Zn(II) dithizonate in Figure V.5.

Figure V.5.- Proton n.m.r. spectrum of zinc(II) dithizonate in deuteriochloroform.

TABLE V.3

Chemical Shifts for the Metal Dithizonates

Compound	Solvent	Chemical Shift (c.p.s.)	
KHDz	DMS	626*	458-446-430-415
Zn(HDz) ₂	CDCl ₃	601*	470-454-440-434
"	DMS	611*	442
"	THF	637*	446-434
Cd(HDz) ₂	DMS	616*	447
Hg(HDz) ₂	DMS	651*	462
Sn(HDz) ₂	CDCl ₃		454-440-418-408
"	DMS	592*	454-441-412-402
Pb(HDz) ₂	DMS	598*	455
Bi(HDz) ₃	CDCl ₃	536*	450-440
"	DMS	622*	460-430
CuHDz	DMS	608*	440
AgHDz	DMS	603*	466-431
HgHDz	DMS	646*	460-444
TlHDz	CDCl ₃	573*	440
"	DMS	592*	456-440
Ni(HDz) ₂	DMS	1200	585 447 411 337 267
Pd(HDz) ₂	DMS		455-440
Pt(HDz) ₂	DMS		460-440
Au(HDz) ₃	DMS		460-440
Mn(HDz) ₂ , Fe(HDz) ₂	{ DMS CDCl ₃	Broad phenyl band	
Co(HDz) ₂ , Cu(HDz) ₂		centred at 450	
HgDz, CuDz, Tl ₂ Dz	DMS	Phenyl band only	
SbCl ₃ -H ₂ Dz	DMS	460-450	340-240*

* Band disappeared on deuteration.

The Zn(II) and Hg(II) complexes have been shown (see Chapter III) to contain the thioenolic tautomer of dithizone. Therefore we can attribute the bands at 611 and 651 c.p.s. respectively in dimethylsulphoxide to the Ph.N.H protons of these two complexes and the presence of a band in this region for the remaining complexes suggests that they are structurally similar .

An indication of the effect of the solvent was obtained by studying the Zn(II) complex in dimethylsulphoxide, tetrahydrofuran and deuteriochloroform and the complexes of Tl(I), Sn(II) and Bi(III) in dimethylsulphoxide and deuteriochloroform. The spectra obtained indicate that the N.H proton is shifted to lower fields as the solvent becomes more strongly hydrogen bonding.

No effect was observed for an increase in temperature from 20°-60° for Zn(II) dithizonate in deuteriochloroform. In particular, the absence of any marked shift in the N.H band suggests that there is no intermolecular solute-solute interaction.

The large chemical shift of 626 c.p.s. for potassium dithizonate in dimethylsulphoxide can be explained as an intramolecular, hydrogen bonded Ph.N.H and may be compared with the band observed at 696 c.p.s. for S-methyldithizone in the same solvent. The free Ph.N.H proton would be expected to have a band at approximately 570 c.p.s. if the change in the chemical shift on hydrogen bonding were comparable to that observed in the S-methyl derivative. The value of 570 c.p.s. is in reasonable agreement with the free Ph.N.H band observed for the metal complexes.

Figure V.6.- Graph showing the correlation between the chemical shift (δ) for the imino proton and the log of the overall stability constant (β_n).

A definite trend is now apparent in the magnitude of the chemical shift for the Ph.N.H proton. There is an increasing shift to lower fields as we go from the dithizonate anion, present in the potassium salt, to the covalently bound metal complexes. The largest shift being observed for $\text{Hg}(\text{HDz})_2$ which is where we would expect to find the strongest covalent bond.

In Figure V.6 the chemical shift (δ), for the Ph.N.H proton, is plotted as a function of the log of the overall stability constant (β_n). The values for β_n are those determined by Pilipenko¹¹ using a spectrophotometric method, and include a term P, the distribution coefficient for the complex between two phases. However, Pilipenko's values are in reasonable agreement with those of subsequent workers¹²⁻¹⁶. The experimental error in the value of δ is indicated by a vertical bar. The errors in the values of β_n are more difficult to gauge although, they are probably at least comparable to that in δ . A linear relationship is shown to exist between $\log \beta_n$ and δ , the shift to lower fields increasing as β_n increases.

Class 2.— The paramagnetic, primary dithizonates of Mn(II), Fe(II), Co(II) and Cu(II) have spectra with only the one broad band, with half band widths > 100 c.p.s.

Class 3.— The primary dithizone complexes of Pd(II), Pt(II) and Au(III) have spectra in which only the bands of the phenyl protons are observed. The spectrum of the Ni(II) complex in dimethylsulphoxide is complicated (see Figure V.7), as it is temperature dependent and has a band as low as 1200 c.p.s. This result is explained by a change in the spin state

Figure V.7.- Proton n.m.r. spectrum of nickel(II) dithizonate in dimethylsulphoxide.

of the Ni(II) ion. Ni(II) dithizonate is a diamagnetic square planar complex in the solid state, but can be isolated as a crystalline paramagnetic complex from pyridine solution. The n.m.r. spectrum in dimethylsulphoxide suggests that the Ni(II) ion is being converted to the high spin octahedral state which thus causes large contact interaction shifts. Similar effects have been observed for paramagnetic Ni(II) and Co(II) acetylacetonates in pyridine-type bases¹⁷.

The absence of any N.H band in the spectra of the Pd(II), Pt(II) and Au(III) dithizonates and the nature of the spectrum of Ni(II) dithizonate suggests that they may be bonded differently to those in classes 1 and 2.

A recent infrared investigation¹⁸ of metal dithizonates indicated differences in the structures of the Ni(II), Pd(II) and Pt(II) complexes as compared with those similar to the Hg(II) complex.

A determination of the formation constants of the Zn(II) and Ni(II) complexes of dithizone and some o- and p-substituted dithizones led Freiser and co-workers¹³ to postulate structure X, involving a planar five membered ring for Ni(II) with four nitrogen donor atoms.

An earlier report¹⁹ on the structures of some Ni(II) formazans agrees with Ni(HDz)₂ being nitrogen bonded, although these workers favoured the six membered ring structure XI.

X

XI

Our results may be explained by structures such as X or XI, involving nitrogen coordination to Ni(II), Pd(II), Pt(II) and Au(III). However, it is also possible that they have a structure similar to that of the dithizonates of class 1, involving nitrogen and sulphur donor atoms (see the structure of $\text{Hg}(\text{HDz})_2$ on p. 29), but having a different stereochemistry.

Class 4.— The 'secondary' dithizonates have spectra with only one broad band due to the phenyl protons. No band attributable to an N.H proton was observed. This is as expected from their infrared spectra, where no N.H vibration is observed, and it also agrees with their being either polymeric or highly conjugated species.

Class 5.— The adduct formed by dithizone with the Lewis acid, SbCl_3 , has a spectrum with a concentration dependent band in the range 240–340 c.p.s. The band is broad and from the relative intensity appears to be due to both N.H protons of dithizone. The dilution shift of the band to higher fields indicates some form of intermolecular bonding.

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CHAPTER VI

ELECTRONIC ABSORPTION SPECTRA

VI.1. Introduction

VI.1.i. Dithizone.- The visible and ultraviolet absorption spectra of dithizone, its oxidised and reduced forms, and their respective oxygen analogues were first seriously studied by Grammaticakis¹.

A comparison of these absorption spectra with those of related azo compounds and formazans led him to conclude that in alcoholic solution dithizone resembled the latter, so that in the tautomeric equilibrium between the thioketo (I) and thioenol (II) forms ($R_1 = R_2 = \text{Ph}$), II is the more important.

I

II

This tautomeric equilibrium has since been investigated by Pel'kis and co-workers²⁻⁴ who studied the effect of the solvent and the electron withdrawing properties of substituents on the phenyl rings ($R_1 = \text{Aryl}$, $R_2 = \text{Aryl}'$). Values of pK_T for dithizone, where

$$pK_T^a = -\log \frac{[\text{Thioketo (I)}]}{[\text{Thioenol (II)}]},$$

^a Reference to this work was only available through the abstract which appears to contain an anomaly in that pK_T is defined as $-\log [\text{Thioenol}] / [\text{Thioketo}]$. Math, Fernando and Freiser (Analyt. Chem., 36, 1762 (1964)) determined values of pK_T for dithizone in H_2O /Dioxane using the method of Pel'kis, but with the correct formula.

were apparently determined at room temperature only and varied from 2.35 in chloroform to 0.85 in methanol. These values are based on the assignment² of a band at approximately 22,000 cm.⁻¹ to the thioenol tautomer and a band at approximately 16,000 cm.⁻¹ to the thioketo tautomer, but the evidence for these assignments is not clear. It appears that considerable over-simplification of the system has occurred, the four possible isomers for each tautomer (see p.29) having been ignored.

The bands of most interest in the absorption spectrum of dithizone are transitions of the azo and thioketo groups of tautomer I and the bands of the formazan system of tautomer II.

In order to identify the transitions of the thioketo group, the spectra of simple thioamides and thiohydrazides will be considered first. Janssen⁵ and Sandstrom⁶⁻⁹ have shown, using simple LCAO-MO theory, that long wavelength low intensity bands ($E \sim 100$) in the spectra of these compounds may be assigned as $n \rightarrow \pi^*$ transitions, and a shorter wavelength more intense band ($E \sim 10,000$) as a $\pi \rightarrow \pi^*$ transition. Both bands are observed to undergo a hypsochromic (blue) shift with increasing solvent polarity, with the shift of the $n \rightarrow \pi^*$ transition being much larger. A bathochromic (red) shift is observed for both bands on conjugation with phenyl or acetyl groups. Shorter wavelength bands in the region 50,000 cm.⁻¹ to 43,000 cm.⁻¹ which undergo a hypsochromic shift with increasing solvent polarity have been assigned¹⁰ as $n \rightarrow \sigma^*$ transitions.

Hypsochromic shifts were observed⁸ for the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in going from a thioamide to its corresponding thiohydrazide.

The electronic absorption bands of the azo group have been studied by a number of workers¹¹⁻¹³, particularly in cis and trans-azobenzene, the absorption bands of which are given in Table VI.1. Included in this table are the absorption bands of their conjugate acids in 70% perchloric acid.

TABLE VI.1

The Electronic Absorption Bands for Cis and Trans-Azobenzene in C_6H_{12} and Their Conjugate Acids in 70% $HClO_4$ ^a

Compound	λ (cm. ⁻¹)								$n \rightarrow \pi^*$
trans-Azobenzene	48,540	44,440	43,670	42,550	31,650	30,400	28,900	22,520	
E_{max}	3.98	4.16	4.17	4.01	4.36	4.31	3.98	2.65	
conjugate acid	48,780		42,370	40,820	33,110		23,750		
E_{max}	3.76		3.85	3.67	3.38		4.47		
cis-Azobenzene	47,850			40,490	35,840		28,820	22,780	
E_{max}	4.01			4.08	3.68		2.60	3.10	
conjugate acid	48,310		43,480	40,650	33,900	29,670	23,920		
E_{max}	4.08		3.81	3.72	3.68	3.75	3.87		

^a Data is from reference (12).

Jaffé observed¹⁴ that the $n \rightarrow \pi^*$ transition of trans-azobenzene is insensitive to solvent effects. However, it has since been shown¹⁵ that there is a small hypsochromic shift with increasing polarity and hydrogen bonding ability of the solvent. The magnitude of the shift was smaller than that for the $n \rightarrow \pi^*$ of the thioketo group, as observed in ethylene trithiocarbonate.

The remaining bands to be considered in tautomer I are those due to the non-conjugated, monosubstituted, benzene ring. In benzene there are two allowed and one forbidden $\pi \rightarrow \pi^*$ transitions. These are observed to undergo bathochromic shifts when groups with lone pair electrons are substituted in the ring¹⁶. In particular, the shift of the two bands of longer wavelength has been shown to be characteristic of the substituent^{17,18}. The band maxima for benzene and aniline in water are given in Table VI.2.

TABLE VI.2

Electronic Absorption Bands of Benzene and
Aniline in Water ^a

	${}^1A_{1g} \rightarrow {}^1B_{1u}$	$E_{\max}$	${}^1A_{1g} \rightarrow {}^1B_{2u}$	$E_{\max}$
Benzene	49,140	3.87	39,370	2.31
Aniline	43,480	3.93	35,710	3.16

^a Data from reference (14).

The electronic absorption bands of the thioketo tautomer of dithizone should therefore be a composite of bands due to the thioketo, phenylazo and phenylthiohydrazide groups of the molecule. Bands due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thioketo group when conjugated with the phenylazo group, will be expected to undergo a bathochromic shift with respect to their positions in an unconjugated thioketone. It is more difficult to predict the shifts that might be expected for the corresponding transitions in azobenzene when a

conjugated thiocarbonyl group replaces one of the conjugated phenyl groups. However, the magnitude of any such shifts should be small. The bands of the phenylthiohydrazide group should be similar to those observed for aniline (see Table VI.2).

The thioenolic tautomer (II) has the formazan skeleton (III) shown below, so that its electronic absorption bands should bear a direct resemblance to those reported for other formazans¹⁹⁻²⁶. There

III

have been no detailed assignments for formazan absorption maxima published, although the intense, long wavelength band (see Table VI.3) can reasonably be assigned as a $\pi \rightarrow \pi^*$ transition of the conjugated azo group.

Where both 'red' and 'yellow' geometrical isomers are observed (see Table VI.3) the change in wavelength and intensity accompanying the conversion of the 'red' to the 'yellow' form parallels the change in converting trans-azobenzene to its conjugate acid (see Table VI.2).

TABLE VI.3

Electronic Absorption Bands of Some Formazans

Substituent R ₁ R ₂ R ₃			Solvent	$\lambda_{\max}$ (cm. ⁻¹)			Ref.
H	Ph	Ph	EtOH	38,460 [4.12]	35,090 [3.87]	23,810 [4.49]	22
H	Ph	Ph	EtOH	38,460 [4.10]	33,330 [3.79]	23,580 [4.36]	20
Ph	Ph	Ph	Benzene	'yellow'		24,630	24
				'red'		20,200	
CH ₃	Ph	Ph	Benzene	'yellow'		24,630 [3.15]	26
				'red'		20,080 [3.93]	

^a Values of $\log E_{\max}$ are given in square brackets.

Having discussed the absorption bands of the constituent groups of dithizone it now remains to interpret the spectra of dithizone in various media in terms of;

- the tautomeric equilibrium,
- the four possible geometrical isomers of each tautomer,
- the acid-base properties of each of the species, and
- the intra and intermolecular hydrogen bonding ability of each of the species.

VI.1.ii. The Metal Dithizonates.— The visible absorption bands of the metal dithizonates have received considerable attention due to the use of dithizone as an analytical reagent for metal ions. However, no attempt has been made to assign either their visible or their ultraviolet bands.

Irving and Cox observed²⁷ an approximately linear relationship between the wavelength of the intense visible absorption band for each

complex and the stability constant of the corresponding metal halide. This was considered to reflect the ability of the metal ion to form dative π -bonds. Irving, Gill and Cross²⁶ have investigated the electronic spectra of Ni(II) formazans and Ni(HDz)₂, but again no band assignments were made nor were any obvious conclusions drawn concerning any resemblance between the two systems.

VI.1.iii. Metal Thiocarbohydrazides.— Most metal ions coordinate to the uncharged form of thiocarbohydrazide, so that few similarities would be expected between the absorption spectra of the metal thiocarbohydrazides and the metal dithizonates. The metal thiocarbohydrazides are of interest, both as a new class of coordination compounds and because, like dithizone, thiocarbohydrazide has dual sites available for coordination to metal ions. The infrared absorption spectra of the metal thiocarbohydrazides suggest that they all coordinate through sulphur and nitrogen donor atoms. It should be possible to confirm this by studying their crystal field bands.

VI.2. Experimental

All spectra were measured on a Unicam SP 700 recording spectrophotometer. Absorption spectra of solutions were obtained using 1 cm. silica cells while reflectance spectra were obtained using an attachment described elsewhere²⁸, with MgCO₃ as the reference.

In the following tables, band frequencies enclosed in parentheses imply either a weak absorption or a shoulder.

VI.3. Results and Discussion

VI.3.i. Compounds Related to Dithizone.- The electronic absorption bands of some simple compounds containing the thioketo group are given in Table VI.4. The assignments are based on the relative intensities of the bands and their behaviour as the polarity of the solvent changes. With the exception of thiocarbohydrazide, absolute energies for the band maxima were not determined for these or any subsequent compounds studied.

In thiocarbohydrazide, it is possible to detect the weak $n \rightarrow \pi^*$ transition as a weak band at approximately $37,000 \text{ cm.}^{-1}$, but in the s-diphenyl derivative this band is presumably masked by the secondary band of the monosubstituted phenyl group. The most intense band in each spectrum is that assigned as the $\pi \rightarrow \pi^*$ transition of the thioketo group. Confirmation that this assignment is reasonable was obtained by a comparison of some of the compounds in Table VI.4 with the spectra of their oxygen analogues (see Table VI.5) which do not show this band.

The absorption bands of s-diphenylcarbazone are also listed in Table VI.5 as this enables the changes in the 'azide' spectrum to be investigated when an azo group is introduced.

Earlier studies of diphenylcarbazone^{1,29,30} included a comparison of its absorption spectrum in ethanol with that of N,N'-diphenylformazan in toluene. It was concluded that diphenylcarbazone existed mainly as the keto tautomer stabilised by the hydrogen bond formed between the lone pair of electrons of the oxygen and the hydroxylic solvent. In both carbon tetrachloride and toluene the appearance of two long wavelength absorption bands was ascribed to the presence of a mixture

TABLE VI.4
The Electronic Absorption Bands of Some Thioamides and
Thiohydrazides

Compound	Solvent	$n \rightarrow \sigma^*$	$\pi \rightarrow \pi^*$	$C:S$	λ (cm. ⁻¹) ^a	$C_6H_5 \cdot NH$ $1A_{1g} \rightarrow 1B_{1u}$ $1A_{1g} \rightarrow 1B_{2u}$
Thiourea	C_6H_{12}	45,500	43,000		(34,000)	
	EtOH	48,500	41,000		(35,000)	
	EtOH ^b		41,300 [4.11]		35,700 [2]	
	n-BuOH	46,700	41,000		35,500	
	H ₂ O	50,700	42,000			
s-Diphenylthiourea	C_6H_{12}	45,600	35,000		(42,500)	(38,000)
	EtOH	47,600	36,000		42,600	38,000
	n-BuOH	46,300	35,500		42,400	38,000
	n-BuOH	47,300	41,200			
Thiosemicarbazide	EtOH ^c		41,320 [4.1]			
Thiocarbonylhydrazide	EtOH	47,800	3.7 41,000 [4.1]		37,300 [2.6]	
	n-BuOH	46,700	41,200		35,100	
	H ₂ O	47,500	42,400		37,600	
	C_6H_{12}	45,300	(36,900)			35,500
s-Diphenylthiocarbamide	n-BuOH	46,700	40,400		42,900	(35,000)
	EtOH	47,100	41,500		43,600	(35,000)
	D.M.S.		(38,000)			(35,000)

^a Values for $\log E_{\max}$ are given in square brackets. ^b Data from reference (5).

^c Data from reference (8).

TABLE VI.5

The Electronic Absorption Bands of some Amides and Hydrazides

Compound	Solvent	$C:O$ $\pi \rightarrow \pi^* \quad n \rightarrow \pi^*$	$C_6H_5.NH$ ${}^1A_{1g} \rightarrow {}^1B_{1u} \quad {}^1A_{1g} \rightarrow {}^1B_{2u}$	λ (cm. ⁻¹) ^a	$C_6H_5.N:N.C(O)$
Urea	EtOH	49,000 (45,000)			
s-Diphenylurea	EtOH	48,600 (45,000)	38,700		
	n-BuOH	46,200 (45,000)	38,400		
Carbohydrazide	EtOH	48,100 (45,000)			
	H ₂ O	49,000 (44,000)			
s-Diphenylcarbazine	EtOH ^b	48,800	42,500	35,000	
	EtOH		42,370 [4,31]	35,000 [3,48]	
	n-BuOH	46,900	42,300	35,000	
s-Diphenylcarbazone	EtOH ^b	48,800	42,200	34,900	
	EtOH		43,480 [4,12]	35,090 [4,11]	20,410 [3,27]
	n-BuOH	47,000	42,400	35,000	21,300
	CCl ₄ ^b			34,480 [4,13]	21,460 [3,52]
	Toluene ^c			34,600 [4,03]	21,410 [3,08]
	CCl ₄ ^c			34,720 [4,10]	21,510 [3,48]
					17,300
					17,760 [2,90]
					17,700 [2,67]
					18,020 [2,96]

^a Values of log E_{max} are given in square brackets.^b Data obtained from reference (30); ^c Data obtained from reference (29).

of the tautomers. The weaker band at $\sim 17,700 \text{ cm.}^{-1}$ was attributed to the keto tautomer and the band at $\sim 21,500 \text{ cm.}^{-1}$ to the enolic tautomer, analogous to Pel'kis's assignments for dithizone².

A more reasonable assignment for both of the long wavelength bands of diphenylcarbazone observed in carbon tetrachloride and toluene is to attribute them to the keto tautomer. The relative intensities of the two bands are very similar to those of the two long wavelength bands of trans-azobenzene (see Table VI.1). The bands are thus assigned as $\pi \rightarrow \pi^*$ ($\sim 21,500 \text{ cm.}^{-1}$) and $n \rightarrow \pi^*$ ($\sim 18,000 \text{ cm.}^{-1}$) transitions. There is a negligible shift in either band as the polarity of the solvent is changed and this is in agreement with previous observations for azobenzene^{14,15}.

In ethanol the two long wavelength maxima are replaced by a single intense band. Contrary to previous views this spectrum is considered to be that of a formazan, implying therefore that the enolic tautomer and not the keto, is predominant in hydroxylic solvents. The more polar enol tautomer would be expected to be more stable in polar solvents.

In neither carbon tetrachloride nor ethanol is it possible to make any distinction between the four possible geometrical isomers of each tautomer. However, it is conceivable that the two bands observed in carbon tetrachloride and toluene are due to the trans-anti and trans-syn configurational isomers of the keto tautomer, although the apparent constancy of their relative intensities in n-butanol, carbon tetrachloride and toluene is evidence to the contrary. The change of solvent would be

expected to affect, to some degree, the position of the equilibrium between the two isomers.

VI.3.ii. Dithizone.- The absorption spectrum of dithizone in non-basic solvents of low polarity (see Table VI.6 and Figure VI.1, curve A) has certain similarities with the spectrum of *s*-diphenylcarbazone in similar media. In particular, an intense band is observed at $\sim 22,000 \text{ cm.}^{-1}$ with a shoulder at $\sim 17,000 \text{ cm.}^{-1}$, which can be assigned as the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the conjugated azo group respectively. One other intense, long wavelength band occurs in the absorption spectrum of dithizone in the above solvents. This is assigned as the $\pi \rightarrow \pi^*$ transition of the thioketo group which has shifted from $\sim 39,000 \text{ cm.}^{-1}$ in diphenylthiocarbazide to $\sim 15,500 \text{ cm.}^{-1}$.

In the proton donor solvents, chloroform and glacial acetic acid, the thioketo $\pi \rightarrow \pi^*$ transition undergoes the expected hypsochromic shift (see Figure VI.1). In hydrochloric acid (S.G. = 1.18) the absorption spectrum (see Figure VI.2) may be interpreted in terms of the protonated form of the thioketo tautomer (I), on the basis of its similarity with the reflectance spectrum of the crystalline solid which is known to have the thioketo structure (see Chapter II). There is an intense band at $18,700 \text{ cm.}^{-1}$ with a weaker band at $27,100 \text{ cm.}^{-1}$. This is comparable with the spectrum of the conjugate acid of *trans*-azobenzene (see Table VI.1) which has bands of similar intensity at $23,750 \text{ cm.}^{-1}$ and $33,110 \text{ cm.}^{-1}$.

In polar, basic solvents, a new band occurs at $\sim 20,000 \text{ cm.}^{-1}$ (see Figure VI, curve D) while in all but the proton donor solvents it

Figure VI.1.- Electronic absorption spectra of dithizone in : A, benzene.,
B, CHCl₃., C, glacial acetic acid., D, methanol.

TABLE VI.6

Electronic Absorption Bands of Dithizone

Medium	λ (cm. ⁻¹)				
Reflectance			27,300	(21,100)(20,300)	18,700 (17,100)(15,700
HCl (conc.)	47,400 41,700	(36,200)	27,100	18,700 (17,100)(15,700	16,500
Glacial HAc	42,300 38,000	37,100 33,200 30,400	22,400		(17,300) 16,100
CHCl ₃		35,500 (33,400)(31,800)	22,000	(23,000) 21,400 (20,000)	(16,700) 15,200
CS ₂	46,700 42,300	37,000 (34,300) 32,900	30,000	21,700 (20,300)	(17,400) 15,500
C ₆ H ₆	(45,400) 41,000	(37,500) 33,300	30,300	21,900 20,400	17,000 15,800
CCl ₄		35,900 33,000	30,100	(23,100) 21,700 (20,500)	(16,500) 15,600
C ₆ H ₆				(23,000) 21,600 (20,500)	(16,500) 15,400
C ₆ H ₅ NO ₂	35,700	(33,400)		19,900	15,900
CH ₃ COCH ₃	35,100 (	(33,000)	27,000	19,300	
CH ₃ COC ₂ H ₅	36,100	30,000		20,400	(16,300)
MeOH	48,700 (44,900)			(23,800) 21,900 (20,500)	(17,400) 16,300
n-BuOH	47,300 44,100	33,600	30,800	(21,900) 20,800	16,300
i-PrOH	48,900 43,300	35,900	(30,000)	21,100 (19,500)	15,700
DMS					(16,100)
Pyridine	39,800 34,100	33,000	30,000	19,400	(17,000) 15,700
Isoquinoline			29,000	(22,000)	
Triethanolamine	35,700		29,700	20,000	
Ethanolamine		32,400	(28,700)	19,700	
Piperidine	34,600	(23,600)		19,300

Figure VI.2.- Electronic absorption spectra of dithizone ; A, solid reflectance and B, solution in conc. hydrochloric acid.

is possible to detect a shoulder in this region. The spectrum is very similar to that of the potassium salt of dithizone (compare Figure VI.3) which is thought to have the formazan structure of tautomer II. Hence in proton acceptor solvents dithizone is present mainly as the thioenolic tautomer.

The solution spectra of dithizone can therefore be interpreted in terms of a predominance of the thioketo tautomer ($I, R_1 = R_2 = Ph$) in proton donor solvents with the equilibrium shifting towards the thioenolic tautomer as the proton accepting strength and polarity of the solvent increases.

The configuration preferred by each tautomer is not evident from their visible absorption spectra. However, the proton n.m.r. spectra of dithizone in deuteriochloroform and tetrahydrofuran suggest that the thioketo tautomer has the trans-syn configuration in these solvents.

The remarkable similarity between the reflectance spectrum of dithizone and its absorption spectrum in concentrated hydrochloric acid (see Figure VI.2) deserves some comment. In solution in hydrochloric acid the spectral changes are indicative of protonation of the thioketo and azo groups. Thus it would seem that the same phenomenon occurs in the solid state. The proton donor in this case must be an N.H proton of an adjacent dithizone molecule. Such an arrangement (IV), with strong $N-H \cdots N$ and $N-H \cdots S$ intermolecular hydrogen bonding, would explain the absence of N.H stretching vibrations from the infrared absorption spectrum of dithizone in the solid state.

IV

This phenomenon of interacting non-conjugated chromophores has been observed³¹ for several complex organic molecules and suggests that solid dithizone might behave as a semiconductor with an energy gap of approximately $18,700 \text{ cm.}^{-1}$.

It should now be possible to interpret the absorption spectra of the derivatives and metal complexes of dithizone in terms of one of the structures illustrated below (V-XI), using the assignments which have been made for dithizone.

V

VI

VII

VIII

IX

X

XI

VI.3.iii. Potassium Dithizonate.— The absorption spectra of the dithizonate anion, soluble only in polar media, are given for a range of such solvents in Table VI.7. The intense absorption band at $\sim 20,000 \text{ cm}^{-1}$ (see Figure VI.3) is analogous to the absorption band assigned to the thioenolic tautomer of dithizone and both are assigned as the characteristic long wavelength formazan absorption band.

Figure VI.3.- Electronic absorption spectra of A, potassium dithizonate and B, dehydrodithizone in methanol.

TABLE VI.7

Electronic Absorption Bands of Potassium Dithizonate

Medium	λ (cm. ⁻¹)			
Reflectance			(22,800)	18,900
MeOH	48,800 (44,200)	36,300 (31,900)	30,000 (27,300)	20,500
EtOH	48,500 (45,700)	36,000 (33,000)	(30,000)	(22,100) 20,500
n-BuOH	47,000 (44,900)	35,900 (32,500)	(30,000)	20,500
i-PrOH	47,800 (45,300)	36,000 (33,700)	(30,000)	20,700
Acetone				19,600
CH ₃ COC ₂ H ₅		35,300	27,100	19,400
DMS			(21,700)	19,000

Based on this assignment, potassium dithizonate should have either structure V or structure VI (R = K). The hypsochromic shift for the long wavelength absorption band in going from the solid or its solution in dimethylsulphoxide and ketone solvents to its solution in alcohols, may be due to the conversion of V to VI. This would be comparable to the 'red' to 'yellow' change observed in other formazans (see Table VI.3). However, the proton n.m.r. spectrum (see p.106) suggests that it has structure VI in dimethylsulphoxide which implies that the trans-syn configuration is always retained.

VI.3.iv. Dehydrodithizone.— This compound has an intense absorption band in the region 21,100–22,300 cm.⁻¹ (see Table VI.8 and Figure VI.3) in proton acceptor solvents, which undergoes a hypsochromic shift in proton donor solvents. A similar shift occurs on forming the S-methyl derivative, 5-methylthio-2,3-diphenyltetrazolium iodide, the reflectance spectrum of which has a shoulder at 24,300 cm.⁻¹. This behaviour is

analogous to that shown by potassium dithizonate which suggests that the latter compound has structure VI which is the structure most like the tetrazole ring of dehydrodithizone.

TABLE VI.8

Electronic Absorption Bands of Dehydrodithizone

Medium	λ (cm. ⁻¹)		
MeOH	48,400	39,300	24,200 (17,700)
n-BuOH	47,000	38,800 (33,000)	22,700
Glacial HAc		38,800	24,200 (16,800)
DMS			22,300
Acetone			21,900
CH ₃ COC ₂ H ₅			21,300
THF		38,000	21,100 (16,700)

VI.3.v. S-Methyldithizone.- This compound has been shown to exist in solution as trans-syn and trans-anti configurational isomers (see p.103). Bands observed in the reflectance spectrum of the solid and in a range of solvents are given in Table VI.9. The reflectance spectrum has a band at 17,200 cm.⁻¹ similar to the intense band at 17,800 cm.⁻¹ in the absorption spectrum of a fresh chloroform solution. A new band at 23,700 cm.⁻¹ slowly appears in the solution spectrum with a corresponding colour change from violet to yellow-brown. A slower change was observed in carbon disulphide (see Figure VI.4) in which the band at 17,200 cm.⁻¹ was replaced by one at 23,100 cm.⁻¹, while a more rapid change occurred in polar, basic media and in hydrogen bonding solvents. The bands at ~17,000 cm.⁻¹ and ~23,000 cm.⁻¹ are the characteristic absorption bands

Figure VI.4.- Electronic absorption spectra of S-methyldithizone in A, methanol, B, CS₂ after 5 min., C, CS₂ after 16 hrs.

Electronic Absorption Bands of S-Methyldithizone

Media	λ (cm. ⁻¹)		
Reflectance			
CS ₂		(27,100)	20,900
C ₆ H ₁₂	45,400	(30,000) (27,000)	(25,900) 23,100
C ₆ C ₆	36,900 (32,100)	(30,000)	23,400
C ₆ H ₅ NO ₂			23,700
CCl ₄	36,900 (32,600)	(25,600)	23,000
CHCl ₃	36,100 (32,000)	(30,000)	23,900
MeOH	48,700	36,700 33,500	23,700
MeOH + NaOH			23,600
n-BuOH	47,100	37,000 (33,200)	23,600
i-PrOH	36,800	(33,000) (30,000)	(27,000)
Acetone			23,800
Acetone + NaOH			(23,900)
Acetone + H ₂ SO ₄			23,800
CH ₃ COC ₂ H ₅		29,500	23,500
DMS	36,000	(33,000) (30,000)	(25,400)
DMS + NaOH			(22,400)
DMS + H ₂ SO ₄			22,900
Glacial HAC	36,600	(33,500)	23,800
			17,200
			17,200
			(18,900) 17,800
			17,900
			17,500
			17,900
			(19,600) 17,800
			18,200
			19,600
			18,100
			18,100
			18,000
			19,000
			(18,000)
			18,100
			17,800
			18,400
			(18,000)
			(18,100)

of 'red' and 'yellow' formazans. The presence of a trace of acid causes the rapid conversion of the 'red' isomer to the 'yellow' isomer, as observed in the proton n.m.r. study (see p.102), while the addition of NaOH causes the reverse change. The slight hypsochromic shift observed for an increase in the basicity of the solvent may be due to deprotonation of the remaining N.H group.

The observed colour change is attributed to the conversion of the trans-anti 'red' isomer (V, $R = S.CH_3$) to the trans-syn 'yellow' isomer (VI, $R = S.CH_3$) which involves an intramolecular hydrogen bond. This is in agreement with both the n.m.r. and the infrared results. The violet solid can therefore be assigned the trans-anti configuration, also found for solid dithizone. The trans-anti configuration is presumably stabilised by intermolecular interactions, which explains the absence of an N.H stretching vibration from the infrared absorption spectrum of the solid.

VI.3.vi. $Hg(HDz)_2$.- The complex $Hg(HDz)_2$ is known (see p.29) to involve coordination of the thioenolic tautomer of dithizone (VII, $R = Hg(II)$), in the solid state. As expected for the formazan skeleton, a strong band is observed in both the reflectance and the solution spectra in the region $18,000\text{ cm}^{-1}$ to $20,400\text{ cm}^{-1}$ (see Table VI.10). The similarity between the reflectance spectrum of the solid and the solution spectra suggests that the solid state configuration is retained in solution.

The bathochromic shift in polar solvents can be attributed to hydrogen bonding of the remaining N.H proton, as in strongly basic solutions the complex turns violet and a 'secondary' complex, $HgDz$, can

Figure VI.5.- Electronic absorption spectra of $\text{Hg}(\text{HDz})_2$ in : A, methanol., B, DMS., C, DMS/ NaOH ., D, DMS/ H_2SO_4 .

TABLE VI.10

Electronic Absorption Bands of $\text{Hg}(\text{HDz})_2$

Medium	λ (cm. ⁻¹)
Reflectance	20,300 (17,700)
CCl_4	37,000 (30,000) 20,300 (17,800)
CS_2	19,300
CHCl_3	(38,100) 37,000 (30,000) 20,100 (17,800)
C_6H_6	20,100
$\text{C}_6\text{H}_5\text{NO}_2$	19,700
MeOH	48,400 (39,300) 37,300 (30,000) 20,300 (18,000)
n-BuOH	47,200 (39,900) 37,000 (30,000) 19,900
Acetone	20,100
Acetone + NaOH	18,700
Acetone + H_2SO_4	20,400
$\text{CH}_3\text{COC}_2\text{H}_5$	20,300
DMS	34,300 (30,000) (19,300) 18,300
DMS + NaOH	18,100
DMS + H_2SO_4	19,800
Glacial HAc	37,900 (30,000) 20,400 (17,700)

in fact be isolated. Addition of a drop of 8N NaOH to a dimethylsulphoxide solution of $\text{Hg}(\text{HDz})_2$ lowers the band from 18,300 cm.⁻¹ to 18,100 cm.⁻¹, while a drop of sulphuric acid raises the band to 19,800 cm.⁻¹. (see Figure VI.5). It appears that the remaining N.H proton of $\text{Hg}(\text{HDz})_2$ is removed at approximately pH 12. The ability of some metal ions, including $\text{Hg}(\text{II})$, to form secondary dithizonates may be attributed to their having lower pK_2 values. These may in turn be attributed to the ability of these metals to 'back-donate' or participate in an interligand π -orbital system, as depicted below (XII).

XII

As the π -bonding ability of the metal diminishes, the energy of the conjugated system should rise causing an increase in the basicity of the N.H proton. This should also result in a decrease in the ability to hydrogen bond which might explain the linear relationship observed between the chemical shift for the N.H proton in dimethylsulphoxide and the stability constant for the metal dithizonates of class 1 (see p.107).

VI.3.vii. $\text{Ni}(\text{HDz})_2$, $\text{Pd}(\text{HDz})_2$, $\text{Pt}(\text{HDz})_2$ and $\text{Au}(\text{HDz})_3$.— The infrared and n.m.r. spectra of the dithizonates of the nd^8 metal ions, Ni(II), Pd(II), Pt(II) and Au(III) have been shown to be different from the remainder. These differences can be attributed to a difference in structure, although it has also been suggested that they might arise because of a difference in configuration (see p.109).

The electronic absorption spectra of the nd^8 metal dithizonates (Table VI.11) also appear to be different from the spectra of complexes typified by $\text{Hg}(\text{HDz})_2$ (see Tables VI.10 and 13) in that additional long wavelength absorption bands are present. They all have an intense band at $\sim 20,000 \text{ cm}^{-1}$ in chloroform (see Figure VI.6) which could be

Figure VI.6.- Electronic absorption spectra of A, Ni(HDz)₂ in methanol., B, Ni(HDz)₂ in CHCl₃., C, Pd(HDz)₂ in CHCl₃., D, Pt(HDz)₂ in CHCl₃., E, Au(HDz)₃ in CHCl₃.

TABLE VI.11

Electronic Absorption Bands of the Dithizone
Complexes of Ni(II), Pd(II), Pt(II) and Au(III)

Compound	Media	λ (cm. ⁻¹)
Ni(HDz) ₂	CS ₂	(20,300) 18,000 (14,500)(10,800)
"	CCl ₄	(23,000) 20,500 17,300 14,800 (11,200)
"	C ₆ H ₆	(22,900) 20,300 17,400 (14,600)(11,200)
"	C ₆ H ₅ NO ₂	23,000 (20,900) 17,300 (14,600)(11,800)
"	MeOH	(23,000) 20,400 17,700 14,400 (10,800)
"	n-BuOH	(22,000) 20,500 17,800 (14,500)(11,400)
"	i-PrOH	(22,800) 20,700 17,500 14,400 (11,600)
"	CH ₃ COC ₂ H ₅	19,800 (17,200)(14,500)(11,500)
"	Acetone	(23,000) 20,900 17,700 14,600 (11,700)
"	CHCl ₃	(30,000)(22,600) 20,200 17,500 14,500 (10,700)
"	CHCl ₃ + py	18,500
"	Glacial HAC	(22,800) 20,900 17,300 14,600 (10,400)
"	DMS	(31,000) 19,400 14,500 (10,800)
Ni(HDz) ₂ (py) ₂	Reflectance	20,700 (18,000) 15,000 (12,000)
Pd(HDz) ₂	CHCl ₃	(30,800) 20,400 (17,800)(15,100)
Pt(HDz) ₂	CHCl ₃	(30,000) 20,060 13,300
Au(HDz) ₃	CHCl ₃	(31,000)(23,200) 20,200 (16,000)

assigned as the band characteristic of the formazan skeleton, suggesting therefore that structures IX and XI are unlikely. The formazan skeleton is capable of coordinating through either sulphur or nitrogen atoms so that structures VII, VIII and X are all possible. Diamagnetic Ni(II) formazans with structure X ($R = \text{Ni(II)}$) have been prepared^{21,26}. These all have a strong absorption band in the range $13,000 \text{ cm}^{-1}$ to $15,000 \text{ cm}^{-1}$ (see Table VI.12) comparable to the band at $14,500 \text{ cm}^{-1}$ in Ni(HDz)_2 in chloroform. However, as no S.H absorption was observed in either the infrared or the n.m.r. spectra of the nd^8 metal dithizonates, whereas N.H stretching bands have been observed, structure X would appear to be unlikely.

The identification of d-d transitions would assist in distinguishing between environments of four nitrogen donors or two nitrogen and two sulphur donors. There have been a number of quantitative treatments of the electronic spectra of square planar nd^8 complexes³²⁻³⁸. Gray and Ballhausen³⁷ have shown, that in systems involving a ligand π -orbital system, there will be three closely spaced metal to ligand charge transfer bands and two well spaced ligand to metal bands. Thus in Ni(HDz)_2 we would expect three weak d-d bands, three metal to ligand and two ligand to metal charge transfer bands as well as the bands due to intraligand transitions. Bands of all four types were identified in nd^8 dithiooxalate complexes³² by carrying out a M.O. treatment of the Ni(II) complex. A complete assignment of the bands of Ni(HDz)_2 would require a similar treatment.

TABLE VI.12

Electronic Absorption Bands of Some Square
Planar Ni(II) Complexes

Compound	Medium	Environment	ν (cm. ⁻¹)	Ref.
Ni(formazan 1) ₂	Benzene	4N	28,010 23,920 12,820	26
Ni(formazan 2) ₂	EtOH	4N	31,250 27,400 14,600	21
Ni(dtc) ₂		4S	32,100 26,000 23,500 20,400 15,600*	40
Ni(exan) ₂		4S	31,600 25,700 23,900 20,800 15,500*	40
Ni(exan) ₂ py ₂		4S, 2N	10,200 9,300*	40
Ni(dtp) ₂		4S	35,700 31,600 26,100 19,100 14,500*	40
Ni(dtp) ₂ py ₂		4S, 2N	14,000 9,000*	40
Ni(dto) ₂ ²⁻	CH ₃ CN	4S	38,600 33,400 19,900 17,700	40
Ni(tscaz) ₂	DMS	2S, 2N	38,200 33,300 22,800(17,000)(10,400)	40
Ni(tscaz) ₂	Ref.	2S, 2N	24,400 19,000(16,700)(10,400)	
Ni(NH ₂ NHCS ₂) ₂	DMS	2S, 2N	30,800(23,800) (16,800)	
Ni(NH ₂ NHCS ₂) ₂	Ref.	2S, 2N	27,000 24,000 18,400 (10,900)	
Ni(thiopic) ₂	CHCl ₃	2S, 2N	15,200*	41
Ni(thiopic) ₂	py	2S, 4N	16,300* 10,600*	41

Abbreviations used: formazan 1 = 3-methyl-1,5-diphenylformazan;
 formazan 2 = 3-acetyl-1,5-diphenylformazan; dtc = diethyl dithiocarbamate;
 exan = ethyl xanthate; dtp = diethyl dithiophosphate;
 dto²⁻ = dithiooxalate; thiopic = N-alkylthiopicolinamide.

* Denotes a band assigned as a d-d transition.

Figure VI.7.- Electronic absorption spectra of : A, $\text{Ni}(\text{tscaz})_2$ solid reflectance., B, $\text{Ni}(\text{tscaz})_2$ in DMS., C, $\text{Ni}(\text{NH}_2\text{NHCS}_2)_2$ solid reflectance., D, $\text{Ni}(\text{NH}_2\text{NHCS}_2)_2$ in DMS.

If we accept the assignment of the band at $\sim 20,000 \text{ cm}^{-1}$ as a ligand $\pi \rightarrow \pi^*$ transition, then the three longer wavelength bands could be assigned as the metal to ligand charge transfer bands. However, there are no bands which can be assigned as d-d transitions.

The other approach is to compare the electronic absorption spectra of square planar complexes with environments of four sulphur, four nitrogen, and two sulphur and two nitrogen donor atoms (see Table VI.12) with the absorption spectrum of $\text{Ni}(\text{HDz})_2$. It can be seen that besides having a band similar to the long wavelength absorption of $\text{Ni}(\text{II})$ formazans, the spectrum of $\text{Ni}(\text{HDz})_2$ also resembles that of $\text{Ni}(\text{tscaz})_2$ (see Figure VI.7) which is known³⁹ to involve a distorted square planar arrangement of two sulphur and two nitrogen donors. The absorption spectrum of $\text{Ni}(\text{NH}_2.\text{NH}.\text{CS}_2)_2$, considered to have an environment comparable to that of $\text{Ni}(\text{tscaz})_2$, is also similar.

In dimethylsulphoxide and pyridine, $\text{Ni}(\text{HDz})_2$ is converted to a high-spin complex, presumably with octahedral symmetry. The absorption spectra in these solvents show a single intense band at $\sim 19,000 \text{ cm}^{-1}$. The reflectance spectrum of the paramagnetic complex isolated from chloroform/pyridine shows an additional weak shoulder at $\sim 12,000 \text{ cm}^{-1}$ which may be the first spin-allowed d-d transition.

It can be concluded that the electronic absorption spectrum of $\text{Ni}(\text{HDz})_2$ shows similarities with $\text{Ni}(\text{II})$ formazans which involve four nitrogen donors and with $\text{Ni}(\text{tscaz})_2$ and $\text{Ni}(\text{NH}_2.\text{NH}.\text{CS}_2)_2$ which involve two sulphur and two nitrogen donors. However, it is not evident from their absorption spectra which of the structures, VII, VIII and X, is preferred by $\text{Ni}(\text{HDz})_2$ or the other nd^8 metal dithizonates.

VI.3.viii. Miscellaneous Dithizone Complexes.- The electronic absorption bands of the remaining metal dithizonates, studied in chloroform solution, are listed in Table VI.13. They all have one intense band in the region 18,000-22,000 cm^{-1} , with some having a shoulder at $\sim 16,000 \text{ cm}^{-1}$ which may correspond to the shoulder observed in the spectrum of the trans-syn isomer of S-methyl dithizone and to the shoulder at $\sim 17,500 \text{ cm}^{-1}$ in $\text{Ni}(\text{HDz})_2$. The intense band can be assigned as the $\pi \rightarrow \pi^*$ transition of the formazan skeleton, as observed in the dithizonates already discussed. Such an assignment would help to explain the apparent absence of any correlation between the wavelength of absorption of individual dithizonates and the electronic structure of the cation from which they are derived, remarked on by Irving and Cox⁴². The wavelength of the $\pi \rightarrow \pi^*$ formazan band should mainly reflect differences in the strength of the metal to nitrogen bond, whereas it is the strength of the covalent, metal to sulphur bond which is the more important variable. Additional evidence for this conclusion can be obtained by considering the absorption bands in the electronic spectra of the metal complexes of s-diphenylcarbazone (see Table VI.13). Both the wavelength and the intensity of the maxima in the s-diphenylcarbazone and the dithizone complexes of a particular metal ion are similar. This can be explained if both series of complexes involve structure VII, and its oxygen analogue, with the band being due to the $\pi \rightarrow \pi^*$ band of the azo group of the formazan. This band should then be little affected by the oxygen or sulphur donor atom, as is in fact observed.

TABLE VI.13

Electronic Absorption Bands of Some Dithizone and
Diphenylcarbazone Complexes

Metal Ion	Dithizone		Diphenylcarbazone
	ν_{CHCl_3} (cm. ⁻¹)	ν_{CCl_4} (cm. ⁻¹) ^a	ν_{Toluene} (cm. ⁻¹) ^b
Mn(II)	19,200 16,200		19,200
Fe(II)	19,100 (16,000) 9,700		19,600
Co(II)	(23,300) 18,000	18,450 [4.77]	18,200
Co(III)	21,300 (18,500)		
Ni(II)	20,200	20,830 [4.48]	20,000
Cu(II)	17,950 (13,200) 6,200	18,180 [4.65]	18,200
Cu(I)	20,000		
Zn(II)	18,400 (15,100)	18,690 [4.97]	18,900
Pd(II)	20,400 (17,800)(15,100)	22,220 [4.53]	
Ag(I)		21,650 [4.43]	
Cd(II)		19,230 [4.94]	20,800
In(III)		19,610 [4.94]	
Sn(II)		19,230 [4.73]	18,900
Pt(II)	20,060 13,300	20,410 [4.50]	
Au(III)	20,200 (16,000)	22,220 [4.50]	
Hg(II)	20,100	20,620 [4.85]	18,200
Tl(I)		19,610 [4.52]	
Pb(II)		19,230 [4.54]	18,500
Bi(III)		20,410 [4.43]	
SbCl ₃ H ₂ Dz	19,300 16,100		
CuDz	22,000 (10,600)		

^a Data from references (43) and (44), with log E in square brackets.

^b Data from reference (45), with log E ~ 4.

Figure VI.8.- Electronic absorption spectra of : A, $\text{Fe}(\text{HDz})_2$ in CHCl_3 ,
 B, $\text{Cu}(\text{HDz})_2$ in CHCl_3 .

Long wavelength bands of weak intensity (see Figure VI.8) observed in the spectra of $\text{Fe}(\text{HDz})_2$ and $\text{Cu}(\text{HDz})_2$ may be assigned as d-d transitions.

A two-dimensional X-ray crystallographic study of $\text{Cu}(\text{HDz})_2$ (see p. 29) was interpreted in terms of a square planar complex. However, the absorption bands at $13,200 \text{ cm.}^{-1}$ and $6,200 \text{ cm.}^{-1}$ in chloroform solution suggest that the complex has tetrahedral symmetry. A band at $13,000 \text{ cm.}^{-1}$ in the tetrahedral anion CuCl_4^{2-} has been assigned as a charge transfer band⁴⁶ while a band at $5,800 \text{ cm.}^{-1}$ in the absorption spectrum of Cu^{2+} in ZnO has been assigned as the crystal field, $^5\text{T}_{2g} \longrightarrow ^2\text{E}_g$, transition⁴⁷. The bands in the absorption spectrum of $\text{Cu}(\text{HDz})_2$ are similarly assigned giving Dq a value of 620 cm.^{-1} .

The band of weak intensity at $9,700 \text{ cm.}^{-1}$ in the absorption spectrum of $\text{Fe}(\text{HDz})_2$ (see Figure VI.8) can be tentatively assigned as a d-d transition, possibly the $^1\text{T}_{2g} \longrightarrow ^1\text{A}_{2g}$ band for a tetrahedral complex.

VI.3.ix. Metal Thiocarbonylhydrazides.— The electronic absorption bands of the $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ and $\text{Pd}(\text{II})$ complexes are listed in Table VI.14. Included for comparison are the electronic absorption bands of the $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ complexes of thiosemicarbazide and the $\text{Ni}(\text{II})$ complex of carbonylhydrazide. Assignments have been made for the $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Co}(\text{III})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ complexes assuming octahedral symmetry about the metal ion.

The double peak for $[\text{Fe}(\text{Htcz})_2\text{NCS}_2]$ at $13,600 \text{ cm.}^{-1}$ and $8,800 \text{ cm.}^{-1}$ (see Figure VI.11) is comparable to that at $10,400 \text{ cm.}^{-1}$ and $8,500 \text{ cm.}^{-1}$

TABLE VI.14

Electronic Absorption Bands of Some Metal Complexes of Htcaz,
Htscaz and Hcaz

Compound	λ (cm. ⁻¹)
[Fe(Htcaz) ₂ NCS ₂]	8,800 (⁵ T _{2g} → ⁵ E _g); 15,400; 18,600; 21,300; 24,100 13,600
[Co(Htcaz) ₂ Cl ₂] violet	8,300 (⁴ T _{1g} → ⁴ T _{2g}); 15,000 (→ ⁴ A _{2g}); 17,800 (→ ⁴ T _{1g} (P)) 20,300
" brown	8,300 ("); 15,000 ("); 17,900 (") 23,000
[Co(Htscaz) ₂ Cl ₂] violet	8,300 ("); 15,600 ("); 17,800 (") 21,700
" brown	8,300 ("); 15,600 ("); 17,900 (") 23,180
Hg[Co(tcac) ₂ Cl ₂]	18,700 (¹ A _{1g} → ¹ T _{1g}); 24,400 (→ ¹ T _{2g}); 28,000
Ni(Htcac) ₃ Cl ₂ ·3H ₂ O	9,500 (³ A _{2g} → ³ T _{2g}); 12,500 (→ ¹ E _g); 16,300 (→ ³ T _{1g} (P)); 26,100 (→ ³ T _{1g} (P)) 10,500
Ni(Htcac) ₃ Cl ₂ ^a	9,500 ("); 16,500 ("); 26,200 (") 10,500
Ni(Htscac) ₃ Cl ₂ ^a	9,600 ("); 16,450 ("); 26,700 (") 10,500
Ni(Hcaz) ₃ Cl ₂ ^a	9,600 ("); 12,500 (→ ¹ E _g); 16,100 ("); 27,400 (") 10,200
Cu(Htcac) ₃ Cl ₂	13,700; 17,200 (² E _g → ² T _{2g}) ?
Pd(Htcac) ₂ Cl ₂	23,000; 26,700

^a These spectra were measured in aqueous solution, the remainder all being reflectance spectra.

Figure VI.9.- Reflectance spectra of : A, $\text{cis-}[\text{Co}(\text{Htcac})_2\text{Cl}_2] \cdot$,
 B, $\text{trans-}[\text{Co}(\text{Htcac})_2\text{Cl}_2] \cdot$, C, $\text{Hg}[\text{Co}(\text{tcac})_2\text{Cl}_2] \cdot$.

in the spectrum of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, where the splitting is attributed⁴⁸ to a Jahn-Teller distortion.

This distorted octahedral environment is also observed for the $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$ complexes.

The band assigned as the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{P})$ transition in each of the isomeric complexes $[\text{Co}(\text{Htc}az)_2\text{Cl}_2]$ (see Figure VI.9) is split, although by different amounts. The corresponding bands in the brown and violet isomers of $[\text{Co}(\text{Hts}caz)_2\text{Cl}_2]$ are also split, and in both cases this splitting can be attributed to a tetragonal or rhombic distortion of the cubic field. The different splitting of the brown and violet isomers suggests that they may be trans and cis geometrical isomers, as a larger splitting is expected for the trans isomer⁴⁹.

The salmon pink $\text{Co}(\text{III})$ complex $\text{Hg}[\text{Co}(\text{tc}az)_2\text{Cl}_2]$, has two bands in the visible region (see Figure VI.9) comparable with those of $\text{Co}(\text{III})(\text{cysteinate})_3^{3-}$ at $17,200 \text{ cm}^{-1}$ and $22,600 \text{ cm}^{-1}$ and $\text{Co}(\text{III})(\text{mercaptoethylamine})_3$ at $17,550 \text{ cm}^{-1}$ and $23,050 \text{ cm}^{-1}$. Both of these ligands provide a cubic field of three sulphur and three nitrogen donor atoms⁵⁰ suggesting that $\text{Hg}[\text{Co}(\text{tc}az)_2\text{Cl}_2]$ involves coordination by two sulphur, two nitrogen and two chloride donors. The report⁵¹ of a $\text{Co}(\text{III})$ complex of thiosemicarbazide, involving an environment of three sulphur and three nitrogen donors, with absorption bands at $23,400 \text{ cm}^{-1}$ and $19,100 \text{ cm}^{-1}$, is additional evidence that the $\text{Co}(\text{III})$ complex of thiocarbohydrazide is coordinated by both sulphur and nitrogen donor atoms.

The splitting of the first spin-allowed band (${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$) in the $\text{Ni}(\text{II})$ complexes (see Figure VI.10) indicates a tetragonal

Figure VI.10.- Electronic absorption spectra of : A, $\text{Ni}(\text{Htcac})_3\text{Cl}_2$ in H_2O ., B, $\text{Ni}(\text{Htcac})_3\text{Cl}_2$ solid reflectance., C, $\text{Ni}(\text{Htscac})_3\text{Cl}_2$ solid reflectance., D, $\text{Ni}(\text{Hcac})_3\text{Cl}_2$ solid reflectance.

Figure VI.11.- Reflectance spectra of : A, $\text{Cu}(\text{Htcac})_3\text{Cl}_2 \cdot$,
 B, $\text{Pd}(\text{Htcac})_2\text{Cl}_2$; C, $[\text{Fe}(\text{Htcac})_2\text{HCS}_2]$, D, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

distortion similar to that observed in $\text{Ni}(\text{Htscaz})_3\text{I}_2$ ⁴⁰ and $\text{trans-Ni}(\text{py})_4\text{Cl}_2$ ⁵². A detailed study of $\text{trans-Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ and $\text{trans-Ni}(\text{NH}_3)_4(\text{NCS})_2$ showed that the tetragonal splitting of the octahedral levels was dependent on the relative positions of the axial and equatorial ligands in the spectrochemical series⁵³. The tetragonal splitting parameters for Ni(II) include the parameter Dt, defined by the splitting of the octahedral ${}^3\text{T}_{2g}(\text{F})$ level into the tetragonal ${}^3\text{E}_g$ and ${}^3\text{B}_{2g}$ levels⁵⁴. Values of Dt for $\text{Ni}(\text{Htcz})_3\text{Cl}_2$, $\text{Ni}(\text{Htscz})_3\text{Cl}_2$ and $\text{Ni}(\text{Hcaz})_3\text{Cl}_2$ are 114 cm^{-1} , 103 cm^{-1} and 60 cm^{-1} respectively. These suggest the environments $3\text{N}, 3\text{S}$ and $3\text{N}, 3\text{O}$ rather than an environment consisting of nitrogen atoms, which would be expected to show negligible splitting. The environment $3\text{N}, 3\text{O}$ for $\text{Ni}(\text{Hcaz})_3\text{Cl}_2$ is contrary to the suggestion of Campi and co-workers⁵⁵ who preferred an environment of four nitrogen donor atoms.

Additional evidence favouring a structure coordinated by three sulphur and three nitrogen donors may be obtained by calculating Dq and B, the interelectronic repulsion term, for the Ni(II) complexes. The spectrochemical position of both thiosemicarbazide and thiocarbonylhydrazide, as measured by Dq, is between ammonia and water, and is also slightly higher than for carbonylhydrazide, where $\text{Ni}(\text{Hcaz})_3\text{Cl}_2$ is thought to have a $3\text{N}, 3\text{O}$ environment. Both facts are in accord with Jørgensen's spectrochemical series for high-spin octahedral Ni(II) complexes containing sulphur ligand atoms⁴⁰. The nephelauxetic parameter β , defined as the ratio of $15B$ for the complexed metal ion over $15B$ for the gaseous metal ion, is usually smaller for ligands with the more

TABLE VI.15

Ligand Field Parameters for Ni(II)
Complexes in Aqueous Solution

Complex	Environment	Dq (cm. ⁻¹)	15B ^a (cm. ⁻¹)	β ^b
Ni(H ₂ O) ₆ ²⁺ ^c	60	850	14,100	0.89
Ni(glycine) ₃ ⁻ ^c	3N, 3O	1,010	13,900	0.88
Ni(NH ₃) ₆ ²⁺ ^c	6N	1,070	13,300	0.84
Ni(Htcac) ₃ ²⁺	3N, 3S	1,000	12,700	0.80 ^d
Ni(Htscac) ₃ ²⁺	3N, 3S	1,005	13,000	0.82 ^d
Ni(Hcac) ₃ ²⁺	3N, 3O	990	13,800	0.87 ^d

^a The secular determinant for the two ${}^3T_{1g}$ eigenvalues was solved using the diagonal sum rule⁵⁷.

^b The value of 15B for the free gaseous ion was taken as 15,840 cm.⁻¹ ⁵⁸.

^c These values are taken from reference (59).

^d These can be considered as upper limit values due to the approximate evaluation of the energy of the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition.

polarisable sulphur donor atom rather than either nitrogen or oxygen⁵⁶.

A comparison of the values tabulated in Table VI.15 shows that this also holds for Ni(Htcac)₃Cl₂. This can be construed as evidence favouring a 3N, 3S environment.

Absorption bands occur at 17,200 cm.⁻¹ and 13,700 cm.⁻¹ in the spectrum of Cu(Htcac)₃Cl₂. Jørgensen has suggested^{59,60} that the ratio $\sigma_{Cu} / \sigma_{Ni}$, between the wavenumber of the first spin-allowed band of the high-spin octahedral Ni(II) complex and the wavenumber of the principal

band of the Cu(II) complex, gives an indication of the stereochemistry of the Cu(II) complex. The ratio ranges from ~ 1.0 for a cubic environment to ~ 1.7 for a strong tetragonal distortion. If we select the band at $17,200 \text{ cm}^{-1}$ as the principal band of $\text{Cu}(\text{Htcz})_3\text{Cl}_2$ then $\sigma_{\text{Cu}} / \sigma_{\text{Ni}} = 1.72$, implying a strong tetragonal distortion.

Thus the thiocarbohydrazide complexes all apparently involve coordination by the thioketo group and one N.H_2 group, as suggested by their infrared spectra. The complexes $[\text{Fe}(\text{Htcz})_2\text{NCS}_2]$, $[\text{Co}(\text{Htcz})_2\text{Cl}_2]$, $\text{Ni}(\text{Htcz})_3\text{Cl}_2$ and $\text{Cu}(\text{Htcz})_3\text{Cl}_2$ also have strongly distorted octahedral environments about the central metal. The thiocarbohydrazidato complex of Co(III) also appears to be bonded through sulphur and nitrogen donors, although it is the thioenolic form of the ligand which coordinates in this case.

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CHAPTER VII

MAGNETIC AND MÖSSBAUER MEASUREMENTS

VII.1. Introduction

Magnetic measurements can yield information about the site symmetry and the electronic configuration of a transition metal ion. In the case of iron compounds it should be possible to correlate magnetic data with the Mössbauer parameters ΔE_q , the quadrupole splitting, and δ , the isomer shift measured with reference to some standard iron compound.

In a cubic crystalline field, ΔE_q for an iron atom should be zero¹ so that any distortion from cubic symmetry is indicated by the magnitude of ΔE_q . Anisotropy in the environment of high spin Fe(II) compounds results in a large ΔE_q due to the $^5T_{2g}$ ground state, whereas low spin Fe(II) compounds usually have smaller values of ΔE_q ². The isomer shift also differs for high and low spin compounds by approximately 1.0 mm./sec. It should therefore be possible to identify the spin state of the iron atom and also obtain some indication of the magnitude of the anisotropy.

VII.2. Experimental

Magnetic measurements at room temperature were made by the Gouy method, using a permanent magnet with a field strength of approximately 7000 gauss. Glass sample tubes were used, with $\text{Hg}[\text{Co}(\text{NCS})_4]$ ³ and $\text{Ni}(\text{en})_3\text{S}_2\text{O}_3$ ⁴ as the calibrants. Diamagnetic corrections were made using Pascal's constants as listed by Figgis and Lewis⁵.

The Mössbauer measurements for fine powdered samples (20 mg. of iron/cm.²) of the compounds were obtained at room temperature with a

standard Mössbauer spectrometer built round an R.I.D.L. 400-channel analyser used in time mode. The velocity modulation was achieved by a transducer vibrated sinusoidally at 30 c./sec. The spectrometer was calibrated with potassium nitroprusside powder and 0.001 inch thick iron foil. Data was obtained by graphing the Mössbauer spectra, the errors being ± 0.03 mm./sec.

VII.3. Results

TABLE VII.1

Magnetic Data for some Metal Dithizonates

Compound	$\chi_M \times 10^6$ c.g.s.u.	$\chi_{Dia} \times 10^6$ c.g.s.u.	μ_{eff}^a B.M.	Temp. °K
Mn(HDz) ₂	9,480	-293	4.80	293
Fe(HDz) ₂	2,990	-294	2.79	293
Co(HDz) ₂	765	-293	1.57	293
Co(HDz) ₃	0	-431	diamagnetic	292
Ni(HDz) ₂	0	-293	diamagnetic	293
Ni(HDz) ₂ ·2py	3,430	-393	3.00	293
Cu(HDz) ₂	1,020	-292	1.76	293
CuDz	550	-149	1.14	293
CuHDz	-140	-152	diamagnetic	292

^a Calculated using $\mu_{eff} = 2.84 (\chi_{Para} \cdot T)^{\frac{1}{2}}$

There is an experimental error of 2% in the value of μ_{eff} .

TABLE VII.2

Magnetic Data for Some Metal Thiocarbonylhydrazides^a

Compound	$\chi_M \times 10^6$	$\chi_{Dia} \times 10^6$	μ_{eff}^b	Temp. °K
	c.g.s.u.	c.g.s.u.	B.M.	
[Fe(Htcz) ₂ NCS ₂]	10,370	-197	5.00	293
cis-[Co(Htcz) ₂ Cl ₂]	9,070	-181	4.65	290
trans-[Co(Htcz) ₂ Cl ₂]	8,850	-181	4.62	292
Hg[Co(tcza) ₂ Cl ₂]	-18	-157	diamagnetic	293
Ni(Htcz) ₃ Cl ₂ ·3H ₂ O	3,787	-281	3.10	293
Cu(Htcz) ₃ Cl ₂	1,650	-241	2.11	291

^a Values quoted are the means obtained from measurements on a minimum of three separate preparations.

^b See footnote to Table VII.1.

TABLE VII.3

Mössbauer Data for Some Fe(II) Compounds Measured at Room Temperature

Compounds High Spin	Environment	μ_{eff}	ΔE_q	δ
		B.M.	mm. sec. ⁻¹	mm. sec. ⁻¹
FeSO ₄ ·7H ₂ O ^a	60	5.20	3.20	1.41
FeSO ₄ ·H ₂ O ^a	60	5.02	2.65	1.30
Fe(NH ₄) ₂ (SO ₄) ₂ ·6H ₂ O ^a	60	5.50	1.75	1.37
FeC ₂ O ₄ ·2H ₂ O ^a	60	5.30	1.70	1.22
[Fe(Htcz) ₂ NCS ₂]	4N, 2S	5.00	2.98	1.00
<u>Low Spin</u>				
[Fe(phen) ₃](ClO ₄) ₂ ^a	6N	diamagnetic	0.00	0.35
[Fe(dipy) ₂ CN ₂] ^a	4N, 2C	"	0.65	0.22
K ₄ [Fe(CN) ₆]·3H ₂ O ^a	6C	"	0.00	0.12
K ₂ [Fe(CN) ₅ NO]·2H ₂ O ^a	5C, 0	"	1.83	-0.18
Fe(HDz) ₂	2N, 2S	2.79	1.56	0.30

^a Data obtained from reference (9).

Abbreviations used are: phen = 1,10 phenanthroline; dipy = dipyrldyl.

VII.4. Discussion

VII.4.1. Metal Dithizonates.- The magnetic moments of $\text{Co}(\text{HDz})_3$, $\text{Co}(\text{HDz})_2$, $\text{Ni}(\text{HDz})_2$, $\text{Cu}(\text{HDz})_2$ and CuHDz are those expected for d^6 , d^7 , d^8 , d^9 and d^{10} metal ions in a strong crystalline field. The low value observed for $\text{Co}(\text{HDz})_2$ can be attributed to the presence of some of the $\text{Co}(\text{III})$ complex.

$\text{Ni}(\text{HDz})_2$ is readily coordinated by bases such as pyridine and dimethylsulphoxide, to give a high spin octahedral complex. The complex with two molecules of pyridine coordinated was isolated and found to have a magnetic moment of 3.0 B.M. Loss of pyridine occurs on standing to give the low spin diamagnetic complex. After two months the value for the magnetic moment was ~ 1.0 B.M.

The primary dithizonates of $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$ and the secondary dithizonate of $\text{Cu}(\text{II})$ all display anomalous magnetic moments at room temperature.

The magnetic moment of $\text{Fe}(\text{HDz})_2$ could be explained by impurities such as $\text{Fe}(\text{OH})_3$. However, values of 3.96 B.M. and 3.6 B.M. have been reported⁶ at room temperature for the planar complexes, $\text{Fe}(\text{II})$ phthalocyanine and bis(pentachlorophenyl)bis(Et_2PhP) $\text{Fe}(\text{II})$. Small magnetic moments, of the order of 1 B.M., have also been reported for the $\text{Fe}(\text{II})$ complex of 5-trifluoromethyltetrazole⁷ and for salts of the complexes $[\text{Fe}(\text{dipy})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{2+}$ ⁸. Explanations for these observations have been the participation of a low-lying, paramagnetic excited state and the presence of $\text{Fe}(\text{III})$ impurities. The value observed for $\text{Fe}(\text{HDz})_2$ is therefore not unreasonable. The Mössbauer parameters for

$\text{Fe}(\text{HDz})_2$ are similar to the values for $\text{K}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ (see Table VII.3) where the large ΔE_q can be attributed to the difference in donor strength of the ligands CN^- and NO^+ . Of the two possible environments for $\text{Fe}(\text{HDz})_2$, consisting of either 2S,2N or 4N, the former should result in a more strongly anisotropic field about the Fe(II) atom. Unfortunately, insufficient data has been accumulated to deduce anything definite about the environment, although, the large ΔE_q could be said to strongly favour that with two sulphur and two nitrogen donors.

The anomalous magnetic moment for $\text{Mn}(\text{HDz})_2$ can also be explained by the presence of impurity. The complex is unstable and could contain $\text{Mn}(\text{OH})_2$ or MnO_2 , both of which would lower the observed high spin ($S = \frac{5}{2}$) value. Other workers, however, have observed magnetic moments in the range 4.74 to 5.7 B.M. at room temperature for Mn(II) Schiff's base complexes of substituted salicylaldehydes and ethylenediamine. The only explanation advanced was that the complexes were not magnetically dilute. A value of 4.5 B.M. was also measured for $\text{Mn}(\text{phthalocyanine})_2$ at 293°K ¹². All of these complexes involve conjugated systems coordinated to the metal ion and should therefore result in a strong delocalisation of charge from the central metal onto the ligands.

The secondary complex of Cu(II) has a room temperature magnetic moment of only 1.14 B.M. This low value is indicative of some form of magnetic exchange, either through Cu-Cu bonds or via the ligands by some super exchange phenomenon. The infrared absorption spectrum has shown that the complex, CuDz , is either polymeric or a highly conjugated

monomer. Either structure would be expected to show a low magnetic moment. However, it is not evident from the magnetic data which of the two structures is the more likely.

VII.4.ii. Metal Thiocarbonylhydrazides.- The complexes $[\text{Fe}(\text{Htc}az)_2\text{NCS}_2]$, $\text{cis}-[\text{Co}(\text{Htc}az)_2\text{Cl}_2]$, $\text{trans}-[\text{Co}(\text{Htc}az)_2\text{Cl}_2]$, $\text{Ni}(\text{Htc}az)_3\text{Cl}_2$ and $\text{Cu}(\text{Htc}az)_3\text{Cl}_2$ have been shown to have distorted octahedral environments which include sulphur and nitrogen donor atoms. This distortion might explain the lowering of the magnetic moments of the $\text{Co}(\text{II})$ and $\text{Fe}(\text{II})$ complexes and the rather high value for the moment of the $\text{Cu}(\text{II})$ complex.

$\text{Hg}[\text{Co}(\text{tc}az)_2\text{Cl}_2]$ is diamagnetic as would be expected for a low spin $\text{Co}(\text{III})$ complex.

Octahedral complexes of $\text{Ni}(\text{II})$ should show magnetic moments which are given by the expression¹³

$$2.83 (1 - 4\mathcal{J}/10D_q),$$

where $\mathcal{J}$ and D_q are electronic spectral parameters. If we use the value obtained for $10 D_q$ of $10,000 \text{ cm}^{-1}$ (see p.143) and put the spin orbit coupling constant, $\mathcal{J}$, = -315 cm^{-1} we have a calculated value of 3.19 B.M. This is in reasonable agreement with the experimental value of 3.10 B.M.

The Mössbauer data for $[\text{Fe}(\text{Htc}az)_2(\text{NCS})_2]$, when compared with that for other high spin $\text{Fe}(\text{II})$ compounds (see Table VII.3), indicates that ΔE_q is comparable whereas δ , the isomer shift, is rather small. The low value for δ may arise from the different type of donor atom about the central metal. The large ΔE_q indicates that whatever the nature of the environment it is strongly anisotropic, as already indicated by both the magnetic moment and the visible absorption spectrum.

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CHAPTER VIII

SUMMARY

VIII.1. The Structure of Dithizone

We have been able to elucidate the structure and in some cases the configuration adopted by the dithizone molecule in different media, by the use of infrared, proton n.m.r., and electronic spectral data. In non-basic solvents of low polarity the thioketo tautomer predominates, the molecule having the trans-syn configuration involving a strong intramolecular hydrogen bond. In solvents of increasing polarity and basicity the thioenol tautomer becomes the more important species.

A detailed interpretation of the electronic spectrum of dithizone has cast doubt on previous calculations of the tautomeric equilibrium constant, pK_T , which were based on a considerably oversimplified picture of the spectrum^{1,2}.

The absence of detectable N.H stretching vibrations from the infrared spectrum of the solid has been explained by the presence of strong intermolecular interactions between the azo, thioketo and imino groups. This type of interaction is suggested by the similarity of the solid reflectance spectrum of dithizone with its spectrum in concentrated hydrochloric acid, which is in turn similar to the spectrum of the conjugate acid of trans-azobenzene.

Diphenylcarbazone, the oxygen analogue of dithizone, has been shown to exist as the keto tautomer in solvents of low polarity and as the enol tautomer in polar or basic media, a conclusion contrary to that previously reached^{3,4}.

VIII.2. S-Methyldithizone

We consider that the results obtained from a study of S-methyldithizone suggest possible misinterpretation of data by previous workers^{5,6}. The 'red' and 'yellow' isomeric formazans were assigned trans-syn and trans-anti configurations by Kuhn and co-workers⁵. Here we have shown that the lowering of both the chemical shift for the N.H proton and the wavenumber of the N.H stretching vibration to lower energies can be explained by the formation of an intramolecular hydrogen bond. We have therefore assigned the trans-syn configuration to the 'yellow' isomer and not to the 'red'. Thus the violet solid containing the 'red' isomer has the same 'open' trans-anti structure present in dithizone and is evidently stabilised by similar intermolecular bonding as indicated by the absence of an N.H stretching vibration from the infrared spectrum of the solid. Further evidence favouring the trans-syn configuration for the 'yellow' isomer is that it has a dipole moment of 4.81 D compared with 2.24 D for the 'red' isomer⁷. A higher value would be expected for the 'ring' trans-syn configuration than for the 'open' trans-anti configuration.

VIII.3. The Structures of the Metal Dithizonates

X-ray crystallographic data for $\text{Zn}(\text{HDz})_2$ shows that the structure involves a five membered chelate ring with coordination by nitrogen and sulphur donor atoms of the thioenol form of the ligand. This structure is essentially the same as that found for $\text{Cu}(\text{HDz})_2$ ⁸ and $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}$ ⁹ from similar crystallographic studies.

Two modifications of each of the dithizonates of Zn(II), Cd(II) and Hg(II) have been obtained. In one the compound occurs as solvated single crystals while in the other it occurs as a powder. X-ray powder diffraction data for the powder modifications of these three compounds and also of $\text{Cu}(\text{HDz})_2$ suggest that they are isomorphous. The single crystal modifications of the zinc(II) and cadmium(II) dithizonates are also isomorphous, both having monoclinic unit cells belonging to the space group C2/c .

Powder diffraction data for $\text{Ni}(\text{HDz})_2$ suggest that it is not isomorphous with the above dithizonates. Further marked differences between the dithizonates of the nd^8 metal ions, Ni(II), Pd(II), Pt(II) and Au(III), and the other dithizonates were observed in the spectroscopic studies. The diamagnetic, primary dithizonates of all except the nd^8 metal ions show a band attributable to the imino proton in their n.m.r. spectra. Coupled modes involving CN and CS stretching and CN stretching and NH deformation in the infrared spectrum of dithizone are raised to higher wavenumbers in the spectra of the dithizonates of the nd^8 metal ions than in the spectra of the other primary dithizonates. Finally, the visible absorption spectra of the primary dithizonates all show an intense band in the vicinity of $20,000 \text{ cm}^{-1}$ with a shoulder sometimes appearing at about $17,000 \text{ cm}^{-1}$, but the dithizonates of the nd^8 metal ions have additional intense, longer wavelength bands.

Previous workers^{10,11} have postulated a structure involving coordination by four nitrogen donors for $\text{Ni}(\text{HDz})_2$ and while this might explain some of our observations we favour a structure similar to that

known to be present in $\text{Zn}(\text{HDz})_2$, $\text{Cu}(\text{HDz})_2$ and $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}$ but with a square planar arrangement of the donor atoms, compared with the tetrahedral or distorted tetrahedral arrangement present for example in $\text{Hg}(\text{HDz})_2 \cdot 2\text{py}$. There are a number of reasons for favouring this essentially common structure for all of the primary dithizonates. Both $\text{Mn}(\text{II})$ and $\text{Fe}(\text{II})$ appear to be sulphur bonded and yet in terms of the 'A', 'B' classification of metal ions by Arhland, Chatt and Davies¹², these are less favourably disposed than $\text{Ni}(\text{II})$ towards sulphur bonding. It is also known that the tendency for the nd^8 metal ions to form square planar complexes is so strong that in both bis (2,2'-dipyridyliminato) palladium(II) and bis(3,3'-p-tolylformazyls)nickel(II)¹³ where the bulky ligand molecules would be expected to prevent a planar arrangement of the donor atoms the ligand is strongly distorted so as to allow square planar coordination. By having a square planar arrangement of the donor atoms the nd^8 metal ion is able to form a very stable π -bonding orbital involving the $(n+1)p_z$ metal orbital and four ligand π -orbitals¹⁴. This could explain the shift to higher wavenumbers of both of the coupled modes involving $\text{N}\equiv\text{CN}$ in their infrared spectra, as the C:N bond order should increase in the presence of π -bonding. The presence of metal to ligand charge transfer bands is also understandable for a complex involving π -bonding.

The bond strength in the other primary dithizonates will depend on the polarisability of the metal ion and for this reason the strongest bonding is present in $\text{Hg}(\text{II})$ dithizonate. The linear relationship between the chemical shift for the imino proton of the diamagnetic, primary dithizonates in dimethylsulphoxide and the log of their overall

stability constant has been explained by the ability of the metal ion to participate in an inter-ligand π -orbital system. This lowers the value of pK_2 thus enabling stronger hydrogen bonding with the solvent.

The ability of the metal ions, Hg(II), Cu(II), Bi(III), Ag(I) and Tl(I) to form secondary dithizonates is explained since these ions form the strongest metal to sulphur bonds. The secondary complex involves the dianion of dithizone and appears to be either a polymer or a highly conjugated monomer.

The absence of any marked relationship between the intense electronic absorption band in the visible spectrum of the primary dithizonates and the electronic structure of the metal ion has also been explained. The band is the characteristic long wavelength formazan absorption and can be assigned as the azo $\pi \rightarrow \pi^*$ transition. To a first approximation it is the covalent metal to sulphur bond which should determine the properties of a particular metal complex and not the donor bond between the azo nitrogen and the metal. Hence it is not surprising that no distinct trend has been observed between the band maxima for the primary dithizonates and some electronic structure parameter of the metal ions.

VIII.4. Metal Complexes of Thiocarbohydrazide

The results of a normal coordinate analysis of the free ligand have been used to show that the metal complexes are all coordinated through the thioketo sulphur atom and the hydrazinic nitrogen atom of each ligand molecule. The electronic absorption spectra and the magnetic properties of the transition metal complexes of the ligand show that a strongly

distorted octahedral environment surrounds the central metal in each complex.

Attempts to isolate metal complexes of the thiocarbohydrazide anion generally led to the isolation of amorphous black products. The only thiocarbohydrazidato complex isolated, $\text{Hg}[\text{Co}(\text{tcz})_2\text{Cl}_2]$, is most probably a polymer in which the $\text{Hg}(\text{II})$ ions are coordinated to the free N.H_2 groups of adjacent $[\text{Co}(\text{tcz})_2\text{Cl}_2]^{2-}$ octahedra. This would have the effect of preventing oxidation of the coordinated ligand, a phenomenon that apparently occurs readily when the ligand is coordinated to $\text{Hg}(\text{II})$, $\text{Ag}(\text{I})$, $\text{Ni}(\text{II})$, $\text{Pt}(\text{II})$ and $\text{Fe}(\text{II})$.

The first stage of the oxidation appears to result in a species involving an azo group but this is followed in most cases by further oxidation. We have isolated $\text{Pt}(\text{II})$ and $\text{Fe}(\text{II})$ compounds having intensely coloured solutions which suggests that for these metal ions the azo intermediate is relatively stable. This behaviour is entirely analogous to that observed in the diphenylthiocarbazide, dithizone system. No complexes of the former compound have been isolated, as the ligand is readily oxidised to dithizone.

In conclusion, it can be said that although thiocarbohydrazide and dithizone are potentially capable of coordinating through either sulphur and nitrogen donors or through only nitrogen, as observed for both thiourea and thiosemicarbazide, both coordinate through sulphur and nitrogen.

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Appendix IX-Ray Powder Diffraction Patterns

The powder patterns are recorded in terms of the d-spacings measured in angstroms and the line intensities, I, measured with respect to the most intense line which is assigned the arbitrary value 100.

d (Å)	I	d (Å)	I	d (Å)	I
13.485	65	4.100	20	2.866	11
11.060	100	4.034	15	2.827	21
8.632	40	4.019	15	2.796	11
8.427	55	3.829	47	2.636	8
6.709	6	3.753	24	2.505	12
5.800	48	3.654	11	2.383	15
5.664	30	3.642	13	2.299	7
5.045	82	3.430	36	2.196	8
4.470	10	3.370	85	2.146	12
4.300	9	3.178	21	2.132	13
4.239	14	2.929	12	1.990	8
4.198	19

d (Å)	I	d (Å)	I	d (Å)	I
12.736	100	3.964	62	2.754	6
11.312	96	3.870	46	2.679	8
10.373	13	3.824	40	2.603	5
9.248	8	3.774	51	2.427	7
7.678	93	3.630	9	2.380	6
7.218	8	3.510	29	2.350	7
6.822	56	3.449	14	2.242	9
6.456	41	3.417	16	2.191	5
6.321	32	3.362	29	2.151	6
6.036	34	3.236	23	2.120	4
5.624	13	3.120	26	2.094	6
5.172	34	3.079	14	2.040	4
4.982	74	2.971	13	2.011	4
4.844	25	2.940	9	1.959	8
4.502	37	2.893	7	1.904	8
4.366	94	2.843	9	1.857	6
4.159	43	2.793	12	1.824	4

Cd(HDz)₂·2py

(Crystalline Modification)

d (Å)	I	d (Å)	I	d (Å)	I
9.455	94	4.230	94	2.925	72
8.950	44	3.902	54	2.839	48
7.617	60	3.779	36	2.734	38
7.500	54	3.715	42	2.483	40
5.862	84	3.583	60	2.380	24
5.698	36	3.523	72	2.329	30
5.070	38	3.449	88	2.213	28
4.972	44	3.320	100	2.123	58
4.871	46	3.131	56	2.107	48
4.450	44	3.106	70	2.058	28
4.340	46				

Cd(HDz)₂

(Powder Modification)

d (Å)	I	d (Å)	I	d (Å)	I
14.356	70	3.276	16	2.161	9
11.030	100	3.211	13	2.118	9
8.827	43	3.130	17	2.006	7
8.590	45	3.038	25	1.950	10
7.148	3	3.028	9	1.930	10
6.052	6	2.930	17	1.912	8
5.470	46	2.787	13	1.888	10
5.050	7	2.737	14	1.861	7
4.315	65	2.659	10	1.821	4
4.288	20	2.578	12	1.773	6
3.957	16	2.504	9	1.716	4
3.731	12	2.404	18	1.686	5
3.669	11	2.346	9	1.640	3
3.568	13	2.294	5	1.576	4
3.503	30	2.242	5	1.394	3
3.370	15	2.181	11	1.351	3
3.337	19				

Hg(HDz)₂

d (Å)	I	d (Å)	I	d (Å)	I
14.890	100	4.007	18	2.762	13
12.242	65	3.872	20	2.610	10
9.881	51	3.701	22	2.451	12
6.593	17	3.448	20	2.399	18
5.811	21	3.363	28	2.358	14
5.452	11	3.258	20	2.198	7
5.220	5	3.169	15	2.108	8
4.927	18	3.009	12	2.060	9
4.716	14	2.957	17	1.944	10
4.427	36	2.831	15		

Ni(HDz)₂

d (Å)	I	d (Å)	I	d (Å)	I
12.490	69	3.933	44	2.998	32
10.978	100	3.914	36	2.935	35
8.272	83	3.541	100	2.731	30
5.339	58	3.466	74	2.617	28
5.029	100	3.419	75	2.271	26
4.450	22	3.368	45	2.183	25
4.122	60	3.274	36	2.094	27
4.050	72	3.104	32	2.063	30

CuDz

d (Å)	I	d (Å)	I	d (Å)	I
22.74	75	10.08	22	5.82	25
16.13	60	9.40	17	4.90	29
15.94	60	8.65	10	4.88	25
13.00	100	8.05	10	4.68	31
11.40	50	7.70	20	4.47	30
11.28	52	7.66	22	4.24	34

APPENDIX IIG Matrix Elements for Thiocarbonylhydrazide

$$G_{r_1}^{r_1} = \mu_N + \mu_C$$

$$G_{r_1}^{r_1'} = -\mu_C/2$$

$$G_{r_1}^{r_2} = -\mu_N/2 = G_{r_1}^{r_3}$$

$$G_{r_1}^R = -\mu_C/2$$

$$G_{r_1}^{\alpha 1} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_C$$

$$G_{r_1}^{\alpha 2} = -\frac{\sqrt{3}}{2} \rho_{CS} \mu_C$$

$$G_{r_1}^{\alpha 2'} = \frac{\sqrt{3}}{2} (\rho_{CS} + \rho_{CN}) \mu_C$$

$$G_{r_1}^{\beta 1} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_{r_1}^{\beta 2} = \frac{\sqrt{3}}{2} (\rho_{NN} + \rho_{NH}) \mu_N$$

$$G_{r_1}^{\beta 3} = \frac{\sqrt{3}}{2} (\rho_{NH}) \mu_N$$

$$G_{r_1}^{\beta 1'} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_C$$

$$G_{r_1}^{\beta 3'} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_C$$

$$G_{r_1}^{\gamma 1} = G_{r_1}^{\gamma 3} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_{r_2}^{r_2} = 2\mu_N$$

$$G_{r_2}^{r_3} = G_{r_2}^{r_4} = G_{r_2}^{r_5} = -\mu_N/2$$

$$G_{r_2}^{\alpha 1} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_N$$

$$G_{r_2}^{\beta 1} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_N$$

$$G_{r_2}^{\beta 2} = -\frac{\sqrt{3}}{2} \rho_{NH} \mu_N$$

$$G_{r_2}^{\beta 3} = \frac{\sqrt{3}}{2} (\rho_{CN} + \rho_{NH}) \mu_N$$

$$G_{r_2}^{\gamma 1} = -\frac{\sqrt{3}}{2} \rho_{NH} \mu_N$$

$$G_{r_2}^{\gamma 2} = \sqrt{3} \rho_{NH} \mu_N$$

$$G_{r_2}^{\gamma 3} = -\frac{\sqrt{3}}{2} \rho_{NH} \mu_N$$

$$G_{r_3}^{r 3} = \mu_N + \mu_H$$

$$G_{r_3}^{\alpha 1} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_N$$

$$G_{r_3}^{\beta 1} = \frac{\sqrt{3}}{2} (\rho_{CN} + \rho_{NN}) \mu_N$$

$$G_{r_3}^{\beta 2} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_{r_3}^{\beta 3} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_N$$

$$G_{r_3}^{\gamma 1} = G_{r_3}^{\gamma 3} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_{r_4}^{r 4} = G_{r_5}^{r 5} = \mu_N + \mu_H$$

$$G_{r_4}^{r 5} = -\frac{\mu_N}{2}$$

$$G_{r_4}^{\beta 1} = G_{r_4}^{\beta 2} = G_{r_5}^{\beta 1} = G_{r_5}^{\beta 2} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_{r_4}^{\gamma 1} = G_{r_5}^{\gamma 3} = \frac{\sqrt{3}}{2} (\rho_{NH} + \rho_{NN}) \mu_N$$

$$G_{r_4}^{\gamma_2} = G_{r_5}^{\gamma_2} = -\frac{\sqrt{3}}{2} \rho_{NH} \mu_N$$

$$G_{r_4}^{\gamma_3} = G_{r_5}^{\gamma_1} = -\frac{\sqrt{3}}{2} \rho_{NN} \mu_N$$

$$G_R^R = \mu_C + \mu_S$$

$$G_R^{\alpha_1} = \frac{\sqrt{3}}{2} (\rho_{CN} + \rho_{CN}) \mu_C$$

$$G_R^{\alpha_2} = G_R^{\alpha_2'} = -\frac{\sqrt{3}}{2} (\rho_{CN}) \mu_C$$

$$G_R^{\beta_1} = G_R^{\beta_1'} = G_R^{\beta_3} = G_R^{\beta_3'} = -\frac{\sqrt{3}}{2} \rho_{CN} \mu_C$$

$$G_{\alpha_1}^{\alpha_1} = 2\rho_{CN}^2 \mu_N + 3\rho_{CN}^2 \mu_C$$

$$G_{\alpha_1}^{\alpha_2} = G_{\alpha_1}^{\alpha_2'} = -\frac{1}{2} \left\{ 2\rho_{CN}^2 \mu_N + [\rho_{CN}(2\rho_{CN} + \rho_{CS} + \rho_{CN}) - \rho_{CS}\rho_{CN}] \mu_C \right\}$$

$$G_{\alpha_1}^{\beta_1} = G_{\alpha_1}^{\beta_1'} = \frac{1}{2} \rho_{CN} [(2\rho_{CN} + \rho_{NN}) \mu_N + (2\rho_{CN} + \rho_{CN}) \mu_C]$$

$$G_{\alpha_1}^{\beta_2} = G_{\alpha_1}^{\beta_2'} = -\frac{1}{2} (\rho_{NH} - \rho_{NN}) \rho_{CN} \mu_N$$

$$G_{\alpha_1}^{\beta_3} = G_{\alpha_1}^{\beta_3'} = \frac{1}{2} \rho_{CN} [(2\rho_{CN} + \rho_{NH}) \mu_N + (2\rho_{CN} + \rho_{CN}) \mu_C]$$

$$G_{\alpha_1}^{\gamma_1} = G_{\alpha_1}^{\gamma_3} = G_{\alpha_1}^{\gamma_1'} = G_{\alpha_1}^{\gamma_3'} = G_{\alpha_2}^{\gamma_1} = G_{\alpha_2}^{\gamma_3} = G_{\alpha_2'}^{\gamma_1'} = G_{\alpha_2'}^{\gamma_3'} = \frac{1}{2} (\cos \tau \cos \tau - 2 \sin \tau \sin \tau) \rho_{NN} \rho_{CN} \mu_N$$

$$G_{\alpha_2}^{\alpha_2} = G_{\alpha_2}^{\alpha_2'} = \rho_{CN}^2 \mu_N + \rho_{CS}^2 \mu_S + (\rho_{CN}^2 + \rho_{CS}^2 + \rho_{CN} \rho_{CS}) \mu_C$$

$$G_{\alpha_2}^{\alpha_2'} = -\frac{1}{2} \left\{ 2\rho_{CS}^2 \mu_S + [\rho_{CS}(2\rho_{CS} + 2\rho_{CN}) - \rho_{CN}^2] \mu_C \right\}$$

$$G_{\alpha_2}^{\beta_1} = G_{\alpha_2}^{\beta_1'} = \frac{1}{2} \rho_{CN} [(2\rho_{CN} + \rho_{NN}) \mu_N + (2\rho_{CN} + \rho_{CS}) \mu_C]$$

$$G_{\alpha_2}^{\beta_2} = G_{\alpha_2}^{\beta_2'} = -\frac{1}{2} (\rho_{NH} - \rho_{NN}) \rho_{CN} \mu_N$$

$$G_{\alpha_2}^{\beta_3} = G_{\alpha_2'}^{\beta_3'} = \frac{1}{2} \rho_{CN} [(2\rho_{CN} + \rho_{NH})\mu_N + (2\rho_{CN} + \rho_{CS})\mu_C]$$

$$G_{\alpha_2}^{\beta_1} = G_{\alpha_2'}^{\beta_1'} = -\frac{1}{2} (\rho_{CS} - \rho_{CN}) \rho_{CN} \mu_C$$

$$G_{\alpha_2}^{\beta_3} = G_{\alpha_2'}^{\beta_3'} = -\frac{1}{2} (\rho_{CS} - \rho_{CN}) \rho_{CN} \mu_C$$

$$G_{\beta_1}^{\beta_1} = \rho_{CN}^2 \mu_C + \rho_{NN}^2 \mu_N + (\rho_{CN}^2 + \rho_{NN}^2 + \rho_{CN} \rho_{NN}) \mu_N$$

$$G_{\beta_1}^{\beta_1'} = \frac{1}{2} (\cos T \cos T - 2 \sin T \sin T) \rho_{CN}^2 \mu_C$$

$$G_{\beta_1}^{\beta_2} = -\frac{1}{2} \left\{ 2\rho_{NN}^2 \mu_N + [\rho_{NN}(2\rho_{NN} + \rho_{NH} + \rho_{CN}) - \rho_{NH} \rho_{CN}] \mu_N \right\}$$

$$G_{\beta_1}^{\beta_3} = -\frac{1}{2} \left\{ 2\rho_{CN}^2 \mu_C + [\rho_{CN}(2\rho_{CN} + \rho_{NH} + \rho_{NN}) - \rho_{NH} \rho_{NN}] \mu_N \right\}$$

$$G_{\beta_1}^{\beta_3'} = \frac{1}{2} (\cos T \cos T - 2 \sin T \sin T) \rho_{CN}^2 \mu_C$$

$$G_{\beta_1}^{\gamma_1} = \frac{1}{2} \rho_{NN} [(2\rho_{NN} + \rho_{NH})\mu_N + (2\rho_{NN} + \rho_{CN})\mu_N]$$

$$G_{\beta_1}^{\gamma_3} = \frac{1}{2} \rho_{NN} [(2\rho_{NN} + \rho_{NH})\mu_N + (2\rho_{NN} + \rho_{CN})\mu_N]$$

$$G_{\beta_2}^{\beta_2} = \rho_{NN}^2 \mu_N + \rho_{NH}^2 \mu_H + (\rho_{NN}^2 + \rho_{NH}^2 + \rho_{NN} \rho_{NH}) \mu_N$$

$$G_{\beta_2}^{\beta_3} = -\frac{1}{2} \left\{ 2\rho_{NH}^2 \mu_H + [\rho_{NH}(2\rho_{NH} + \rho_{NN} + \rho_{CN}) - \rho_{NN} \rho_{CN}] \mu_N \right\}$$

$$G_{\beta_2}^{\gamma_1} = \rho_{NN} [(2\rho_{NN} + \rho_{NH})\mu_N + (2\rho_{NN} + \rho_{NH})\mu_N]$$

$$G_{\beta_2}^{\gamma_3} = \rho_{NN} [(2\rho_{NN} + \rho_{NH})\mu_N + (2\rho_{NN} + \rho_{NH})\mu_N]$$

$$G_{\beta_3}^{\beta_3} = \rho_{CN}^2 \mu_C + \rho_{NH}^2 \mu_H + (\rho_{CN}^2 + \rho_{NH}^2 + \rho_{CN} \rho_{NH}) \mu_N$$

$$G_{\beta_3}^{\beta_1'} = \frac{1}{2} (\cos T \cos T - 2 \sin T \sin T) \rho_{CN}^2 \mu_C$$

$$G_{\beta_3}^{\beta_3'} = \frac{1}{2} (\cos \tau \cos \tau - 2 \sin \tau \sin \tau) \rho_{CN}^2 \mu_C$$

$$G_{\beta_3}^{\gamma_1} = -\frac{1}{2} (\rho_{CN} - \rho_{NH}) \rho_{NN} \mu_N$$

$$G_{\beta_3}^{\gamma_3} = -\frac{1}{2} (\rho_{CN} - \rho_{NH}) \rho_{NN} \mu_N$$

$$G_{\gamma_2}^{\gamma_2} = 2\rho_{NH}^2 \mu_H + 3\rho_{NH}^2 \mu_N$$

$$G_{\gamma_2}^{\gamma_1} = G_{\gamma_2}^{\gamma_3} = -\frac{1}{2} \left\{ 2\rho_{NH}^2 \mu_H + [\rho_{NH}(2\rho_{NH} + \rho_{NH} + \rho_{NN}) - \rho_{NH} \rho_{NN}] \mu_N \right\}$$

$$G_{\gamma_1}^{\gamma_1} = G_{\gamma_3}^{\gamma_3} = \rho_{NH}^2 \mu_H + \rho_{NN}^2 \mu_N + (\rho_{NH}^2 + \rho_{NN}^2 + \rho_{NH} \rho_{NN}) \mu_N$$

$$G_{\gamma_1}^{\gamma_3} = -\frac{1}{2} \left\{ 2\rho_{NN}^2 \mu_N + [\rho_{NN}(2\rho_{NN} + 2\rho_{NH}) - \rho_{NH}^2] \mu_N \right\}$$

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