STUDIES OF SOME TRANSITION METAL COMPLEXES OF BIGUANIDE AND RELATED LIGANDS

by

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SUMMARY

The major part of this project consists of a study of some structural problems relating to biguanide complexes. As an adjunct to this work the reactions of the sulphur-containing ligands, guanylthiourea and dithiobiuret, with transition metal ions have been examined. The coordination chemistry of the related oxy-compounds, biuret and guanylurea which have been studied extensively by previous authors, has been reviewed.

A series of chromium(III) complexes with 1-substituted biguanides has been prepared, some for the first time. The electronic spectra of the chromium complexes have been interpreted in favour of coordination via unsubstituted nitrogen atoms only. This hypothesis is in accord with deductions made from studies of molecular models.

A systematic investigation has been made of the cobalt(II) complexes of 1-substituted biguanides. Temperature-dependence studies of the magnetic properties and measurements of the diffuse reflectance spectra in the near infrared, visible and ultraviolet regions and of the infrared absorption spectra have demonstrated that two stereochemistries exist in the series of compounds examined. It has been shown that the red complexes obtained from the reaction of cobaltous salts and 1-arylbiguanides in neutral solutions are pseudo-tetrahedral. In alkaline solutions the same reactants afford yellow, square-planar complexes. The reactions of cobalt salts with 1-alkylbiguanides yield the yellow square-planar complexes under both neutral and alkaline conditions. The bonding in these complexes and the reasons for the formation of two different stereochemistries are discussed.

The infrared spectra of a number of complexes of unsubstituted biguanide with chromium(III), cobalt(II) and copper(II) have been studied for the first time. Measurements were made on both the cationic and neutral complexes. The observation that N-H bending frequencies are higher and C-N stretching frequencies lower in the cationic complexes than in the corresponding neutral complexes, is in agreement with a proposed bonding scheme for the biguanide complexes.

As an extension of the work on biguanide complexes the reaction of guanylthiourea and dithiobiuret with transition metal ions have been studied. It has been demonstrated that cupric sulphate is reduced by dithiobiuret and a cuprous complex is precipitated. Guanylthiourea and cupric salts react with the formation of mixed valence Cu(II) Cu(I) complexes. A chromium(III) complex of guanylthiourea has been shown to exist in solution although the pure complex has not been isolated in the solid state.

ACKNOWLEDGEMENTS

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Discussions with other members of the staff, especially Dr. I.R.C. Bick in connection with chapter 3, and research students are gratefully acknowledged.

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Finally, I acknowledge the receipt of a Commonwealth Postgraduate Scholarship.

To the best of my knowledge and belief, this thesis contains no material which has been accepted for the award of any degree or diploma in any university and contains no copy or paraphrase of material previously published or written by another person, except when due reference is made in the text.

R. H. Skabo.

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CHAPTER 1

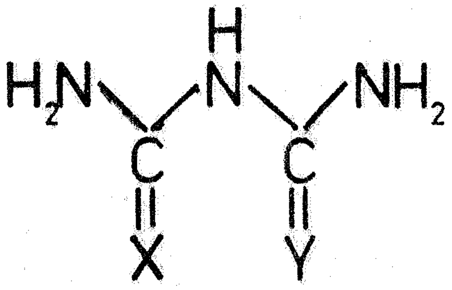
Survey of the Chemistry of some Oxygen-, Nitrogen-, and Sulphur-Containing Ligands

A great deal of interest has been taken in the group of compounds with structures based on I, overleaf. Here X and Y represent oxygen, sulphur or the imino group as shown in II through VII. The importance of the compounds, and their derivatives, arises from the usefulness of many of them, both as drugs and as ligands in forming complexes with transition metal ions. These properties have stimulated research into the chemistry of the compounds and, indeed, a number of attempts have been made to correlate the complex forming ability of the compounds with their biological activity (e.g. 42, 109).

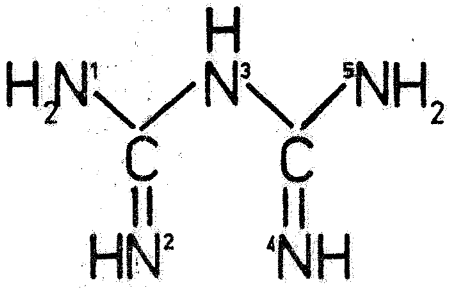
1.1. Biguanides

Biguanide, II, and its derivatives have been more extensively studied than any of the other compounds. The parent compound (II) was reported first by Rathke in 1878 (76). The syntheses of the hundreds of substituted biguanides reported since then have been greatly stimulated by the fact that many of them possess useful medicinal properties. Thus biguanides have found uses as hypoglycemic agents, trypanocides, bactericides, antirheumatic and anti-inflammatory drugs and in the treatment of skin and mental disorders.

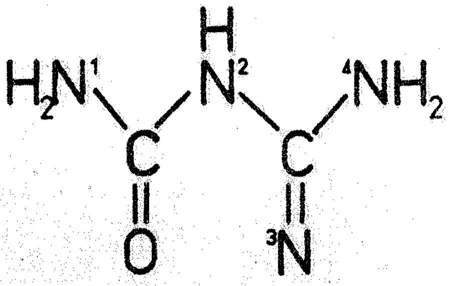
The first biguanide complex was made by Rathke (76), who obtained a pink precipitate, of bisbiguanidecopper(II) sulphate, by heating a solution containing cupric sulphate, ammonia, and a crude preparation of biguanide. Numerous complexes of biguanide and its derivatives with a majority of the transition metals have been prepared since. Most of



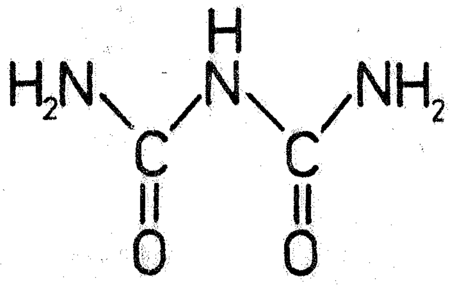
I



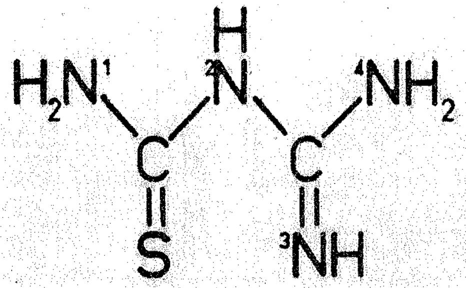
II Biguanide



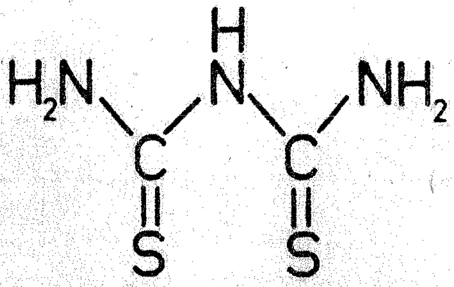
III Guanylurea



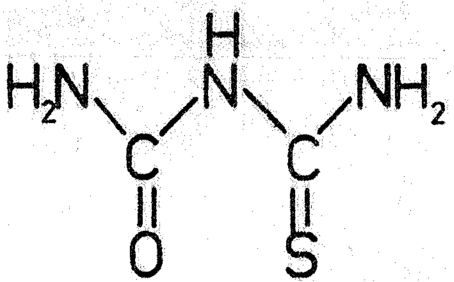
IV Biuret



V Guanylthiourea



VI Dithiobiuret



VII Thiobiuret

(The superscript figures demonstrate the numbering system for the nitrogen atoms in each of the compounds.)

these have been reported within the last thirty years by Ray and co-workers, who have carried out an extensive study of the preparation and properties of biguanide complexes. Ray (78) has prepared a fairly comprehensive review of the chemistry of biguanides and biguanide complexes, covering the literature up to about 1960. Table I, page 8 in this chapter is an up-dated version of a table in Ray's review, and lists all the biguanide complexes reported before July 1968.

a) Preparation of the Biguanides

Since Ray (78) has given a fairly extensive review of the methods of preparing the various biguanides, a brief summary is all that is necessary here.

Biguanide itself can be prepared quite satisfactorily by heating a finely ground, intimate mixture of dicyandiamide and ammonium chloride at 160-165°C for about 10 minutes. The biguanide is isolated from the byproducts as its copper complex and then liberated from the complex in acid solution (53). The disadvantages of the method are the low yield (ca 15%) and the necessity for the tedious separation as the copper complex.

A method which has neither of these disadvantages was reported by Shirai and Sugiro (95). In their procedure, O-alkylisourea, guanidine and guanidine hydrochloride are heated in alcoholic solution, affording biguanide hydrochloride in yields of about 60%.

Substituted Biguanides

1-mono- or 1,1-di- substituted biguanides are readily prepared by the reaction of dicyandiamide with the appropriate amine hydrochloride

(100, 45).

$H_2N.C(:NH).NH.C{\vdots}N + RR'NH.HCl \longrightarrow RR'N.C(:NH).NH.C(:NH)NH_2.HCl.$

(R = H, alkyl or aryl; R' = alkyl or aryl).

1,5-disubstituted biguanides can be prepared fairly readily by a two-step synthesis (24).

$NaN(CN)_2 + RR'NH.HCl \longrightarrow RR'N.C(:NH).NH.C{\vdots}N + NaCl.$

$RR'N.C(:NH).NH.C{\vdots}N + R''R'''NH.HCl \longrightarrow RR'N.C(:NH).NH.C(:NH).NR''R'''.HCl$

(R = H, alkyl or aryl; R' = alkyl or aryl;
R" = H, alkyl or aryl; R"' = alkyl or aryl).

Biguanides substituted at the 2- or 3- position have been reported. Cramer (23) prepared 1,2-disubstituted biguanides by the reaction of N,N'-disubstituted thioureas with guanidine in the presence of mercuric oxide.

$(H_2N)_2C:NH + RHN.C(:S).NHR \xrightarrow{HgO} RHN.C(:NR').NH.C(:NH).NH_2.$

1,2,3-triphenylbiguanide has been prepared by the reaction of symtriphenylguanidine and cyanamide (98).

$NH\O.C(:N\O).NH\O + NH_2.CN \longrightarrow NH\O.C(:N\O).N\O.C(:NH).NH_2$

Curd et. al. have reported the preparation of a number of 1-aryl-2-alkyl-5-alkylbiguanides as part of their work on synthetic antimalarials (24).

$ArNCS + NaHN.CN \longrightarrow ArN:C(.SNa).NH.CN.$

$ArN:C(.SNa).NH.CN + RI \longrightarrow ArN:C(.SNa).NH.CN.$

$ArN:C(SR).NH.CN + RNH_2 \longrightarrow ArN:C(NHR).NH.CN.$

$ArN:C(.NHR).NH.CN + R'R''NH.Ha \longrightarrow ArN:C(.NHR)NH.C(:NH)NR'R''.$

(Ar=aryl; R=alkyl; R'= alkyl, R"= alkyl).

1,1,4,4,5,5,-hexamethyl"-iso-" biguanide has been prepared (49) according to the following series of reactions:

$$2\ (CH_3)_2N.CN.2Ha \xrightarrow{\Delta} (CH_3)_2N.C(:NH).N:CCl.N(CH_3)_2.HCl.$$

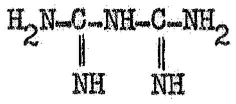
$$\xrightarrow{(CH_3)_2NH} (CH_3)_2N.C(NH).N:C(.N(CH_3)_2).\ \ N(CH_3)_2.$$

The foregoing review of the literature concerning the preparation of biguanides, demonstrates that quite a variety of these compounds has been reported.

However there are quite a few types of biguanide derivatives which have not yet been prepared and some of these would be interesting as potential ligands in complex formation with transition metals. These are discussed in a later section of this chapter.

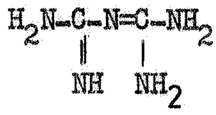
b) The Structure of Biguanide and its Derivatives

Structure II is only one of a number of possible bonding schemes for the biguanide molecule, an alternative, proposed by Wellman and Harris (110) being VIII below



$$H_2N{-}\underset{\underset{NH}{\|}}{C}{-}NH{-}\underset{\underset{NH}{\|}}{C}{-}NH_2$$

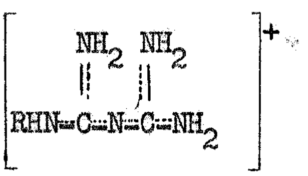
II



$$H_2N{-}\underset{\underset{NH}{\|}}{C}{-}N{=}\underset{\underset{NH_2}{|}}{C}{-}NH_2$$

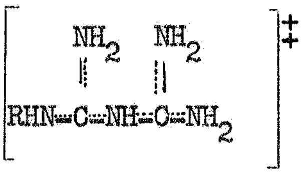
VIII

Since both 3-substituted- and 1, 1,4,4,5,5- hexasubstituted-biguanides are known, both structures II and VIII must exist at least in some biguanide derivatives. Thus structure VIII cannot have a substituent in the 3- position while II cannot give rise to 1,1,4,4,5,5-hexasubstituted products. No conclusive evidence has yet been reported which establishes the structure of the parent compound. On the other hand, Wellman and Harris (110) by using N.M.R. spectroscopy to study some substituted biguanides in acid solutions have found evidence for the existence of mono-, di- and tri-protonated biguanide ions in solutions of varying acidity (see IX, X and XI below).



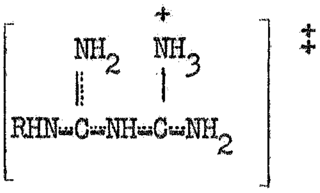
$$\left[\mathrm{RHN{-}\overset{\overset{NH_2}{\|}}{C}{-}N{-}\overset{\overset{NH_2}{\|}}{C}{-}NH_2}\right]^{+}$$

IX



$$\left[\mathrm{RHN{-}\overset{\overset{NH_2}{\|}}{C}{-}NH{-}\overset{\overset{NH_2}{\|}}{C}{-}NH_2}\right]^{++}$$

X



$$\left[\mathrm{RHN{-}\overset{\overset{NH_2}{\|}}{C}{-}NH{-}\overset{\overset{\overset{+}{NH_3}}{|}}{C}{-}NH_2}\right]^{++}$$

XI

1.2. Guanylurea and Guanylthiourea

Ray (78) has reviewed the preparation and properties of guanylureas and guanylthioureas. The review is comprehensive and, in most respects, quite satisfactory, though one important error should be pointed out. The reaction of dicyandiamide with aliphatic alcohols in the presence of cupric salts was described as proceeding according to the equation:

$$\mathrm{H_2N.C(:NH).NH.C\vdots N + ROH \xrightarrow{Cu(OAc)_2} H_2N.C(:NH).NH.C(:O).NHR.}$$

It has been shown recently (27) that the reaction affords, not the N^1-alkylguanylurea as suggested by Ray, but the O-alkylguanylurea as shown in the reaction:

$$\mathrm{H_2N.C(:NH).NH.C\vdots N{+}ROH \xrightarrow{Cu(OAc)_2} H_2N.C(:NH).NH.C(.OR):NH}$$

The review and a series of papers published by him and his coworkers relating to these so-called N^1-alkylguanylureas should in fact, definitely refer to the corresponding O-alkylguanylureas.

1.3. Biuret, Dithiobiuret and Thiobiuret

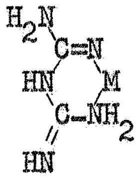
The preparation and properties of these compounds and numerous derivatives of them have been described by Kurzer (54). Only the parent compounds biuret and dithiobiuret have been shown to form complexes with transition metals and a discussion of these is presented later in this chapter. Complexes of thiobiuret have not been reported.

1.4. Biguanide Complexes

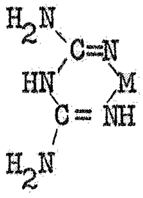
Biguanide, like many other ligands, is a moderately strong base (PKa=12.8 at 25°C). The neutral molecule acts as a bidentate chelating agent, bonding to metal ions through two of its terminal nitrogen atoms thus forming a six-membered chelate ring. The numerous substituted biguanides which have been shown to form complexes with transition metal ions (see Table 1.1) are all bases with pKa values comparable with that of the parent compound.

In strongly alkaline solutions, a biguanide loses a proton and under these conditions neutral complexes are formed with transition metal ions - i.e. bis-biguanide complexes with divalent metal ions and tris-complexes with trivalent cations.

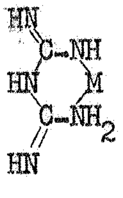
Although it is accepted that two of the four terminal nitrogen atoms act as donors in complex formation, it has not been proved which two they are. Thus there are at least four bonding schemes which may be correct (see XII to XV) for neutral complexes.



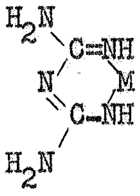
XII



XIII



XIV



XV

(M represents the required fraction of a co-ordinated metal ion i.e. one half or one third).

Table 1.1

Known Biguanide Complexes of the first row transition metals

	Metal Ion										
Ligand	V^{IV}	Cr^{III}	Mn^{III}	Mn^{IV}	Fe^{II}	Fe^{III}	Co^{II}	Co^{III}	Ni^{II}	Cu^{II}	Zn^{II}
Biguanide	+	+	+	+	+	+	+	+	+	+	+
1-methyl-biguanide	+							+	+	+	+
1-ethyl-	+							+	+	+	+
1-propyl-									+	+	
1-isopropyl-									+	+	
1-butyl-									+	+	
1-hexyl-	+	+						+	+	+	
1-(2-hydroxyethyl)-		+						+	+	+	
1-(3-hydroxypropyl)-									+	+	
1-(2-methoxyethyl)-									+	+	
1-(3-methoxypropyl)-									+	+	
1-phenyl-		+						+	+	+	
1-benzyl-		+						+	+	+	
1-(p-tolyl)-									+	+	
1-(p-ethoxyphenyl)-									+	+	
1-(p-acetylaminophenyl)-									+	+	
1-(4-sulphophenyl)-							+	+	+	+	

Table 1.1 (Cont'd)

Known Biguanide Complexes of the first row transition metals (continued)

Metal Ion.

Ligand	V^{IV}	Cr^{III}	Mn^{III}	Mn^{IV}	Fe^{II}	Fe^{III}	Co^{II}	Co^{III}	Ni^{II}	Cu^{II}	Zn^{II}
1-(p-sulphamoyl-phenyl)-								+	+	+	
1-(1-naphthyl)-									+	+	
1-(2-sulpho-1-naphthyl)-								+	+	+	
1,2-(o-phenylene)-							+	+	+	+	+
1,2-(ethylene)-									+	+	
1,1-dimethyl-	+							+	+	+	
1,1-diethyl-								+	+	+	
1,5-diphenyl-									+	+	
1-methyl-1-phenyl-									+	+	
1-ethyl-5-phenyl-									+	+	
1-(p-chlorophenyl)-5-isopropyl-								+	+	+	
1,1-diethyl-5-phenyl-									+	+	
1,1,5,5-tetramethyl.										+	

Table 1.1 (Cont'd)

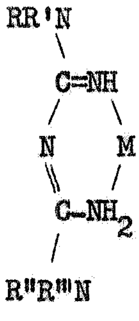
Known biguanide complexes of 2nd and 3rd row transition metals

Metal Ion

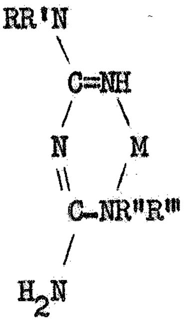
Ligand	Ru^{III}	Rh^{III}	Pd^{II}	Pd^{IV}	Re^{V}	Os^{VI}	Ir^{III}	Pt^{II}	Pt^{IV}	Au^{I}	Au^{III}
Biguanide	+	+	+	+	+	+	+	+	+	+	+
1-methylbiguanide			+								
1-ethyl-			+								
1,1-dimethyl-			+								
1-(2-hydroxyethyl)-			+								
1-(3-hydroxypropyl)-			+								
1-(2-methoxyethyl)-			+								
1-(3-methoxypropyl)-			+								
1-phenyl-			+								
1-benzyl-			+								
1,5-diphenyl-			+								
1,1-diethyl-5-phenyl-			+								
1-(p-chlorophenyl)-5 isopropyl-			+								

Note: Complexes reported after 1960 are those of iron(II) and iron(III) (Ref. 90), ruthenium(III) (Ref. 89), rhodium(III) (Ref. 96), iridium(III) (Ref. 97), platinum(II) (91), platinum(IV) (Ref. 93) and gold(I) and gold(III) (Ref. 92).

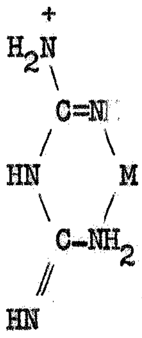
When a proton is added to each ligand molecule, so that the complex becomes a cation with the ligands formally neutral, even more possibilities arise. Ray and coworkers (78,86) have proposed XII and XVI as the structures which best account for the chemical properties of neutral and cationic biguanide complexes, respectively. In the latter case (XVI) the biguanide molecule is supposed to act as a zwitterion.



XVII



XVIII

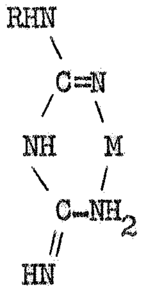


XVI

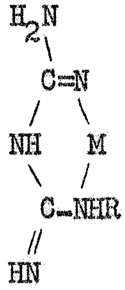
In Ray's opinion, then, an imino nitrogen is deprotonated in both the neutral and cationic complexes, the proton in the latter case being accommodated on a quarternary nitrogen. He pointed to the preparation of complexes of 1,1,5,5-tetrasubstituted biguanides as evidence in favour of this hypothesis, reasoning that in these complexes only the imino-nitrogens could be deprotonated. He appears to have neglected the possibility that the imido nitrogen, N^3, could be deprotonated in this case. (see XVII and XVIII).

The structure (XIII) proposed by Curd and Rose (25) was discounted by Ray (78) because it did not explain adequately the chemical properties of biguanides as observed by him. However, Ray's arguments and experiments have not proved conclusively that XIII or XVII or XVIII are incorrect. The preparation of a complex with an N^3-substituted biguanide would eliminate structures XVII and XVIII, but no such preparation appears to have been reported.

Further structural isomers must be considered when complexes of some substituted biguanides are studied. In the case of an N^1-substituted biguanide it is not only necessary to decide whether amino- or imino-nitrogens are co-ordinated, but, also whether the substituted amino group is co-ordinated or not (as in XIX and XX).

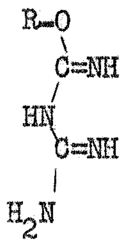


XIX

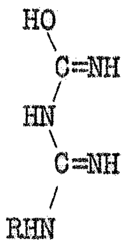


XX

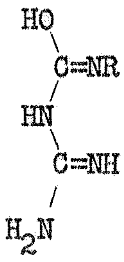
For N^1-substituted biguanides Ray and Saha (86) have postulated structure XX on the basis of their chemical evidence and once again their hypothesis is open to some doubt. In postulating XX they have made the assumption that biguanides are able to co-ordinate through a substituted nitrogen atom. Since many ligands, notably N-substituted ethylenediamines and salicylaldimines, are known to do just that, their assumption would appear at first sight to be quite reasonable. However they seem to have ignored the fact that Cramer (23) and Slotta and Tschesche (98), having prepared 1,2-di-substituted biguanides, found that they could not isolate copper complexes of them. This fact suggests that biguanides may not readily co-ordinate through substituted nitrogen atoms. Furthermore it has been shown by Diana et. al. (27) that although O-substituted guanylureas (XXI) and N^3-substituted guanylureas (XXII) readily form complexes with metal ions, the N^1-substituted guanylureas (XXIII) do not. They attributed these properties to the steric hindrance between the metal ion and the substituent which cannot be avoided when compounds of type XXIII co-ordinate with a metal ion through the substituted nitrogen atom.



XXI

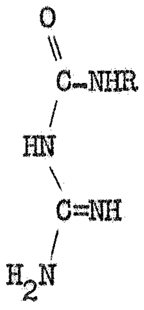


XXII

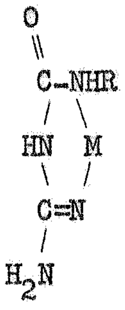


XXIII

It should be noted that Ray and Dutta (82) had previously, and mistakenly, assigned structure XXIV to the compounds which were in fact O-substituted guanylureas XXI. Ray and Dutta thus thought they had proof that guanylureas, at least, could co-ordinate through substituted nitrogen atoms (as in XXV).



XXIV



XXV

Studies of the chemical properties of biguanide complexes appear to have left us with very little definite information about their structures. Thus there is still uncertainty about which two of the four terminal nitrogen atoms in the parent biguanide are actually co-ordinated in metal complexes; it is not known whether the chelate ring is conjugated (structure XV) or not, and in the complexes of substituted biguanides there is some doubt that the substituted nitrogen atoms are able to co-ordinate with the metal.

Very little use has been made of physical techniques in structural studies of the biguanide complexes.

The infrared spectra of some copper and nickel complexes with substituted biguanides have been used to demonstrate (77) that isomerism of some kind may exist in these supposedly square planar complexes. No attempt was made to assign any of the bands in these spectra to vibrational modes of the complexes.

Electronic spectroscopy has been used to a limited extent in studies of biguanide complexes. Single-crystal spectra of some bis-biguanide-copper(II) and -nickel(II) halides (15) and of tris-biguanide chromium(III) (5) have been reported recently. Banerjea and Basu (6) have recently studied the solution and diffuse reflectance spectra of a silver(III) complex of the tetradentate ethylenedibiguanide. The absorption and circular-dichroism spectra of the tris-biguanide complexes of chromium(III) and cobalt(III) have been reported by Michelsen (59).

These studies have been concerned not with the bonding in the ligands but rather with the environment of the metal ions.

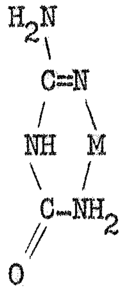
A number of thermodynamic studies of biguanide complexes of copper(II), nickel(II), cobalt(III) and chromium(III) have been made. Both spectroscopic and potentiometric techniques have been used in these studies.

The kinetics of the dissociation of some tris-biguanide complexes of chromium(III) and cobalt(III) were investigated by Banerjea and coworkers (8). They followed changes in concentration of the various species spectrophotometrically at suitable wavelengths. A similar technique has been used by Ray and coworkers in determining the stabilities of quite a number of copper and nickel biguanide complexes (78). The potentiometric (pH) method has been used to determine the stability constants of Cu(II), Ni(II) Co(III) and Cr(III) complexes (78). No definite correlations have been found between the base strength of the biguanides and the stability of their complexes. An interesting problem has been posed by earlier studies of biguanide complexes of cobalt(II). It has been found (84,85) that some of these compounds are yellow, with magnetic moments in the range 2.0 to 2.8 B.M. while others are red and have magnetic moments of the order of 4.8 B.M. It has been postulated (78) that the yellow complexes are low-spin, square planar. There has been no systematic study of this phenomenon and the structures of these complexes have been only tentatively assigned.

1.5. Guanylurea Complexes

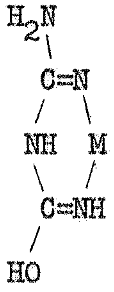
Table 1.2 which lists the known guanylurea complexes collates data from a review by Ray (78) and the literature after 1961. As mentioned earlier (page 6) the alkylguanylureas are now referred to correctly as O-alkylguanylureas rather than N^1-alkylguanylureas as described in many earlier papers.

The similarity of the visible absorption spectra of biguanide and guanylurea complexes was cited by Ray and coworkers as evidence for nitrogen bonded structures for the latter (78). Structures proposed by Ray (78), and others are shown below, XXVI to XXVIII, as are the alternative structures XXIXa and XXIXb which are analogous to structure XV, proposed earlier for biguanide complexes.



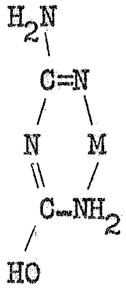
XXVI

(Ref. 78)



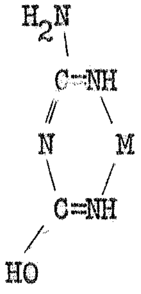
XXVII

(ref. 27)

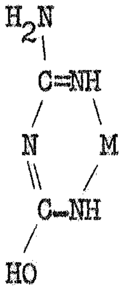


XXVIII

(ref. 27)



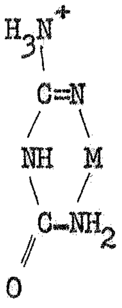
XXIXa



XXIXb

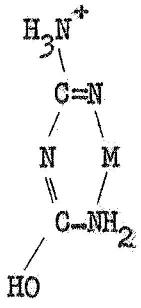
Structure XXVI cannot hold in the case of an O-alkylguanylurea and is therefore most probably incorrect also for the parent compound. There is no real evidence available which enables a choice to be made between the other structures, although XXIX has the advantage that it allows stabilisation of the chelate ring by delocalisation of π - electrons.

In the cationic guanylurea complexes the extra proton on each ligand molecule must presumably be accommodated on a nitrogen atom. Once again there are several possible structures which could account for the protonation and some of these, XXX to XXXIII, are shown below with appropriate references if they have appeared in the literature.



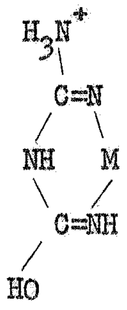
XXX

(Ref. 78)



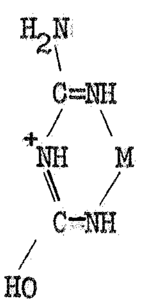
XXXI

(ref. 27)



XXXII

(ref. 27)



XXXIII

Table 1.2

Known Guanylurea Complexes

Metal Ion

Ligand	V^{IV}	Cr^{III}	Co^{II}	Co^{III}	Ni^{II}	Cu^{II}	Zn^{II}	Pd^{II}
guanylurea		+		+	+	+		+
O-methylguanylurea	(a)	+		+	+	+	+	+
O-ethyl-	(a)	+		+	+	+	+	+
O-isopropyl-					+	+		
O-n-butyl	(a)	+		+	+	+		+
O-iso-butyl-		+		+	+	+		+
O-iso-amyl-		+		+	+	+		+
O-n-hexyl-		+		+	+	+		+
O-(2-hydroxyethyl)-						+		
O-(2-methoxyethyl)-					(b)	(b)		(b)
O-(2-ethoxyethyl)-	(a)				(b)	(b)		(b)
O-(2-butoxyethyl)-	(a)				(b)	(b)		(b)
O-benzyl-					+	+		
N^4-phenyl			+	+	+	+		

Note: + Represents a known complex listed previously by Ray (Ref. 78, p323).

(a) and (b) represent complexes reported after 1960 as follows:

(a) Dutta R.L. and Lahiry S., Ref. (32).

(b) " " " " " " (31).

Structure XXX, proposed by Ray (78), can be assumed to be incorrect on the same grounds used for excluding XXVI.

There is at this stage no means of choosing between the remaining structures.

Complexes of N-substituted-guanylureas are not well known. It has been shown that N^1-substituted-guanylureas do not form complexes (27) and apart from this, the only work on N-substituted-guanylurea complexes was the preparation of a copper(II) complex of N^4-phenylguanylurea by Ray and Bandyopadhayay (79).

Physiochemical studies of guanylurea complexes have been even less numerous than in the case of biguanide complexes. Quantitative studies of the stabilities of some copper(II) and nickel(II) complexes have been conducted by Dutta (29), who measured concentrations spectrophotometrically at suitable wavelengths.

The electronic spectra in the visible region, for a number of copper(II) and nickel(II) (29) and some cobalt(III) complexes (30) of alkyl-guanylureas have been measured. Room temperature magnetic moments of some complexes have been determined (31,32) but no temperature dependence studies have been reported.

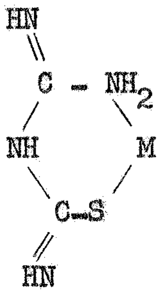
1.6. Guanylthiourea Complexes

Complexes of guanylthioureas have been studied to a very much lesser extent than have those of the biguanides and guanylureas. Table 1.3 lists the known complexes of guanylthioureas:

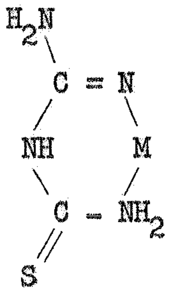
Table 1.3

Ligand	Co^{II}	Ni^{II}	Cu^{II}	Pd^{II}
guanylthiourea	+	+	+	+ (Ref. 78)
S-ethylguanylthiourea	+	+	+	(Ref. 69)

Ray and coworkers (80,78,73) have suggested that, unlike guanylurea, guanylthiourea may coordinate with a metal ion either through two nitrogen atoms or through one nitrogen and the sulphur atom. Structure XXXIV was proposed for the palladium(II), cobalt(II) and (III) and the copper(II) complexes while the nitrogen-bonded structure, XXXV was assigned to the nickel complex. These structural assignments were based on the colours of the complexes and the reactions of the complexes with warm alkali. It was suggested that the decomposition of the cobalt, copper and nickel compounds to the corresponding metal sulphides in the presence of warm alkali implied sulphur to metal bonding in these complexes. The nickel complex was unaffected by warm alkali and resembled the biguanide and



XXXIV



XXXV

guanylurea complex in colour and was therefore believed to contain nitrogen - metal bonds only.

Cobalt(II), nickel(II) and copper(II) complexes of S - ethylguanylthiourea were prepared by Paigankar and Haldar (69). The magnetic properties of the cobalt(II) and copper(II) compounds were studied between 85°K and 300°K. Both complexes obeyed the Curie-Weiss law; the cobalt complex had a magnetic moment of 2.26 B.M. at 297°K and a θ value of 17°K while the copper complex had a moment of 1.82 B.M. at 292°K and a θ value of 4°K.

Colour and chemical properties implied metal-sulphur bonding in the cobalt complex and metal-nitrogen bonding only, in the copper and nickel complexes.

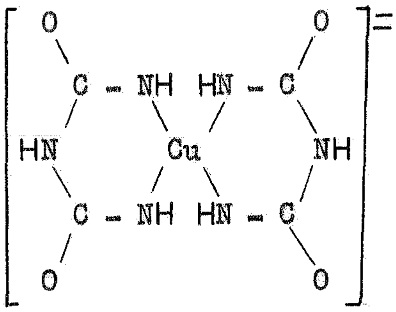
The analytical applications of guanylthiourea were studied by Trimble (104). Of twenty metal ions studied, he found that only five (Cu(II), Co(II), Ni(II), Pd(II) and Ag(I)) afforded precipitates with the ligand. Analyses of these precipitates showed that the compounds formed were not stoichiometric, although in some cases they were almost so. For these complexes the metal to ligand ratios were as follows: copper 1:1, nickel 1:2 and cobalt 1:2.

The ratio for palladium was indeterminate and the silver compound was not analysed.

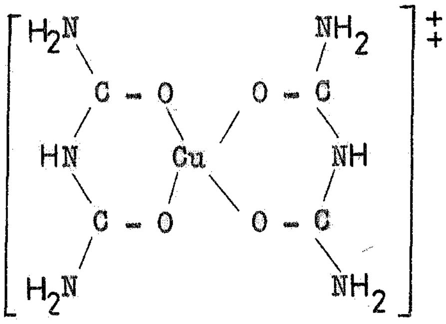
1.7. Biuret Complexes

There have been relatively few biuret complexes reported, but most of these have been studied in detail. The X-ray structures of the copper complexes $K_2\ [Cu(C_2H_3O_2N_3)_2]\ 4H_2O$ and $[Cu(C_2H_5O_2N_3)_2]\ Cl_2$ have been determined (43,44) Nardelli and coworkers have determined structures for the zinc(II) cadmium(II) and mercury(II) complexes (61,62,63). Structures of several other complexes have been inferred from spectroscopic evidence (17,57,58).

Three distinct types of coordination have been found in biuret complexes. In the anionic copper complex mentioned above, biuret is a bidentate ligand, coordinating through two nitrogen atoms as shown in XXXVI. The complex is square planar although there are weak axial interactions between the copper ion and two nitrogen atoms from adjacent complex molecules. (Such a situation is depicted for a hypothetical biguanide complex in figure 3.4a on page 55).



XXXVI



XXXVII

The situation is different in cationic copper biuret complex where it was found (43,44) that biuret is bonded to the metal via two oxygen atoms as shown in XXXVII. Again, the complex is square planar and in this case there are weak axial interactions with the two chloride anions. A similar structure has been determined for the cationic zinc(II) complex (63).

Nardelli et. al. (61) have been determined the complete structure of the complex $CdCl_2.2C_2H_5O_2N_3$. They found that each cadmium ion is surrounded by an octahedron consisting of four chloride ions and two oxygen atoms, one from each of the two monodentate biuret molecules. The octahedra are joined, by shared edges made up of bridging chlorines, into long chains.

The same authors have shown that the corresponding mercury(II) complex is isostructural (62). Melson and McClellan (57) have used infrared and electronic spectroscopy to determine the structures of a number of biuret complexes of divalent metals. For complexes with the general formula $[M^{II}(C_2H_5O_2N_3)]Cl_2$, where M is Ni, Cu, Co or Mn, they concluded that the ligand is bidentate and coordinated via oxygen. A similar structure has been postulated for tris (biuret) chromium(III) perchlorate by Chatterjee and Porter (12).

It appears, then, that the type of coordination undergone by biuret with transition metal ions depends largely upon the conditions maintained during the reaction. In the cationic complexes obtained from neutral solutions the bonding is via oxygen while the anionic complexes obtained from alkaline solution, coordination is via deprotonated amino groups.

1.8. Dithiobiuret Complexes

The only one of these complexes to have been obtained pure and properly characterised is a silver(I) derivative reported by Stephen and Townshend (100) as having the formula $[Ag_2(C_2H_5N_3S_2)_3](NO_3)_2$. The authors interpreted the infra-red spectrum of this complex as indicating monodentate coordination of dithiobiuret via a sulphur atom.

Bandyopadhayay (4) obtained a number of coloured dithiobiuret derivatives when he caused dithiobiuret to react with transition metal salts in aqueous solutions. Most of these compounds were stable to dilute mineral acids but decomposed to the metal sulphides in alkaline solution or upon heating. The compounds were neither characterised nor analysed in any way.

The only other dithiobiuret complex reported previously is the yellow cuprous compound obtained from the reaction of dithiobiuret and cuprous chloride in an aqueous medium (3). This complex was not characterised in any way.

1.9. Conclusions

The gross structural features of the complexes mentioned in this review have been established to a large extent. Thus it is obvious that biguanides are able to coordinate only through nitrogen donor atoms, and it appears that guanylureas do the same (10). There is some evidence, however, that guanylthioureas are coordinated through nitrogen-sulphur in some complexes and nitrogen alone in others. The type of coordination in biuret complexes appears to depend mainly upon the method of preparation. Little can be said at this stage about the complexes of dithiobiuret since they have been so little studied.

The only complexes for which detailed structural data are available are the biuret complexes of copper (43,44) and zinc (63). Clearly the most useful way to obtain similar details for the other complexes is to undertake X-ray diffraction studies on them. However, it seems certain that the application of other, less time-consuming, techniques should provide some insight into the bonding in these complexes.

It should be possible to determine which are the donor atoms in most complexes, by means of electronic spectroscopy. Such studies have already been used in determining the type coordination in some biuret and guanylurea complexes and should be applicable to guanylthiourea and perhaps dithiobiuret complexes.

Infrared spectroscopy has been used to a limited extent in studies on biuret complexes. Its use in other cases may be restricted somewhat by the complexity of the molecules involved. Magnetochemical studies should provide information on the stereochemistries of the metal ion in some complexes and will thus be indirectly useful only, in studies of the bonding in the ligands.

Complexes of biguanide and its derivatives have been studied more extensively than the complexes of any of the other ligands mentioned above and yet very little definite detailed structural information is available. In the case of the N^1-substituted biguanides, for example, it is not known whether the substituted nitrogen is coordinated with the metal or not. The possibility of conjugation in the chelate ring has not even been discussed previously although the ligand would probably lend itself readily to stabilisation by this means. Finally, the arrangement of the protons in these complexes is not at all certain. A more detailed study of the compounds by chemical and physical techniques should lead to a better understanding of at least some of these points.

In conjunction with studies of the biguanide complexes it should be interesting to investigate the complexes of some of the other ligands. A comparison of the properties of biguanide with those of guanylurea and guanylthiourea in which one nitrogen is replaced by oxygen or sulphur and with biuret or dithiobiuret, where two nitrogens are replaced, should be instructive.

CHAPTER 2

BIGUANIDE COMPLEXES

Studies of the Coordination of Biguanide and Substituted Biguanides

The bonding in biguanide complexes has not been studied previously in any detail. Some features on which evidence is required are the following:

(i) the correct formulation of biguanide complexes as either cationic or neutral species

(ii) the arrangement of protons on the ligands in these complexes

(iii) the degree of conjugation in the chelate ring

(iv) the ability of substituted nitrogens to act as donor atoms in complex formation.

In this study it has been demonstrated that biguanide complex bases should, in fact, be formulated as the hydrated, neutral species rather than as the corresponding hydroxides. Infrared and visible - U.V. spectra have been used to establish formulae for these complexes.

Points (ii) and (iii) are closely related since the arrangement of protons on the ligand skeleton is dependent upon whether or not there is conjugation in the chelate ring. Attempts have been made to devise a suitable synthesis for N^3-substituted biguanides which should be of use in an investigation of these features.

Complexes of some N^1-substituted biguanides have been studied and it has been shown that in none of these complexes does a substituted nitrogen act as donor atom.

2.1. Formulation of Biguanide Complexes

In general it is accepted that biguanide complex salts contain the cationic species, $[M(BgH)^{*}_{n}]^{n+}$, associated with anions, nX^-. However, in the case of the corresponding complex bases both the formulae $[M(BgH)_n](OH)_n$ and $[M(Bg)_n].nH_2O$ have been used indiscriminately. It is clear that these two formulations imply the existence of two distinctly different complex species, one cationic the other uncharged. In the former species the ligand is formally uncharged, in the latter it is deprotonated and therefore negatively charged.

Some indication of the correct formulation of the complex bases can be obtained from the fact that they can be dehydrated easily to the anhydrous compounds which can only be formulated $[M(Bg)_n]$. Now if the hydrated complex base is actually $[M(BgH)_n](OH)_n$, then dehydration has resulted in a change in the nature of the complex species, from $[M(BgH)_n]^{n+}$ to $[M(Bg)_n]$. Thus dehydration should also be accompanied by some changes in the properties of the complex. The infrared spectra of several hydrated and anhydrous complex bases have been measured, and while a detailed discussion of these spectra is reserved for chapter 4, the following points are of significance here. The only changes observed in the infrared spectra of the complexes after dehydration were the absence of bands in the 3 micron region, which could be attributed to O-H stretching vibrations. No shifts were observed in the N-H deformation and C-N stretching bands, which occur below 1700 cm^{-1}. It has similarly been found that dehydration does not result in any changes in the electronic spectra of biguanide complex bases. Thus these observations, which should be fairly sensitive to changes in the nature of the complex species,

* BgH = Biguanide

suggest that the hydrated and anhydrous complexes should be similarly formulated as $[M(Bg)_n].xH_2O$ and $[M(Bg)_n]$.

In support of this hypothesis it has been shown that there are, on the other hand, marked differences between the properties of a complex base and the corresponding salt. A detailed study of the infrared spectra of a number of these complexes is described in chapter 4. It has been found that for a complex salt the N-H deformation frequencies are higher and the C-N stretching frequencies lower than for the corresponding base. Furthermore the electronic spectra of complex bases and salts are significantly different. From table 2.1 it may be seen that there is a hyposochromic shift of the spin allowed bands on passing from base to salt, in the octahedral complexes of chromium(III) and cobalt(III).

Table 2.1

Electronic Spectra of Biguanide Complexes

Complex	Diffuse Reflectance spectrum (cm^{-1})
$[Cr(Bg)_3]$	20,000; 26,200
$[Cr(BgH)_3]Cl_3$	20,700; 27,100
$[Co(Bg)_3]$	19,600; 26,800
$[Co(BgH)_3]Cl_3$	20,200; 27,800

This evidence favours different formulations for biguanide complex bases and salts and it would appear that the species should be formulated as $[M(Bg)_n].xH_2O$ and $[M(BgH)_n]X_n$ respectively.

2.2. Coordination of 1-Substituted Biguanides

a) Studies with Molecular Models

The steric interactions caused by the addition of substituents to one coordinated nitrogen atom in each of the ligands in a tris-biguanide complex were examined qualitatively by means of covalent molecular models (Catalin).

It was found that although three unsubstituted biguanide molecules could be accommodated easily around a metal ion, the addition of even a small substituent, such as a methyl group, gave rise to a certain amount of steric interaction. As the size of the substituent increased from methyl, to isopropyl or phenyl, the steric interaction became more severe. However, it appeared that most mono-substituted biguanides could be accommodated even though coordinated through the substituted nitrogen atoms.

For the 1,1-disubstituted biguanides the steric interactions were much greater. It seemed to be possible for 1,1-dimethyl biguanide to coordinate through N^1, although steric interactions were considerable. However, substituents as large or larger than isopropyl or phenyl groups made coordination via N^1 impossible. Thus, should the tris (1,1-diisopropyl-biguanide) or tris (1,1-diphenyl-biguanide) complexes of a transition metal be formed, coordination would necessarily be by means of the unsubstituted N^2.

It is possible, then, that the tris-complexes of biguanides substituted at N^1 could fall into two classes, those in which the ligands are coordinated through N^1 and those in which coordination is through N^2. While many complexes could belong to either class, those of

1,1-diphenylbiguanide or 1,1-diisopropyl-biguanide are restricted, by steric considerations, to the latter class. Furthermore, since even small substituents produce some steric interactions, it seems more likely that all N^1-substituted biguanides would coordinate in a similar manner; i.e. through N^2.

In order to make a study of the coordination of N^1-substituted biguanides, a series of chromium(III) complexes was prepared. Ligands ranging from the parent biguanide, to 1,1-diphenylbiguanide, all formed complexes quite readily with chromium(III). Analytical data collected in table 2.3, together with spectroscopic and magnetic data contained in tables 2.2 and 2.4 respectively, all point to the fact that these compounds are tris-biguanide complexes with pseudooctahedral structures.

In the case of tris (1,1-diphenylbiguanide) chromium(III) there is no doubt that the ligand is coordinated only through unsubstituted nitrogen donor atoms. For the other complexes, however, the type of coordination cannot be decided by steric considerations alone. The electronic spectra of all the chromium complexes have been measured, therefore, so that the type of coordination in the diphenylbiguanide complex can be compared with that in the complexes of other biguanides.

b. Electronic Spectra

The absorption spectra, in aqueous or alcoholic solutions, and the diffuse reflectance spectra of several chromium(III) biguanide complexes, measured in the 1000 to 220 millimicron region, are listed in table 2.2. Some of the spectra are reproduced in figure 2.1. The assignments given in table 2.2 are based on the assumption that the chromic ion is situated in an octahedral ligand field (28). Although the low symmetry of the biguanides means that the symmetry of the ligand field is necessarily lower than D_3, the absence of any noticeable splitting in the spin-allowed bands indicates that the perturbations of the octahedral energy levels are small.

This apparent high symmetry of the ligand fields in the chromium complexes may be used as evidence that the biguanides are coordinated through unsubstituted nitrogen atoms in all cases studied here. The unsymmetrical addition of substituents to donor nitrogen atoms in the ligands would be expected to cause far more severe distortions of the ligand field than the addition of substituents to non-donor nitrogen atoms. The absence of any apparent change in the symmetry of the ligand field as substituents are introduced can thus be taken to indicate that the substituents are not attached to donor nitrogen atoms.

Additional evidence on the type of coordination in these complexes can be obtained by considering the energies of the absorption maxima in the electronic spectra.

The position of the first spin allowed band in these spectra gives the value of the ligand field parameter, 10 Dq or Δ. This parameter is a measure of the interaction between the metal and ligand orbitals and may have contributions from several sources.

Pavkovic and Meek (70) studied the spectra of some nickel(II) complexes of N-substituted ethylenediamines. They found that 10 Dq changes from 11200 cm^{-1} for $[(Ni\ en_3)]Cl_2$ to 10,000 cm^{-1} for $[Ni(N,N\text{-dimethylen})_3]Cl_2$ and a spectrochemical series could be established

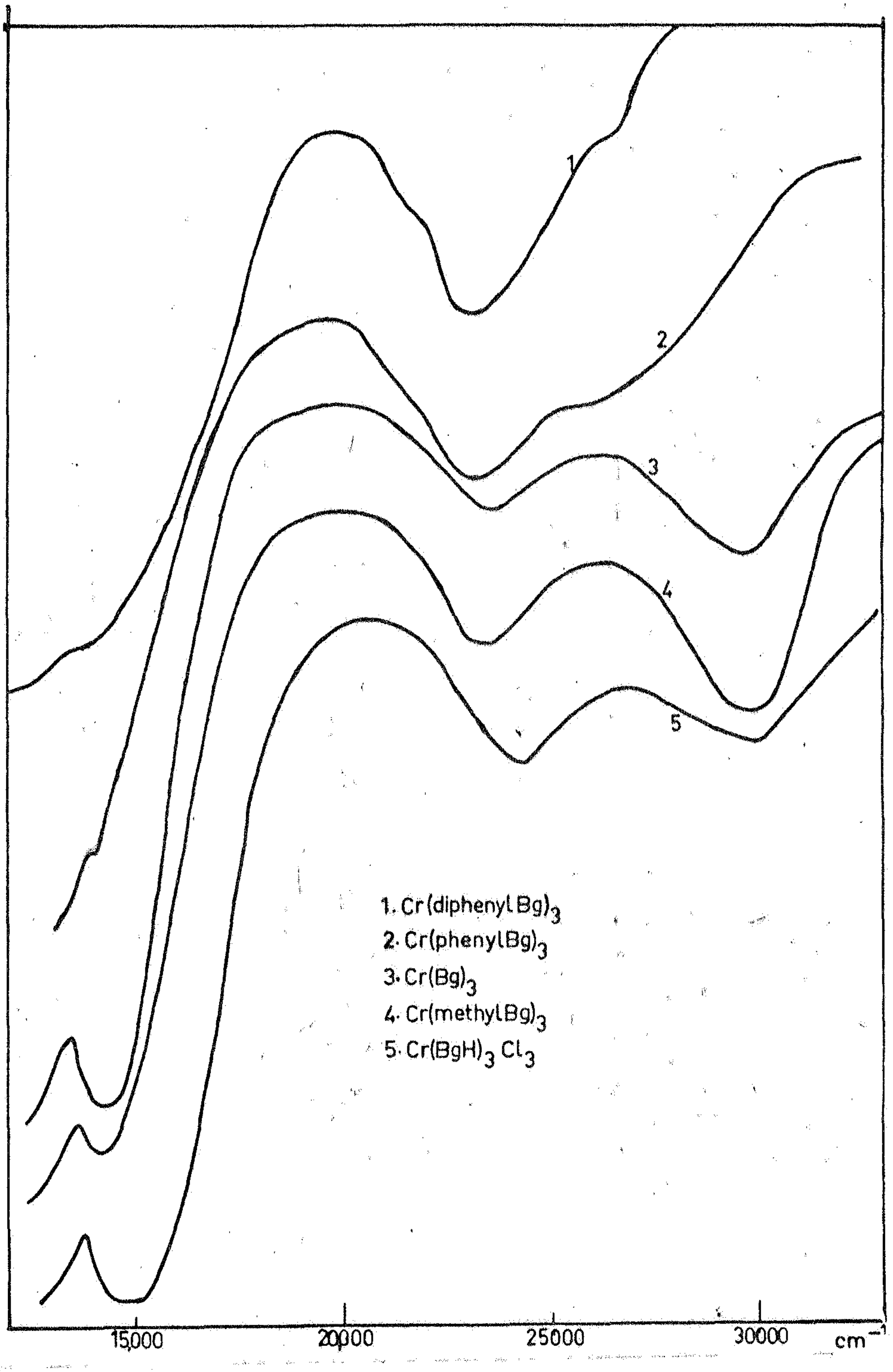


Figure 2.1. Diffuse Reflectance Spectra of Chromium(III) Biguanide Complexes

Table 2.2 Electronic Spectra of Chromium(III)

Biguanide Complexes

Band positions in cm^{-1} (molar ext. co-effs).

Complex*	Mode (Solvent)	$(^2Eg \leftarrow {}^4A_{2g})$	$^4T_{2g}(F) \leftarrow {}^4A_{2g}$	$^4T_{1g}(F) \leftarrow {}^4A_{2g}$
$[Cr(Bg)_3]$	Transmission (H_2O)		20,200(90)	26,000(57)
	Refl.	13,550	20,000	26,200
$[Cr(Methyl\ Bg)_3]$	Transmission (H_2O)		20,000(63)	25,300(56)
	Refl.	13,700	20,000	26,200
$[Cr(phenyl\ Bg)_3]$	Transmission (EtOH)		20,400	
	Refl.	14,000(sh)	20,000	25,500(sh)
$[Cr(O\text{-}chlorophenyl\ Bg)_3]$	Transmission (EtOH)	- -	20,200	- -
	Refl.	13,800	20,200	26,300(sh)
$[Cr(diphenyl\ Bg)_3]$	Transmission (EtOH)		20,400	
	Refl.	13,700(sh)	20,000	26,400(sh)
$[Cr(BgH)_3\ Cl_3]$	Refl.	13,900	20,700	27,100

* Formula written without water of crystallisation.

for the group of ligands studied. The series, in order of decreasing ligand field strength, was:

en>N-methylen>N-ethylen>N-propylen>N,N'-dimethylen>N-methyl-Nethylen>N,N-dimethylen. The shifts in the Dq values were attributed entirely to "steric effects" since they were in the opposite direction to any which might be expected to arise from "inductive effects". A slightly different spectrochemical series was arrived at by Watt and Alexander (107), when they made a study of a series of rhodium(III) complexes of the type $[Rh(diamine)_2Cl_2]Cl$. The differences in the two series can be attributed to the smaller steric effect in the rhodium complexes where only two diamine molecules are present in the complex ions. In this case the inductive effect may determine the position of some of the ligands in the series.

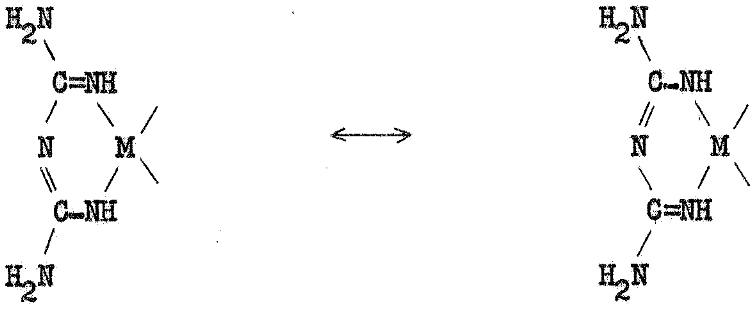
It seems clear, from the above, that in a series of complexes in which the same metal ion is complexed by several ligands differing only in the substituents on the donor atoms, some observable differences should appear in their electronic spectra.

It can be seen, however, that in the spectra of the chromium(III) biguanide complexes, no such differences are displayed. Thus Dq is virtually the same for all of the complexes examined and this suggests that the ligands are all coordinated to the metal ion in the same way. Since the studies with molecular models have demonstrated that in the diphenylbiguanide complex coordination must be via unsubstituted nitrogen atoms only, it is suggested that in all the complexes examined, similar situations will be found.

It does not necessarily follow, of course, that in all complexes of N^1-substituted biguanides the ligands are coordinated through unsubstituted nitrogen atoms only. However, the evidence outlined above, together with that discussed in chapter 1, certainly suggests that such a situation is more likely than one in which the ligand is coordinated through the substituted nitrogen atoms.

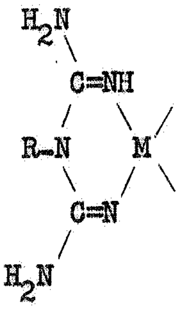
2.3. N^3-Substituted Biguanides

The possibility of conjugation in the chelate ring in biguanide complexes has already been mentioned briefly, and bonding schemes such as XV have been proposed for these complexes.



XVa XVb

For a bonding scheme like XV it is necessary that deprotonation of the ligand occurs at N^3 and it is obvious that if a substituent can be introduced at N^3 it will act as a barrier to conjugation as shown in XXXVIII.



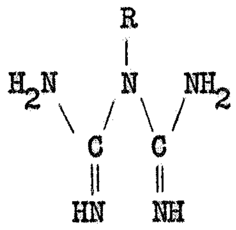
XXXVIII

Furthermore, for an N^3-substituted biguanide, deprotonation must occur at some other nitrogen atom, probably N^2, as shown in XXXVIII.

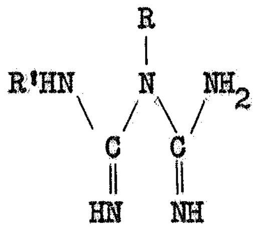
Thus a comparison between complexes of N^3-substituted biguanides with those of other biguanides might well be useful both in deciding upon the degree of conjugation in these complexes and in determining how the protons are attached to the ligands. Differing degrees of conjugation and deprotonation of different nitrogen atoms would be expected to give rise to changes in the electronic spectra of the complexes, since the charge distribution of the ligands would be altered. A comparison of the electronic spectra of complexes of N^3-substituted biguanides with those of other biguanides should enable any differences in the bonding in these complexes to be discerned.

The only N^3-substituted biguanide reported in the literature is 1,2,3-triphenylbiguanide which was prepared by Slotta and Tschesche in 1929 (98). These authors found that this biguanide would not form the usual pink complex with the cupric ion and it has been suggested earlier in this thesis that this lack of coordinating ability is due to the presence of substituents at both N^1 and N^2. Thus for this compound to form a chelate complex it must coordinate through a substituted nitrogen atom.

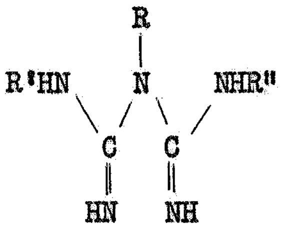
It was necessary, therefore, to seek a suitable method for the preparation of an N^3-substituted biguanide which would be able to form a chelate complex in which two unsubstituted nitrogen atoms are coordinated to the metal ion. Several biguanide derivatives which would fulfil this requirement are shown below as structures XXXIX to XLI.



XXXIX



XL



XLI

The 1,3,5-trisubstituted biguanide, XLI, suggested itself as the compound which could probably be prepared most readily. A survey of the literature had revealed that aryldicyanamides could be prepared quite easily and that they are quite stable at temperatures up to about 60°C (106). It seemed likely that an aryldicyanamide could be caused to react with two moles of an amine or amine hydrochloride in a similar procedure to that used for the preparation of 1,5-disubstituted biguanides (see page 4). Such a reaction was envisaged as proceeding according to the equation:

$$N{\equiv}C - N(Ar) - N - C{\equiv}N + 2RNH_2 \longrightarrow RHN{-}C({=}NH){-}NH{-}C({=}NH){-}NHR$$

Alkyldicyanamides are unstable even at room temperature and would therefore be unsuitable for such a preparation.

Accordingly, phenyldicyanamide was prepared by the literature method (12,106) which involves a three step reaction between aniline and cyanogen bromide.

$$2C_6H_5NH_2 + CNBr \longrightarrow HN(C_6H_5)CN + C_6H_5NH_2HBr$$

$$HN(C_6H_5)CN + KOH \longrightarrow KN(C_6H_5)CN + H_2O$$

$$KN(C_6H_5)CN + CNBr \longrightarrow C_6H_5N(CN)_2 + KBr$$

Several means of effecting a reaction between the phenyldicyanamide and amines or amine-hydrochlorides were tried. However, no reaction at all was caused by refluxing the compounds in alcoholic solution, and fusion of a mixture of the compounds at temperatures above 60°C resulted only in the formation of a yellow polymer of the dicyanamide (106).

Thus at this stage no satisfactory synthesis has been arrived at and further progress in this study must await the preparation of a suitable biguanide derivative.

2.4. EXPERIMENTAL

(a) Preparation of the Ligands

N^1-substituted biguanides were prepared according to literature methods as follows: Biguanide (53); 1-methylbiguanide (45); 1-phenylbiguanide, 1-(o-chlorophenyl)-biguanide and 1,1-diphenylbiguanide (100).

(b) Preparation of the chromium(III) Complexes

Tris(biguanide) chromium(III) and tris(1-methylbiguanide) chromium(III) were prepared by the literature method (77a). Analytical data for the complexes are contained in table 2.2.

Complexes of chromium(III) with 1-arylbiguanides were prepared by the dropwise addition of a concentrated solution of chrome alum to a hot (70°C) solution of the appropriate biguanide sulphate or hydrochloride in 2N aqueous sodium hydroxide. The arylbiguanide complexes separated from the solution as dark red oils which solidified on cooling to room temperature. The complexes were isolated by decanting the supernatant solution while it was still warm. The oily residue was washed, by decantation, with warm water. Purification was then effected by dissolving the complex in the minimum amount of alcohol filtering the alcoholic solution, and reprecipitating it by pouring the alcoholic solution into twice its volume of cold water. The pink, powdery precipitate which formed was filtered in a sintered glass crucible and dried over silica gel.

Typical quantities used in these preparations were 0.01 moles of the chromic salt and 0.03 moles of the biguanide salt in 50 mls. of 2N aqueous sodium hydroxide. The yields of the complexes varied but were normally quite low, and in the vicinity of 30 to 50%.

Tris(biguanide) chromium(III) chloride was prepared from the complex base by the literature method (78).

(c) Analyses

The analytical data for the chromium biguanide complexes are presented in table 2.3.

Chromium was determined by heating a known amount of the finely powdered complex base to constant weight in a tared porcelain crucible. The residue was taken to be chromic oxide, Cr_2O_3. In all cases, duplicate analyses were carried out with an error of less than 4% of the metal determined.

Nitrogen was determined by a standard, semi-micro Kjehldahl method, using a potassium sulphate, selenium metal, mercuric sulphate catalyst (9). Duplicate determinations were carried out with an error of less than 2% of the nitrogen determined.

Table 2.3

Complex	Found					Calc.				
	Cr	C	H	N	Cl	Cr	C	H	N	Cl
[Cr(Bg)$_3$]H$_2$O	14.20			56.6		14.04			56.7	
[Cr(methyl Bg)$_3$]2.5H$_2$O	11.96	24.54	6.56	47.9		11.83	24.75	6.67	47.8	
[Cr(phenyl Bg)$_3$]3H$_2$O	8.33	46.07	5.80	33.3		8.20	45.46	5.73	33.15	
[Cr(o-chlorophenyl Bg)$_3$] H$_2$O	The complex was prepared but not analysed									
[Cr(BgH)$_3$]Cl$_3$.0.5H$_2$O		15.27	4.78	22.6			15.30	~~4.93~~ 4.71		22.6
[Cr(diphenyl Bg)$_3$]3H$_2$O	6.10	58.56	5.04	24.4		6.03	58.45	4.92	24.4	

Carbon and Hydrogen analyses were carried out by the Alfred Bernhardt microanalytical service of the Max Planck Institute, Mülheim, West Germany.

Chlorine was determined as follows (108).

A small quantity of the complex, containing up to about 0.1 gm of chlorine was weighed into a 250 ml. beaker. Five mls. of 5N silver nitrate solution and 15 mls. of conc. HNO$_3$ were added in that order. The resulting suspension was protected from light, warmed gently and carefully swirled from time to time. After about one hour the precipitate was filtered in a porosity 4 sintered glass crucible and washed with 1:1 HNO$_3$. The crucible and contents were dried at 130°-150° and the precipitate weighed as AgCl.

(d) Magnetic Measurements

The room temperature magnetic moments (at approximately 20°C) were determined by the Gouy technique. A permanent magnet with a field strength of about 7 kilogauss was used in conjunction with a Stanton model SM12 balance.

Gouy tubes were packed to a length of 5 cm., and a weight which was constant to within 1% over several packings.

Diamagnetic susceptibilities for the ligands were calculated from Pascal's constants as listed in : Magnetochemistry, by P.W. Selwood, 2nd edition, Interscience, page 92, 1964.

The magnetic results are as follows:-

Table 2.4

Complex	χ_g	χ_D	$\chi_A 10^3$	μ_{eff}(B.M.)	T°C
$[CrBg_3]H_2O$	16.13	85	6070	3.79	20.0
$[Cr(methyl\ Bg)_3]2.5H_2O$	13.89	140	6245	3.84	19.4
$[Cr(phenyl\ Bg)_3]3H_2O$	9.81	258	6478	3.91	20.1
$[Cr(diphenyl\ Bg)_3]3H_2O$	7.02	405	6450	3.88	19.0
$[Cr(BgH)_3]Cl_3\ 0.5H_2O$	12.90	157	6228	3.86	23.5

Electronic Spectra

The diffuse reflectance spectra were measured on a Unicam SP500 modified as described by Smith and Wedd (99).

Transmittance spectra were measured in either alcoholic or aqueous solution, according to the solubility of the complex, on a Perkin-Elmer model 4000A spectrophotometer.

CHAPTER 3

BIGUANIDE COMPLEXES OF COBALT(II)

Introduction

The curious fact that some biguanide complexes of cobalt(II) are yellow, low-spin compounds while others are red and high-spin, has been mentioned earlier, in chapter 1. No systematic study and, consequently, no explanation of this phenomenon has been reported and it is obvious that some investigation of it should be worthwhile. Accordingly, a series of complexes of cobalt(II) with 1-substituted biguanides was prepared and their magnetic and spectral properties were studied. A list of the biguanide complexes reported previously together with new complexes prepared in this work, is contained in Table 3.1.

The data in Table 3.1 allow a certain number of observations to be made regarding the biguanide complexes. Firstly, all the red complexes are those of aryl-substituted biguanides and furthermore they are all, with one exception, cationic complexes (i.e. they are sulphates or chlorides). Thus protonation of the ligand appears to cause the changeover from yellow to red form, only in the case of the aryl-substituted complexes. There appears to be one exception to this generalisation, the neutral complex of 1-(4-sulphophenyl)-biguanide which is reported (83) to be red and high-spin. One possible explanation of this is that the sulphonic acid group in the ligand is capable of acting as an anion, so that the complex would be an "internal salt" or zwitterion.

Table 3.1 Cobalt(II) Complexes with N^1-Substituted Biguanides.

Known Complexes †	Colour	μ_{eff}** (B.M.)	Ref.
$[Co(Bg)_2]$*	Yellow	2.49	84
$[Co(BgH)_2]SO_4$*	Yellow	2.75	84
$[Coen(BgH)_2]SO_4$	Yellow	2.74	84
$[Co$ 4-sulphophenyl $Bg)_2]$	Red	4.97	83
$[Co$ m-phenylene$(BgH)_2]Cl_2$	Red	4.84	81
New Complexes †			
$[Co($cyclohexyl $Bg)_2]$	Yellow	2.48	
$[Co($cyclohexyl $BgH)_2]SO_4$	Yellow	2.49	
$[Co($phenyl $Bg)_2]$	Yellow	2.62	
$[Co($o-chlorophenyl $Bg)_2]$	Yellow	2.15	
$[Co($o-chlorophenyl $BgH)_2]SO_4$	Red	4.23	
$[Co($m-chlorophenyl $Bg)_2]$	Yellow	—	
$[Co($m-chlorophenyl $BgH)_2]SO_4$	Red	4.94	
$[Co($diphenyl $Bg)_2]$	Yellow	—	
$[Co($phenyl $BgH)_2]SO_4$	Red	4.80	
$[Co(\beta$-naphthyl $Bg)_2]$	Yellow	—	
$[Co(\beta$-naphthyl $BgH)_2]SO_4$	Red	4.70	

BgH = biguanide ($C_2H_7N_5$).

*Studied in this work;

**At room temperature.

† For Complete formulations see Table 3.6 P. 80

The room temperature magnetic moments of the yellow complexes lie within the range usually observed in four-coordinate, square-planar complexes of cobalt(II), and on this basis it would be reasonable to assume that they had this structure. Tetrahedral structures could well be assigned to the red complexes on similar grounds.

In order to verify these tentative stereochemical assignments the spectra of the compounds, both electronic and vibrational, and the temperature dependence of their magnetic susceptibilities, were measured.

3.1 Electronic Spectra

The theoretical basis for the interpretation of the electronic spectra of both tetrahedral and octahedral complexes of cobalt(II) is well established. However, no such theory has been developed for the square-planar complexes of divalent cobalt, and indeed it is only recently that this stereochemistry has been recognised as fairly common.

a) Tetrahedral Complexes of Cobalt(II)

At least two bands are usually observed in the visible and near infrared region of the spectra of tetrahedral cobalt(II) complexes (14). These have been assigned as the transitions $^4A_2 \rightarrow {}^4T_1$ (F) and $^4A_2 \rightarrow {}^4T_1$ (P), usually designated ν_2 and ν_3 respectively (see figure 3.1). A third band, ν_1 ($^4A_2 \rightarrow {}^4T_2$), has not been observed often. This has been due both to its position at the low energy end of the near infrared region (ca 3000 - 5000 cm^{-1}) and to the fact that it is electric dipole forbidden in complexes of T_d symmetry and will often have a very low intensity. Goodgame et. al. (46) observed fairly strong absorptions

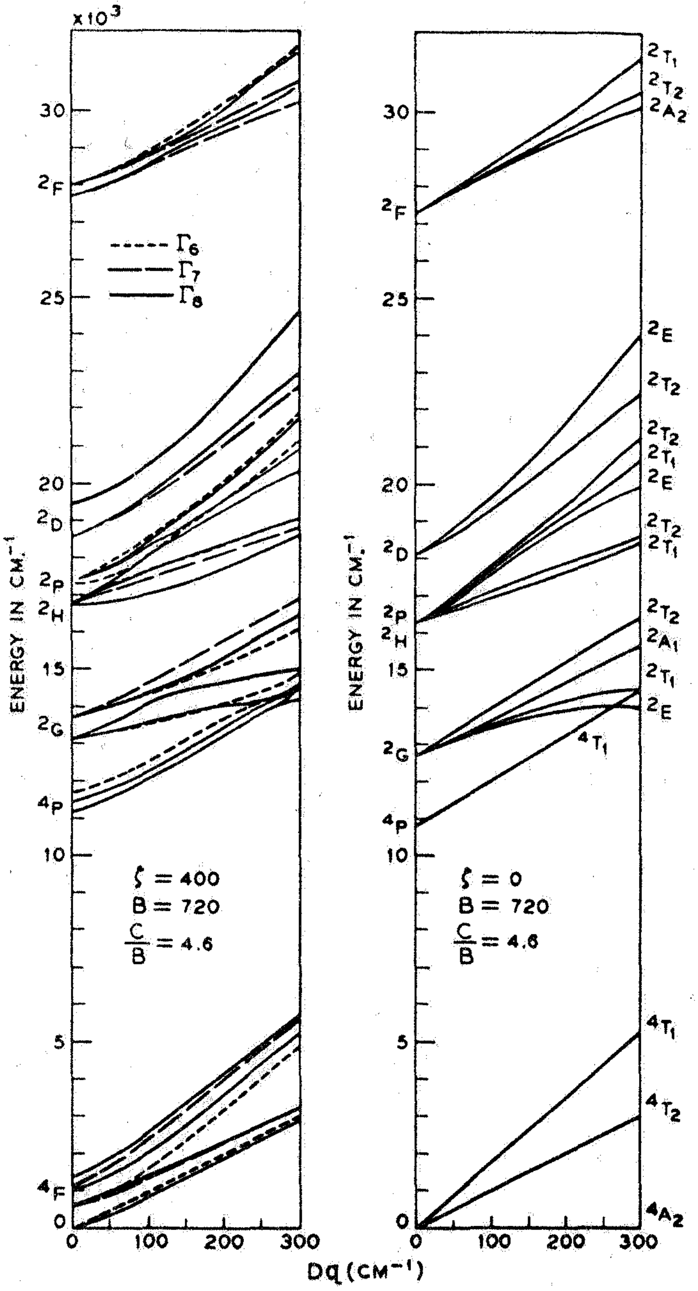


Figure 3.1

Energy Level Diagram for Tetrahedral d^7 (Ref.14)

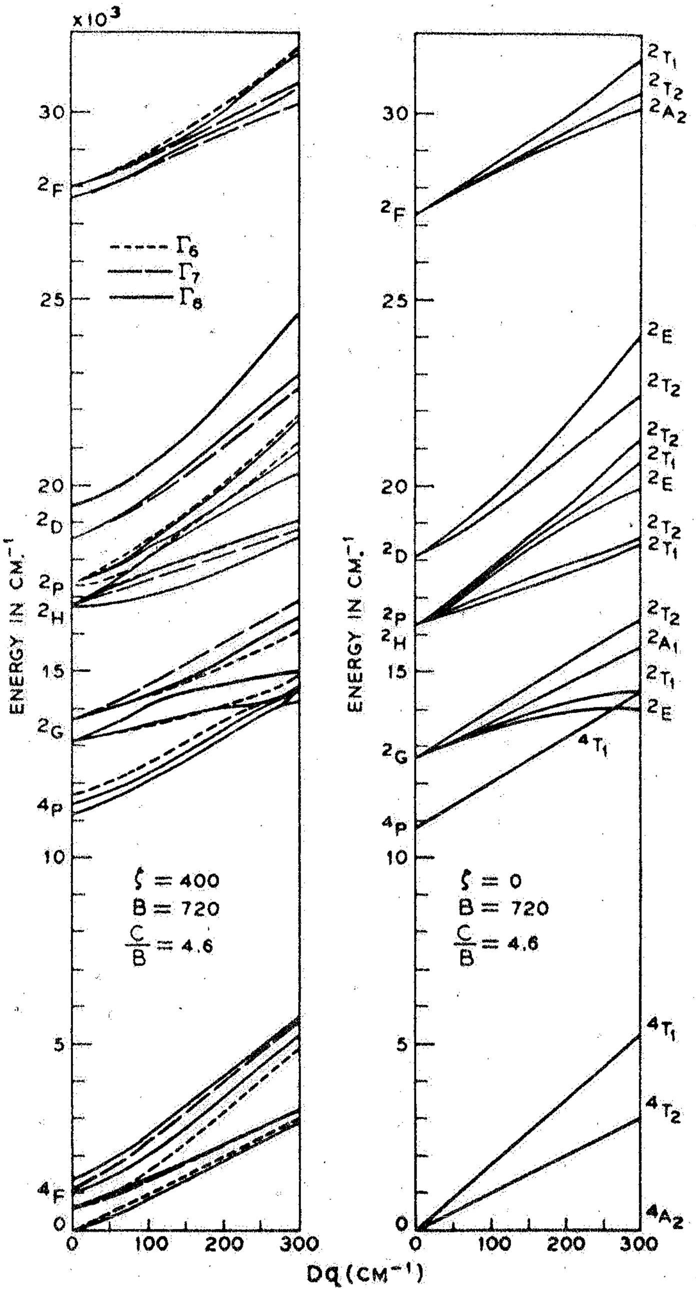


Figure 3.1

Energy Level Diagram for Tetrahedral d⁷ (Ref.14) due to ν_1 in a number of pseudo-tetrahedral complexes of cobalt(II) (with C_{3v} and C_{2v} symmetry).

In general, tetrahedral complexes are characterised by the broad and usually, intense absorption due to ν_3 in the visible region (15,000 - 20,000 cm^{-1}) and a weaker absorption (ν_2) in the near infrared. Colour is not an infallible guide to stereochemistry (14). Although most tetrahedral complexes of divalent cobalt are blue or violet, a number of red tetrahedral complexes have been reported during the past ten years. Thus Cotton and Soderberg (20,21) have reported the pink complex bis-(dipivaloylmethanato) cobalt(II) whichhas been shown to be tetrahedral by X-ray diffraction (22). They noted that the extinction coefficient of the complex in solution for the ν_3 absorption was unusually low (ca. 40) for a tetrahedral complex while the Racah parameter, B', was fairly high. It was possible to rationalise these abnormal values to some extent by showing that a good correlation could be obtained between the intensities of the absorption and the values of ΔB ($\Delta B = B - B'$) for a number of tetrahedral complexes. This relationship was postulated as arising from the fact that the intensities of the spectral bands in tetrahedral complexes are dependent on the amount of orbital mixing, of which the nephelauxetic parameter, β, (equal to B'/B) is a measure.

A number of red complexes of cobalt(II) with salicylideneimenes have been reported (16,26,64,65,111) and all are considered to be tetrahedral. This stereochemistry has been assigned on the basis of spectroscopic (64,65), magnetic (111) and X-ray diffraction (88) studies of the compounds. Tsuchida et. al. (65) have suggested that the low molar extinction coefficients for ν_3 in some of these compounds may be due to a symmetry lower than tetrahedral.

b) Octahedral Complexes of Cobalt(II)

The energy level diagram for a d^7 ion in an octahedral ligand field, calculated by Tanabe and Sugano (103), is reproduced in figure 3.2. In weak and medium fields the ground state is a $^4T_{1g}$ level arising from the free ion ^4F term, while in strong fields a ^2E level (from the free ion ^2G term) becomes the ground state. Most octahedral complexes of divalent cobalt have the quartet ground state although a few low-spin complexes are known (11,75).

Four bands have been observed for spin-free, octahedral cobalt(II) and they have been assigned as follows (28):

$^4T_{2g}$ (F) $\leftarrow$ $^4T_{1g}$	8 - 9000 cm^{-1}
^2E_g $\leftarrow$	$\approx$ 11000 cm^{-1}
$^4A_{2g}$ (F) $\leftarrow$	16 -18000 cm^{-1}
$^4T_{1g}$ (P) $\leftarrow$	20 -21000 cm^{-1}

All of the bands have very low intensities ($\varepsilon < 10$ normally) since they are electric dipole forbidden. The weak absorption actually observed have been shown by Holmes and McClure (51) to be vibration - induced electric dipole transitions.

It is unusual to find four separate bands in the spectrum of an octahedral complex of cobalt(II). For example the spectrum of the hexaquo cobalt(II) ion contains a band at 8000 cm^{-1}, assigned as the $^4T_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F) transition and a split band at 16000 - 22000 cm^{-1} assigned as a combination of the $^4A_{2g}$ (F) $\leftarrow$ $^4T_{1g}$ (F) (at 19600 cm^{-1}) and $^4T_{1g}$ (P) $\leftarrow$ $^4T_{1g}$ (F) (at 21600 cm^{-1}) bands (37,65).

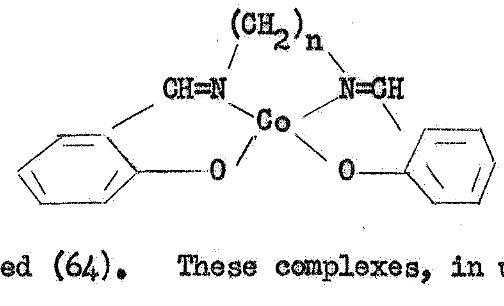
c) Square-Planar Cobalt(II)

The spectra of a number of complexes of divalent cobalt, believed to have this stereochemistry, have been reported. Everett and Holm (35), who studied the equilibrium:

$$\text{square-planar} \rightleftharpoons \text{tetrahedral}$$

in a series of bis (β-ketoamino) cobalt(II) complexes, published the spectra of both the square-planar and tetrahedral species. The former compounds gave rise to a band at approximately 8500 cm^{-1}, often with a shoulder on the high energy side. No further ligand field bands are shown before the charge transfer bands, which appear in each case above about 15000 cm^{-1}.

The spectra of some disalicylidene-diaminato-cobalt(II) complexes of the type:



(n = 2 or 3)

have been reported (64). These complexes, in which the ligands are constrained to square-planar coordination, each give rise to a single band at 8300 - 8500 cm^{-1}.

Although there is, as yet, no theoretical basis for interpreting these spectra there seems to be some justification for expecting that square-planar cobalt(II) gives rise to a band or possibly two bands in the region of 8000 cm^{-1}.

d) Biguanide Complexes - Spectra

The diffuse reflectance spectra of a number of biguanide complexes are listed in table 3.2 where the compounds are grouped according to colour and room temperature magnetic properties (see Table 3.1). Typical spectra are shown in figure 3.3.

It may be seen that each of the yellow, low-spin, complexes gives rise to only one band in the region examined, at 9000 - 10,000 cm^{-1}. The red complexes each exhibit two bands, one near 10,000 cm^{-1} and one at about 18500 cm^{-1}.

There is a close resemblance between the spectra of the low-spin biguanide complexes and the spectra of the square-planar complexes discussed in the previous section. A band position of 10,000 cm^{-1} for the biguanide complexes compared with 8500 cm^{-1} for the β-ketoamino complexes is not unreasonable since ligands with nitrogen donor atoms are usually higher in the spectrochemical series than those with oxygen donor atoms. Thus the electronic spectra are consistent with the assignment of a square-planar stereochemistry to these complexes.

The interpretation of the spectra of the red, high-spin, compounds could be approached on the basis of either pseudo-tetrahedral or a pseudo-octahedral stereochemistry. In the former case the two bands would be assigned as the ν_2 and ν_3 absorptions, corresponding to the

Table 3.2

Diffuse Reflectance Spectra of Cobalt(II) Biguanide Complexes

Yellow, Low-spin complexes	Band positions (cm^{-1})	
[Co(Bg)$_2$]2H$_2$O	9,900	
[Co(BgH)$_2$] SO$_4$ 1.5H$_2$O	10,100	
[Co(cyclohexyl Bg)$_2$] 1.5H$_2$O	10,000	
[Co(cyclohexyl BgH)$_2$] SO$_4$	9,200	
[Co(phenyl Bg)$_2$] 0.5H$_2$O	9,800	
[Co(o-chlorophenyl Bg)$_2$] 0.5H$_2$O	10,000	
[Co(m-chlorophenyl Bg)$_2$]	9,900	
[Co(diphenyl Bg)$_2$] 2.H$_2$O	10,000	
Red, High-spin Complexes		
[Co(phenyl BgH)$_2$] SO$_4$	9,800	18,500
[Co(o-chlorophenyl BgH)$_2$] SO$_4$.2.5H$_2$O	9,800	18,450
[Co(m-chlorophenyl BgH)$_2$] SO$_4$	9,800	18,500
[Co(β-naphthyl BgH)$_2$] SO$_4$	9,800	18,400

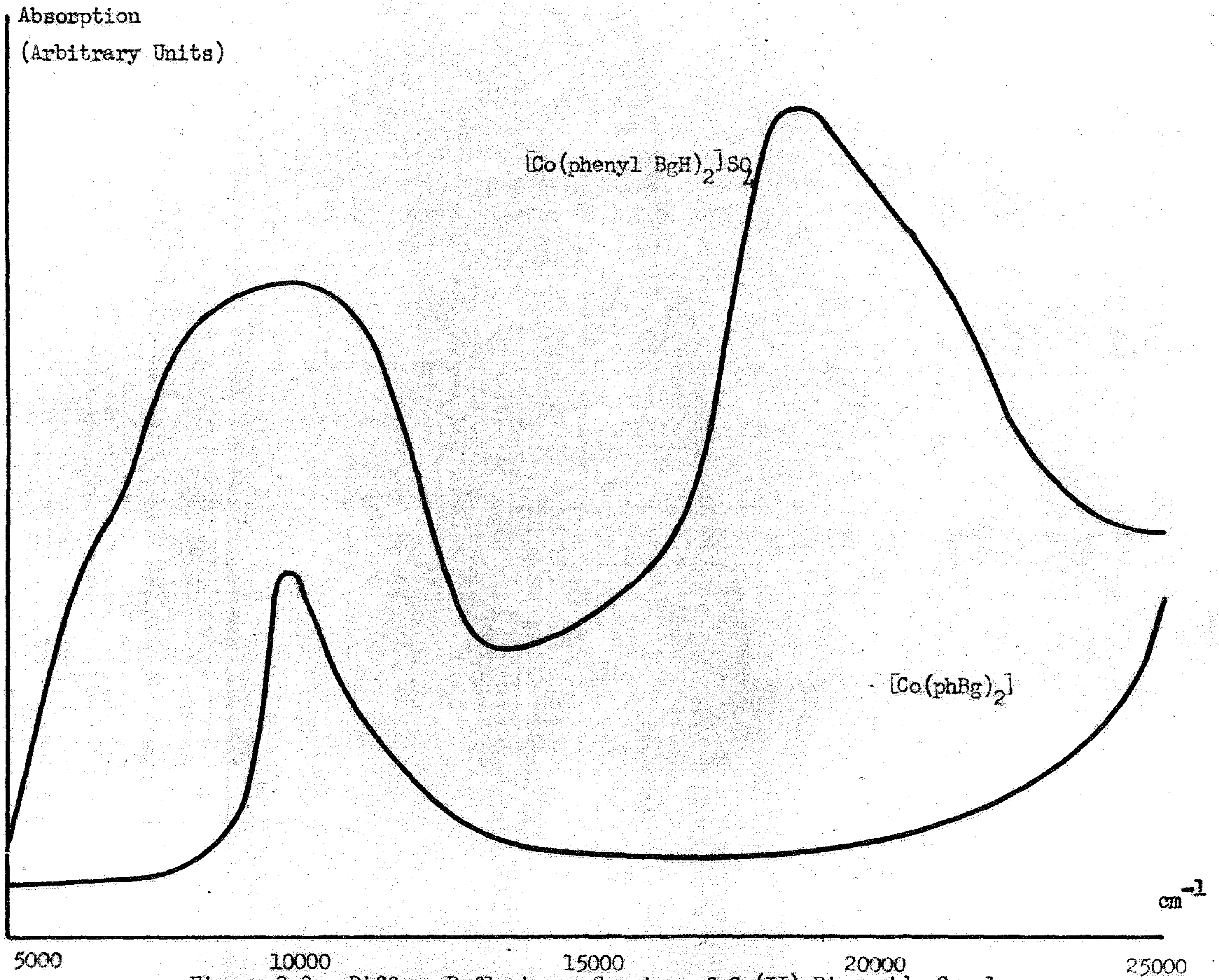


Figure 3.3. Diffuse Reflectance Spectra of Co(II) Biguanide Complexes.

$^4T_1(F) \leftarrow {}^4A_2$, $^4T_1(P) \leftarrow {}^4A_2$ transitions in T_d symmetry. On the other hand, if the complexes are considered to be pseudo-octahedral the low energy band would be assigned to the $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ while the high energy absorption would be expected to contain both the $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ bands.

Although a tetrahedral structure is easily visualised for a complex with the formula $Co(aryl\ BgH)_2\ SO_4$, octahedral stereochemistry would require either that sulphate is coordinated or that each biguanide is coordinated to two cobalt atoms as shown in figures 3.4 a and 3.4b. The infrared spectra of these complexes, discussed later in section 3.4 make it quite clear that sulphate is not coordinated. This leaves structures such as 3.4a and 3.4b as the only possibilities providing octahedral coordination of the cobalt ion. Although axial interactions such as these are known to exist in some complexes (44,50) they would be expected to be much weaker than an actual coordinate bond. Furthermore it is difficult to see why protonation of the ligands should bring about an interaction such as this, strong enough to impose pseudo-octahedral stereochemistry on the metal ion.

In order to gain some further indication of the stereochemistry of the complexes, some attempts were made to measure the intensities of the absorptions. It was found that the pressed alkali halide disc technique (13) was unsatisfactory in this case, because clear dispersions of these complexes in the halides could not be produced. Solution measurements were made difficult by the fact that the complexes, once prepared and dried, would not readily redissolve in water. This was overcome by some

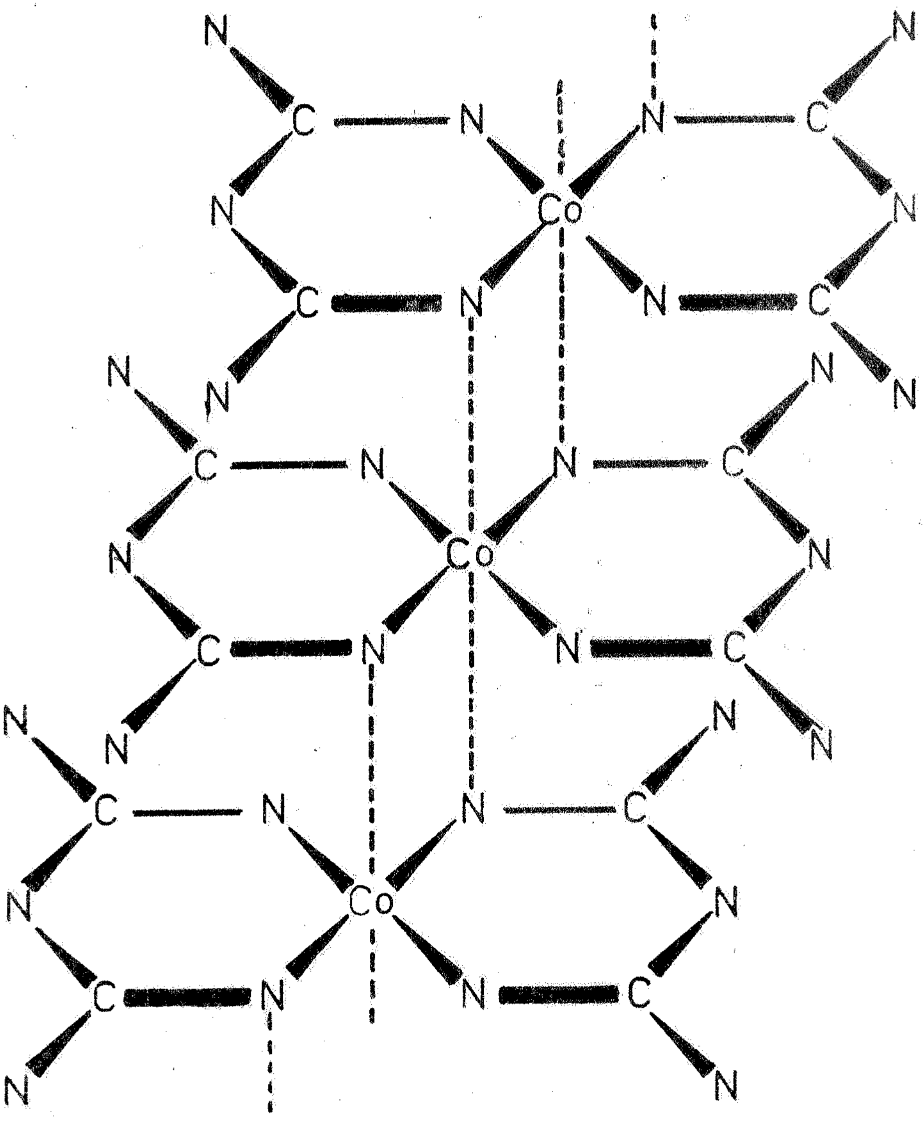


Figure 3.4 a

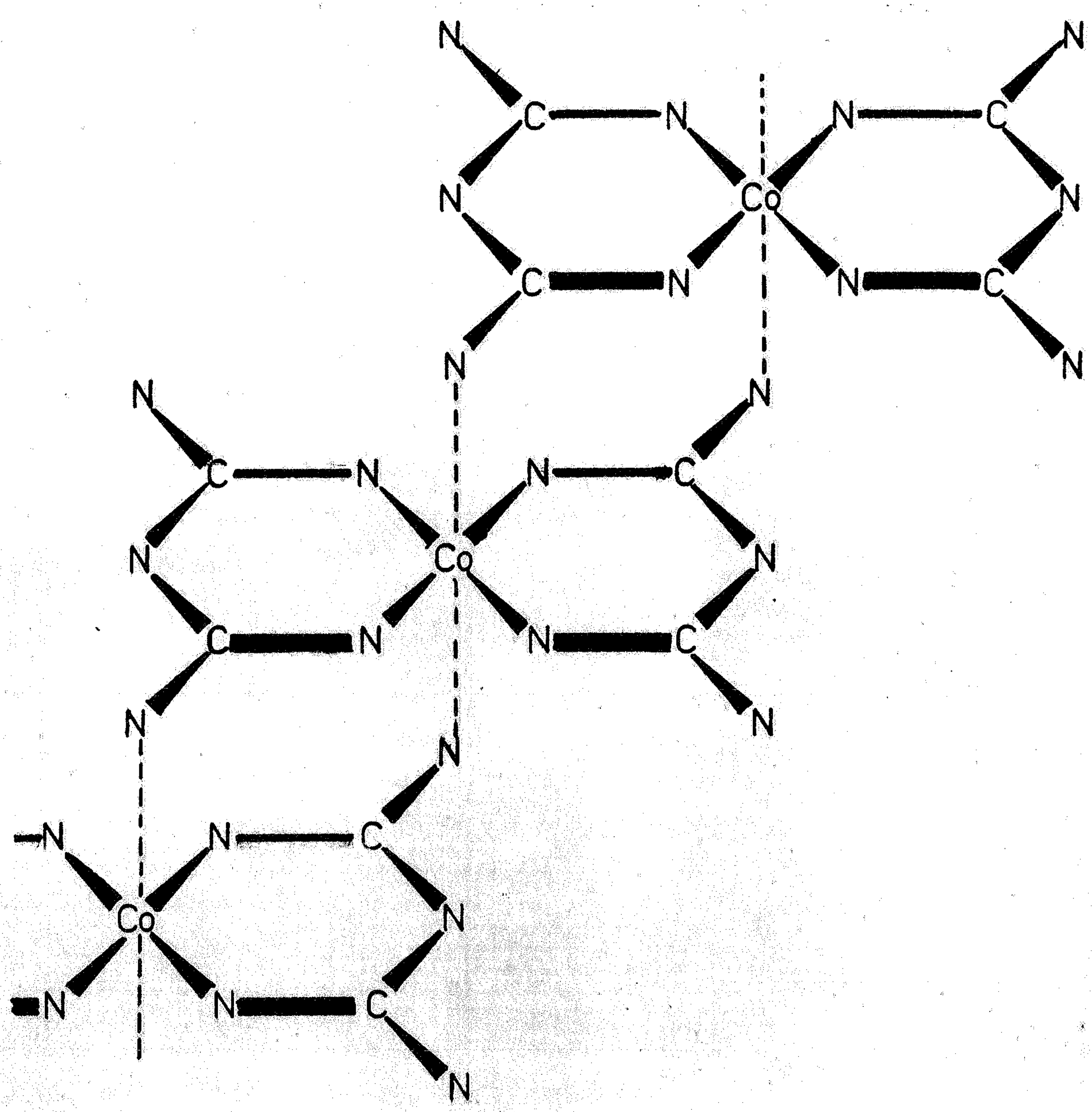


Figure 3.4 b

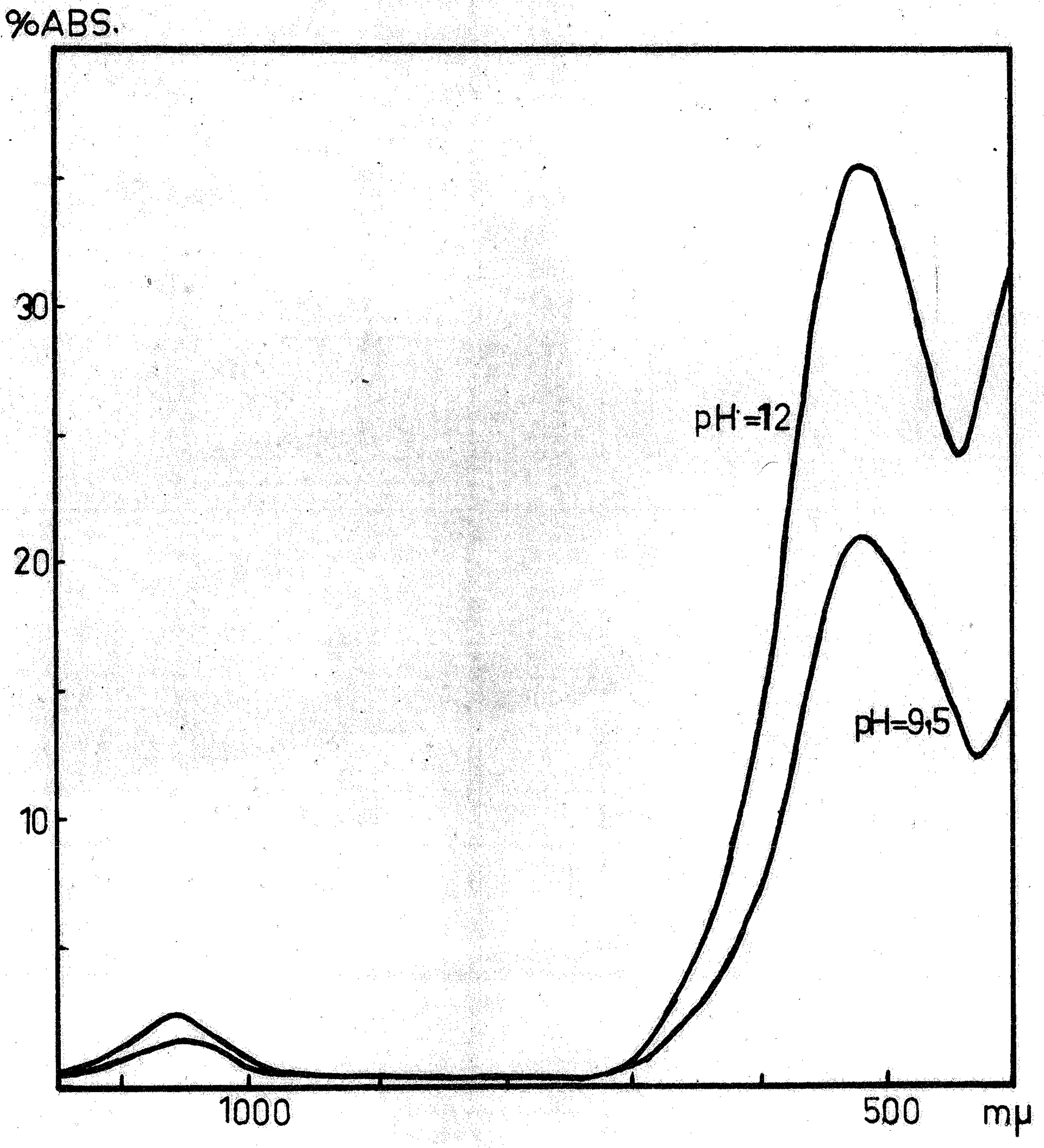
extent by dissolving one of the complexes in weakly acid solution, in which some dissociation takes place, then increasing the pH by addition of alkali. Measurements of the spectrum of $[Co(\text{m-chlorophenyl BgH})_2]SO_4$ made at two different pH values are shown in figure 3.5. A molar extinction coefficient of 126 was found for ν_3 at pH value of 12. This is likely to be less than the true value since there is most probably some dissociation of the complex. Thus the molar extinction coefficient (ε max) for the ν_3 band is considerably higher than might be expected for an octahedral complex, yet is well within the range of values expected of pseudo-tetrahedral complexes.

For tetrahedral cobalt(II) the parameters Dq and B can be obtained by solution of the equations:

$$\nu_2 = E[{}^4T_1\ (F)] - E\ {}^4A_2\ (F) = 15\ Dq + 7.5\ B - Q$$
$$\nu_3 = E[{}^4T_1\ (P)] - E\ {}^4A_2\ (F) = 15\ Dq + 7.5\ B + Q$$

where $Q = \frac{1}{2}[(-6\ Dq + 15\ B)^2 + 64\ (Dq)^2]^{\frac{1}{2}}$

which are derived (14) from the matrices of Tanabe and Sugano (103). Values for these parameters in the biguanide complexes are in all cases very close to 600 cm^{-1} for Dq and 700 cm^{-1} for B. The figure for B lies well within the range usually observed for tetrahedral cobalt(II) (usually 600 - 800 cm^{-1}) whereas the Dq value is higher than any reported previously. However, it is not unreasonably high since the figures available for comparison, pertain to nitrogen - donor ligands which are lower in the spectrochemical series. Furthermore, it has been shown (36) that the theory upon which these calculations are based is only qualitatively useful, especially for compounds with symmetry lower than T_d.



Solution Spectrum of Co(m-chlorophenylBgH)$_2$·SO$_4$

Figure 3·5

Thus the values of Dq and B' quoted may well be subject to large errors and the calculations are of little importance in determining the structures of the complexes.

3.3. Magnetochemistry

Satisfactory theoretical treatments for the magnetic properties of tetrahedral and octahedral cobaltous complexes have been developed so that explanations are available for most of the phenomena observed.

a) Tetrahedral Cobalt(II)

For tetrahedral cobalt(II) with an orbital singlet ground state, the orbital contribution to the magnetic moment is explained by the mixing into the ground state, by means of spin-orbit coupling, of an orbitally degenerate upper level. The expression for the magnetic moment then takes the form (14):

$$\mu_{\text{eff}} = 2\left[1-\frac{4\lambda}{10\ \text{Dq}}\right]\left[S(S+1)\right]^{\frac{1}{2}}\ \text{B.M.} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.1)$$

Where λ is the spin-orbit coupling constant for a single electron and 10 Dq is the separation between the ground state and the level being mixed in.

This mechanism satisfactorily accounts for the range of magnetic moments (4.0 to 4.8 B.M.) actually observed in tetrahedral cobalt(II) complexes. The slight temperature dependence of the magnetic moments of these complexes has been accounted for by the introduction of a temperature independent term into the expression for the magnetic susceptibility. This is given by (38):

$$\chi_{T.I.P.} = 8N\beta^2/10\,Dq = 2.09/10\,Dq \ldots\ldots\ldots\ldots\ldots\ldots \quad (3.2)$$

Cotton et. al. (19) appear to have used these expressions with a good deal of success in correlating the magnetic and spectroscopic properties of a number of cobalt(II) complexes.

b) Octahedral Cobalt(II)

In octahedral cobalt(II) complexes the orbital degeneracy of the ground state ($^4T_1$) gives rise to an orbital contribution to the magnetic moments, which should therefore lie between the limits $[4S(S+1)]^{\frac{1}{2}}$ and $[4S(S+1) + L(L+1)]^{\frac{1}{2}}$. The values actually found depend upon the amount of quenching of the orbital contribution and are usually between 4.8 and 5.2 B.M. (11).

A few octahedral complexes are known in which the ligand field is so strong that the doublet state, ^2E, has crossed the $^4T_1$ (F) level and become the ground state. In these complexes the magnetic moments are close to the spin only value of 1.73 B.M. although there is a slight orbital contribution.

c) Square-Planar Cobalt(II)

No satisfactory theory has yet been developed for the low-spin, four-coordinate complexes of cobalt(II). These are assumed to be square-planar although the X-ray structures of very few have been determined. Jeffrey (52) has shown that the cobalt(II) phthalocyanine complex is square-planar. Rodley et. al. (33,87) have demonstrated that bis (o-phenylenebisdimethylarsine) cobalt(II) perchlorate exists in two isomeric forms, both of which contain weakly coordinated perchlorate although in one form the coordination is stronger than the other. Both forms may be considered as square-planar cobalt(II) with weak axial interactions.

Magnetic moments of these and other complexes (39) which are thought to be square-planar fall within the range 1.9 - 2.8 B.M. and temperature dependence studies have shown (41) that the orbital contribution is maintained down to low temperatures. It has been found that not all of the low-spin complexes obey the exact Curie-Weiss law so that in some cases it is only possible to obtain approximate values for the Weiss constant.

The fact that both the spin and orbital contributions to the magnetic moments of cobalt(II) complexes vary with stereochemistry and ligand field strength, makes the magnetochemical method a powerful tool in structural studies on these compounds. Although room temperature magnetic moments alone are often a useful guide to stereochemistry temperature dependence studies are more conclusive.

d) Magnetochemistry of Cobalt(II) Biguanide Complexes

The temperature dependence of the magnetic properties of a number of cobalt(II) biguanide complexes have been studied here for the first time. Results from these studies are summarised in table 3.3 and figures 3.6 to 3.8. It may be seen that three distinct types of magnetic behaviour have been encountered.

The yellow, low-spin compounds, with one exception, have magnetic properties consistent with those expected for square-planar cobalt(II). That is, the magnetic susceptibilities follow the Curie-Weiss law with only minor deviations from the linearity expected. The lack of any recognised theory for this stereochemistry precludes further discussion.

The sole exception in this series of compounds is bis-(biguanide) cobalt(II) sulphate which is antiferromagnetic, with a Curie temperature below and probably quite close to 120°K. Above 140°K the susceptibility obeys the Curie-Weiss law with a θ value of 320°K. No detailed examination of this phenomenon was made and it can only be postulated that there is some interaction between the cobalt atoms in adjacent layers of the solid compound. It is not readily apparent why this complex should be the only one giving rise to such behaviour and a more detailed investigation might prove interesting.

For the red, high-spin complexes the magnetic properties may be explained on the basis of pseudo-tetrahedral stereochemistry. Curie-Weiss law behaviour is observed in all cases, with θ values up to 10°K. The temperature dependence of the magnetic moments is slight and the moments lie within the range expected for tetrahedral cobalt(II).

The magnetic moments of these complexes could equally well arise in pseudo-octahedral coordination. However, the small temperature dependence of the magnetic moments is not typical of Cobalt(II) complexes with this stereochemistry.

The fact that it is not possible to correlate by means of equation 3.1, the magnetic moments of the red complexes with the tetrahedral Dq values obtained in the previous section does not necessarily invalidate the assignment of pseudo-tetrahedral structures to them. Any apparent discrepancy can be explained by noting that the symmetry of the complexes

Magnetochemical Properties of Cobalt(II) Biguanide Complexes

$[Co(Bg)_2].2H_2O$			$[Co(BgH)_2]SO_4$ $1.5H_2O$		
T°K	χ_A x 10^6	μ_{eff}	T°K	χ_A x 10^{-6}	μ_{eff}
290.5	2133	2.24	290.5	2373	2.36
269.5	2310	2.24	274.0	2441	2.32
256.0	2415	2.23	244.5	2614	2.27
236.0	2597	2.22	227.5	2662	2.21
218.0	2781	2.21	211.8	2730	2.16
197.5	3027	2.20	194.0	2839	2.11
177	3300	2.17	177.5	2903	2.04
164	3601	2.18	161	3061	1.99
156.5	3758	2.18	141	3117	1.88
136.5	4260	2.17	121	3234	1.78
118	2926	2.17	102.5	3252	1.64
104.5	5452	2.14			
91.5	6149	2.13			

Table 3.3 (Cont'd)

$[\text{Co(cyclohexyl Bg)}_2]1.5\text{H}_2\text{O}$

$T^{o}K$	$\chi_A \times 10^{-6}$	μ_{eff}
291.9	2608	2.48
268.8	2792	2.46
241.0	3070	2.44
213.0	3450	2.43
186.0	3867	2.41
160.4	4487	2.41
139.1	5107	2.39
119.8	5803	2.37
100.0	7011	2.38

$[\text{Co(cyclohexyl BgH)}_2]\text{SO}_4$

$T^{o}K$	$\chi_A \times 10^{-6}$	μ_{eff}
293.2	2626	2.49
256.3	2991	2.49
221.4	3381	2.46
185.3	4017	2.45
147.0	4924	2.42
121.0	5883	2.40
100.0	7044	2.38

$[\text{Co(phenyl Bg)}_2]5\text{H}_2\text{O}$

$T^{o}K$	$\chi_A \times 10^{-6}$	μ_{eff}
290.5	3075	2.68
273.1	3276	2.68
252.3	3533	2.68
230.3	3840	2.67
210.5	4163	2.66
191.7	4619	2.67
170.7	5140	2.66
150.5	5808	2.66
130.7	6620	2.64
114.5	7498	2.63

$[\text{Co(o-chlorophenyl Bg)}_2]0.5\text{H}_2\text{O}$

$T^{o}K$	$\chi_A \times 10^{-6}$	μ_{eff}
286.5	2005	2.16
270.0	2122	2.15
253	2250	2.14
233	2423	2.13
216	2579	2.12
200	2757	2.11
186	2918	2.10
162	3330	2.07
142.5	3792	2.09
123.5	4377	2.09
101.4	5301	2.08

Table 3.3 (Cont'd)

$[Co(phenyl\ BgH)]SO_4\ 1.5H_2O$

T°K	$\chi_A \times 10^{-6}$	μ_{eff}
292.7	9813	4.80
267.5	10684	4.80
240.0	11871	4.79
213.0	13291	4.78
186.0	15175	4.77
158.5	17675	4.75
132.0	21195	4.75
112.5	24803	4.74
95.5	28967	4.73

$[Co(\beta\text{-}naphthyl\ BgH)_2]\ SO_4$

T°K	$\chi_A \times 10^{-6}$	μ_{eff}
293.7	9327	4.70
273.6	9966	4.69
253.5	10690	4.68
232.2	11590	4.66
212.4	12590	4.64
191.9	13870	4.63
164.7	16070	4.62
138.0	19100	4.62
119.0	22120	4.61
96.9	26710	4.58

$[Co(m\text{-}chlorophenyl\ BgH)_2]\ SO_4$

T°K	$\chi_A \times 10^{-6}$	μ_{eff}
295.7	10213	4.94
267.0	11332	4.94
239.8	12578	4.93
212.9	14086	4.92
186.0	16078	4.91
158.0	18813	4.90
131.3	22538	4.89
105.0	27741	4.85

$[Co(o\text{-}chlorophenyl\ BgH)_2]\ SO_4.2.5H_2O$

T°K	$\chi_A \times 10^{-6}$	μ_{eff}
290.7	8036	4.33
274.0	8531	4.33
251.5	9203	4.32
231.2	9957	4.31
211.5	10846	4.30
190.0	11889	4.28
164.1	13809	4.27
149.8	15034	4.26
137.1	16389	4.23
124.3	17814	4.23
110.0	19952	4.21
94.5	23009	4.19

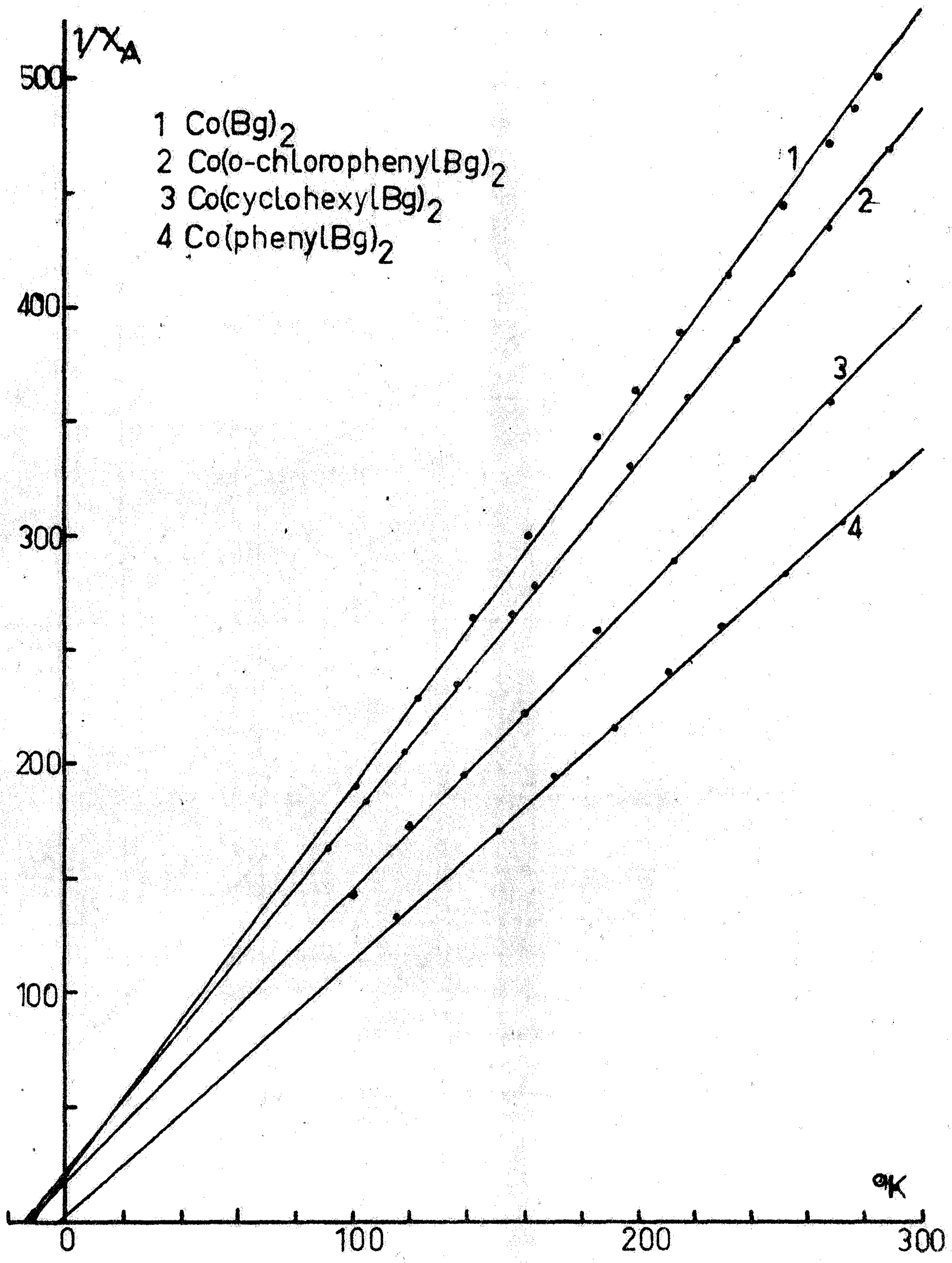

1/χA
500
400
300
200
100
0
100
200
300
°K
1 Co(Bg)2
2 Co(o-chlorophenylBg)2
3 Co(cyclohexylBg)2
4 Co(phenylBg)2
1
2
3
4

Figure 3.6

is most probably a good deal lower than T_d and, as mentioned before, these calculations are only qualitative in such circumstances.

3.4 Infrared Spectra of the Cobalt(II) Biguanide Complexes

A detailed study of the infrared spectra of biguanides and biguanide complexes is left until chapter 4. However, it is of interest to consider here the use of infrared spectroscopy in deciding whether or not the sulphate radicals are coordinated to the cobalt(II) ions in the biguanide complex salts.

The free sulphate ion has tetrahedral (T_d) symmetry and gives rise to two infrared active vibrations, denoted ν_3 and ν_4, which are both triply degenerate. Two other vibrations ν_1 and ν_2 are Raman active only. If the symmetry of the sulphate ion is lowered, e.g. by coordination to a metal ion, the vibrations ν_1 and ν_2 become infrared active and the degeneracies of ν_3 and ν_4 are lowered according to the correlation table, 3.4. Nakamoto et. al. (60) found that ν_3 and ν_4 were each split into two bands for monodentate coordinated sulphate and into three bands in the case of bidentate sulphato group. Furthermore they observed enhanced intensities in bands assigned to ν_1 and ν_2 for coordinated sulphate ions.

The infrared spectra of all the biguanide complex sulphates contained bands which could be assigned to the ν_3 and ν_4 modes of the sulphate ion, see table 3.5, but none which could be attributed to ν_1 or ν_2. Furthermore, in all cases but one, the bands assigned to ν_3 and ν_4 were single maxima, that due to ν_3 being fairly broad in all cases. In all the complex bases a number of weak to medium bands appeared in the 9 μ region and in most cases these were swamped by the intense, broad, Correlation Table for T_d, C_{2v} and C_{3v} (Reference 60).

Table 3.4

Point Group	ν_1	ν_2	ν_3	ν_4
T_d	A_1 (R)	E (R)	F_2 (I,R)	F_2 (I,R)
C_{2v}	A_1 (I,R)	E (I,R)	A_1 (I,R) + E (I,R)	A_1 (I,R) + E (I,R)
C_{3v}	A_1 (I,R)	A_1 (I,R) + A_2 (R)	A_1 (I,R) + B_1 (I,R) + B_2 (I,R)	A_1 (I,R) + B_1 (I,R) + B_2 (I,R)

Table 3.5

Vibrational frequencies of the sulphate ion in Co(II) biguanide complexes

Complex	Assignment	
	ν_3	ν_4
$[Co(phenyl\ BgH)_2]SO_4$	1081 v.s. br	610 s
$[Co(o\text{-}chlorophenyl\ BgH)_2]SO_4$	1071 v.s. br	611 s
$[Co(m\text{-}chlorophenyl\ BgH)_2]SO_4$	1075 v.s. br	610 s
$[Co(\beta\text{-}naphthyl\ BgH)_2]SO_4$	1085 v.s. br	608 s
$[Co(BgH)_2]SO_4$	1122, 1087, 1066 v.s.	617 s
$[Co(cyclohexyl\ BgH)_2]SO_4$	1082 v.s. br	610 s

sulphate (ν_3) absorption which appears in the complex salts. However, in the spectrum of $[Co(BgH)_2]SO_4$ a series of three maxima was observed in this region. Since only a single maximum was found at around 600 cm^{-1} (ν_4) and since no bands attributable to ν_1 and ν_2 could be found, the only reasonable explanation for the apparent splitting of the ν_3 vibration is that it is actually due to a superposition of the biguanide absorption in this region on the sulphate absorption.

Thus the infrared spectra demonstrate that none of these complexes contain coordinated sulphate, and the structural assignments made previously are supported.

3.5 Bonding in the Cobalt(II) Biguanide Complexes

Reasons for the change from Square-Planar to Tetrahedral Structures

The evidence obtained in this study on the biguanide complexes of cobalt(II) points to the existence of two types of compounds, namely those with square-planar and those with pseudo-tetrahedral stereochemistries. The latter group comprises those compounds with the general formula $[Co(ArBgH)_2]^{2+}$ (i.e. the cationic complexes of 1-arylbiguanides) while all of the other complexes investigated fall into the former group. Thus the structural properties of the cobalt(II) biguanide complexes may be summarised as follows:

(i) Neutral biguanide complexes of cobalt(II) are yellow, low-spin, and square-planar.

(ii) The cationic complexes of biguanide and 1-alkylbiguanides with cobalt(II) are also yellow, low-spin, and square-planar.

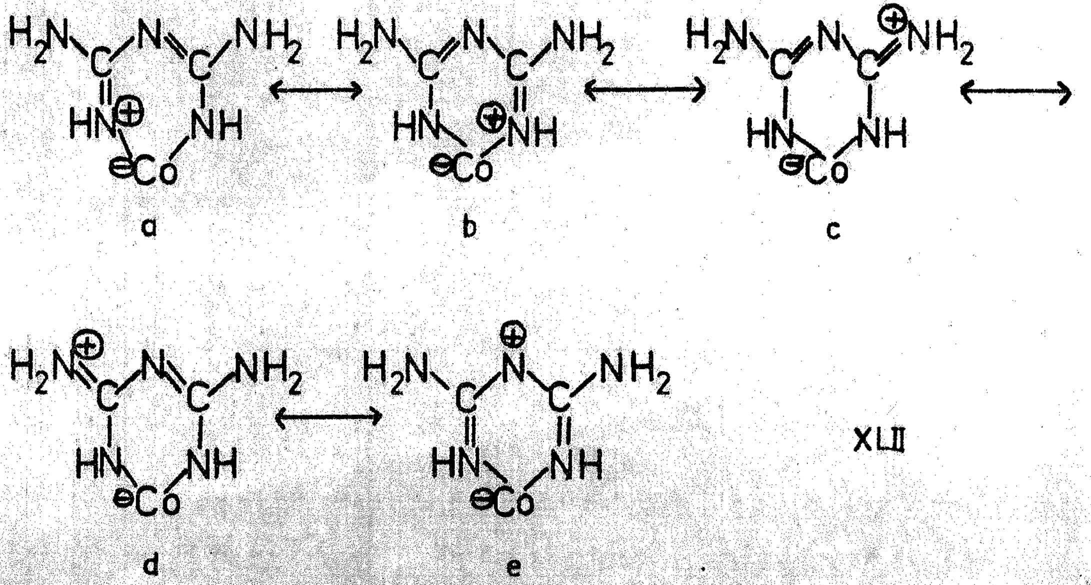
(iii) The cationic complexes of cobalt(II) with 1-arylbiguanides are red, high-spin, and pseudo-tetrahedral.

It has been observed before that the stereochemical configuration of complexes formed by cobalt(II) and nickel(II) with a series of β-ketoamino ligands changes from square-planar to pseudo-tetrahedral as the substituent on the nitrogen donor atom is increased in size (34,35). In these cases it was postulated that the change in configuration was caused mainly by steric interaction between the N-substituted chelate rings.

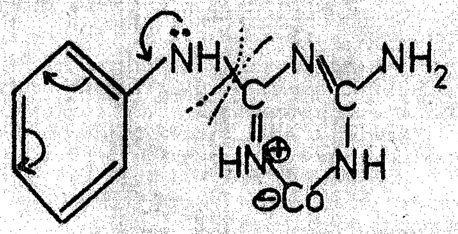
The change from square-planar to tetrahedral stereochemistry in the case of the cobalt(II) biguanide complexes, on the other hand, seems fairly certain to be almost entirely an electronic effect. This is suggested by the fact that whereas the $[Co(cyclohexylBgH_2]^{2+}$ cation is low-spin and square-planar, the $[Co(phenylBgH)_2]^{2+}$ cation is high-spin and tetrahedral. In these two complexes the steric effect should be almost identical so that the difference in stereochemistry can be attributed to the difference between the electronic properties of the cyclohexyl- and phenyl-groups.

A theory has been developed here which accounts for the facts (i - iii) mentioned above and which is based on the differences in properties of alkyl (alicyclic) and aryl substituents. It is postulated that a resonance hybrid of structures XLII (a - e) represents the bonding in $[Co(Bg)_2]$.

Thus the delocalisation of the formal positive charge over all the nitrogen atoms in the ligand provides a stabilising effect on the planar chelate ring. An alkyl substituent on N^1, being essentially an "electron donor", enhances the ability of conjugated system to accommodate



XLII



XLIII

the positive charge and increases the stability of the planar system. On the other hand, an aryl substituent (see figure XLIII) competes with the conjugated system for the lone pair electrons on N^1 and effectively isolates N^1 from the system. Thus the stability of the planar configuration is lowered.

Protonation of the ligand adds another positive charge to the system. In the complexes with biguanide and the alkyl-biguanides this charge can still be accommodated by delocalisation over all five nitrogen atoms and the planar configuration is retained although it is destabilised to some extent. However in the 1-arylbiguanide complexes, in which N^1 is isolated, the extra charge cannot be delocalised sufficiently by the conjugated system (in which only four nitrogen atoms remain) and the chelate ring reverts to a puckered configuration. This distortion of the chelate ring might be expected to destroy the planarity of the complex ion and result in the change to a pseudo-tetrahedral structure.

3.6. EXPERIMENTAL

(a) Preparation of the ligands

The biguanides were all prepared by well known literature methods which are summarised in chapter 2.

(b) Preparation of the Complexes

For the complexes all preparative operations were carried out on a vacuum line under an atmosphere of pure nitrogen, with the strict exclusion of atmospheric oxygen. The complexes are extremely sensitive to aerial oxidation when wet, but reasonably stable when dry. They were stored in an atmosphere of pure nitrogen.

(i) Complexes of the type $[Co(R\text{-}Biguanide)_2].nH_2O.$ (R=H or alkyl)

These complexes were prepared by the dropwise addition of a concentrated aqueous solution of cobaltous chloride or sulphate to a vigorously stirred solution of the biguanide sulphate or chloride in 2N aqueous sodium hydroxide. To avoid precipitation of cobalt hydroxide, an excess of ligand was used. The yellow precipitate was filtered on sintered glass, washed with water, water-alcohol then alcohol, and dried in vacuo until it had attained the consistency of a fine, dry, powder.

(ii) Complexes of the Type $[Co(R - Bg)_2]$ (R = aryl)

Arylbiguanides though insoluble in water, are readily soluble in alcohol. Thus it was found that the arylbiguanide cobalt(II) complex bases could be prepared most conveniently from alcoholic solution.

A concentrated aqueous solution of cobaltous chloride hexahydrate was added slowly, to a vigorously stirred solution of the arylbiguanide base in normal alcoholic sodium hydroxide. A slight excess of the ligand was used. The yellow complex was filtered, washed with alcohol, and dried as in (i).

(iii) Complexes of the type $[Co(R - BgH)_2]SO_4$ (R=H or alkyl)

Dilute aqueous ammonia (2N) was added dropwise to a vigorously stirred aqueous solution of cobaltous sulphate and the appropriate biguanide sulphate until a greenish yellow or yellow precipitate was obtained.

The reaction mixture was then stirred until the precipitate became bright yellow, which sometimes took several hours. A fifty percent excess of the ligand was used in each preparation to avoid precipitation of cobaltous hydroxide.

The complexes were filtered, washed and dried as described in section (i).

(iv) Complexes of the type $[Co(R\text{-}BgH)_2]SO_4$ (R = aryl)

Of several methods which were tried, the following was found to be the most satisfactory:

An ice-cold, concentrated methanolic solution of an arylbiguanide base was added slowly to three times its volume of an ice-cold aqueous solution of cobaltous sulphate. The reaction mixture was stirred continuously during the addition of the ligand. The red precipitate was filtered immediately and washed with a few mls. of very cold (-10°C) water/methanol mixture. It was then dried in vacuo. Stoichiometric amounts of the ligand and cobaltous sulphate were used. It is interesting to note that the complexes dissolved quite readily in the supernatant liquid if the temperature were allowed to rise appreciably or in the wash solution if it were not kept cold. However, once dried, the complexes would not dissolve in water or alcohol unless these were made slightly acid.

(c) Analyses

Analytical data for the complexes discussed are set out in table 3.6.

Cobalt analyses were carried out by first fusing the complexes with sodium pyrosulphate (approximately 3 gm. $Na_2S_2O_7$ per 100 mgm. complex) until a clear melt was obtained. The cooled melt was then dissolved in water and the cobalt estimated by the gravimetric pyridine - thiocyanate method.

Carbon and Hydrogen microanalyses were carried out by Alfred Bernhardt, Mülheim, Germany.

Nitrogen was determined by a semi-micro Kjehldahl method (9).

(d) Electronic spectra were measured as described on page 41

(e) Magnetic Measurements were carried out by the Gouy method on a temperature-variable balance constructed in this department. The design is based upon that published by Figgis and Nyholm (40).

Table 3.6

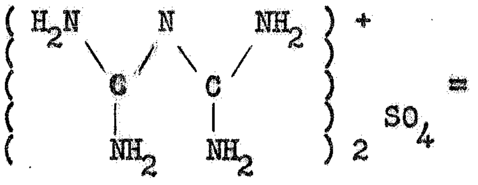
Analyses of Cobalt(II) Biguanide Complexes

Complex	Found					Calculated				
	Co	C	H	N	$SO_4^{=}$	Co	C	H	N	$SO_4^{=}$
$[\text{Co(Bg)}_2]2\text{H}_2\text{O}$	20.3	16.43	5.35	47.3		20.0	16.27	5.43	47.5	
$[\text{Co(BgH)}_2]\text{SO}_4.1.5\text{H}_2\text{O}$	15.4	–	–	36.3		15.4			36.5	
$[\text{Co(cyclohexyl Bg)}_2]1.5\text{H}_2\text{O}$	13.1	–	–	31.1		13.1			31.0	
$[\text{Co(cyclohexyl BgH)}_2]\text{SO}_4$	11.27	–	–	26.8	18.2	11.3			26.9	18.4
$[\text{Co(phenyl Bg)}_2]0.5\text{H}_2\text{O}$	14.3	–	–	32.9		14.0			33.3	
$[\text{Co(phenyl BgH)}_2]\text{SO}_4.1.5\text{H}_2\text{O}$	10.87	–	–	26.1	18.1	11.0			26.1	17.9
$[\text{Co(o-chlorophenyl Bg)}_2]0.5\text{H}_2\text{O}$	11.7	39.29	3.98	28.6		12.0	39.30	3.90	28.6	
$[\text{Co(o-chlorophenyl BgH)}_2]\text{SO}_4.2.5\text{H}_2\text{O}$	9.2	30.67	3.96	22.5	15.9	9.5	30.83	4.05	22.5	15.4
$[\text{Co(m-chlorophenyl BgH)}_2]\text{SO}_4$	11.0	–	–	23.9	17.0	10.2			24.2	16.6
$[\text{Co}(\beta\text{-naphthyl Bg})_2]$	11.3	–	–	26.5		11.2			26.4	
$[\text{Co}(\beta\text{-naphthyl BgH})_2]\text{SO}_4$	9.8	–	–	22.7	15.65	9.7			23.0	15.77
$[\text{Co(diphenyl Bg)}_2]2\text{H}_2\text{O}$	9.9	–	–	23.2		9.8			23.4	

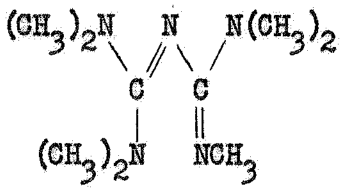
CHAPTER 4

Infrared Spectra of Biguanide Complexes

The correlation of the infrared spectra and structures of biguanides and biguanide complexes have not been studied before. Indeed there have been only two occasions on which the spectra of such compounds have been reported. Ray (77) used the infrared spectra of copper(II) and nickel(II) complexes with 1,1-disubstituted biguanides to show that certain of these compounds exist in two different forms, which he postulated were the cis- and trans-isomers. The other instance was the publication by Colthup et. al. (18) of the infrared spectra of biguanide sulphate (XLV) and 1,1,2,2,4,5,5-heptamethylbiguanide (XLVI)



XLV



XLVI

For XLVI they assigned a band at 1600 cm^{-1} to the C=N stretching mode while a band at about 1550-1600 cm^{-1} in the spectrum of XLV was assigned to a N - C - N stretch. It was postulated that in XLV the lower frequency indicated an equivalence of the C - N bond orders brought about by resonance.

One of the difficulties experienced in interpreting the infrared spectra of biguanide complexes arises from the large number of atoms in the ligand. For example, the bis(biguanide)copper(II) molecule contains 27 atoms, and gives rise to 75 normal vibrations. Although some of the vibrations will be degenerate and some infrared-inactive, the spectrum will remain complicated.

Furthermore, in the absence of X-ray structural data for biguanide complexes, the data necessary for a normal coordinate analysis are not known. Thus it is necessary to make use of the less rigorous, though useful, group-frequency approach in interpreting the infrared spectra.

In this study the spectra of free biguanide base and several of its complexes are reported for the first time. Progress is made in correlating these spectra with structures that are proposed for the complexes and a number of assignments are made.

Most of the assignments made here are based upon assignments reported in the literature for compounds with functional groups resembling those found in biguanides. The correlation table shown below is based upon results obtained previously for such compounds as urea (71, 112), the guanidinium ion (2) and ethylendiamine (74).

Correlation Table for Compounds Related to Biguanide

Frequency Range (wave numbers)	Assignment
3600 - 3000	N-H stretch
1600 - 1750	NH_2 bending
1600 - 1700	C = N stretch
1350 - 1600	N - C - N stretch
1000 - 1250	NH_2 rock
<1000	skeletal modes

Results and Discussion

4.1 The 4000 - 2000 cm^{-1} Region

Biguanide and its complexes all give rise to strong broad bands in the region 2800 - 3500 cm^{-1} (see figure 4.1). These bands may be assigned with certainty to N - H symmetric and antisymmetric stretching modes. A fairly complex series of maxima is usually observed between 3000 and 3500 cm^{-1} with a long shoulder of lower intensity below 3000 cm^{-1}. This lower energy absorption together with the breadth and complexity of the whole band system is characteristic of hydrogen bonding (18, 72).

The complexity of the absorption in this region makes a detailed analysis virtually impossible and, therefore, the spectra were recorded without any attempt being made to interpret them further.

Deuteration experiments, which were carried out primarily to assist in the assignment of bands below 2000 cm^{-1}, showed that bands in the 3 μ region were displaced to 4 - 5 μ in good agreement with the expected isotopic shift. (Compare figures 4.1 and 4.2).

4.2 The 2000 - 700 cm^{-1} Region

Between 1150 and 1700 cm^{-1} a number of bands, most of them fairly intense, appear in the spectra of biguanide and its complexes. (See figure 4.3) According to the correlation table presented earlier in this chapter, (page 82) the vibrational modes which give rise to absorption in this region are the NH_2 bending and rocking and the C = N (or N - C - N) stretching modes. Below 1150 cm^{-1} it is expected that absorption due to various skeletal modes will appear.

As mentioned earlier the spectra of some deuterated compounds were measured so that absorptions due to N - H vibrations could be distinguished from those due to skeletal vibrations. The spectra of biguanide and partially deuterated biguanide are listed in table 4.1 and those of tris(biguanide) chromium(III) in its normal and deuterated forms, in table 4.2. A number of spectra of complexes of biguanide with transition metal ions are summarised in table 4.3.

The remainder of this chapter contains an analysis of the spectra, first of free biguanide, then of its complexes. It will be demonstrated that assignments made for the spectrum of the ligand are in agreement with those made for its complexes. Certain regular differences between the spectra of the cationic and neutral complexes will be pointed out and attempts made to rationalise them. Finally, the correlation of the spectra with the structures proposed in an earlier chapter are discussed.

(a) Spectrum of Biguanide Base

Partial deuteration of biguanide was accomplished by dissolving it in 99.5% D_2O, allowing the solution to stand for several hours, then evaporating the solution to dryness under reduced pressure. Because the free base is not particularly stable, the dissolution and evaporation were not repeated. However, sufficient evidence was obtained with the partially deuterated compound to enable some tentative assignments to be made.

Bands which appear at 1600 and 1625 cm^{-1} and at 1200 cm^{-1} in the spectrum of the undeuterated compound are diminished in intensity upon

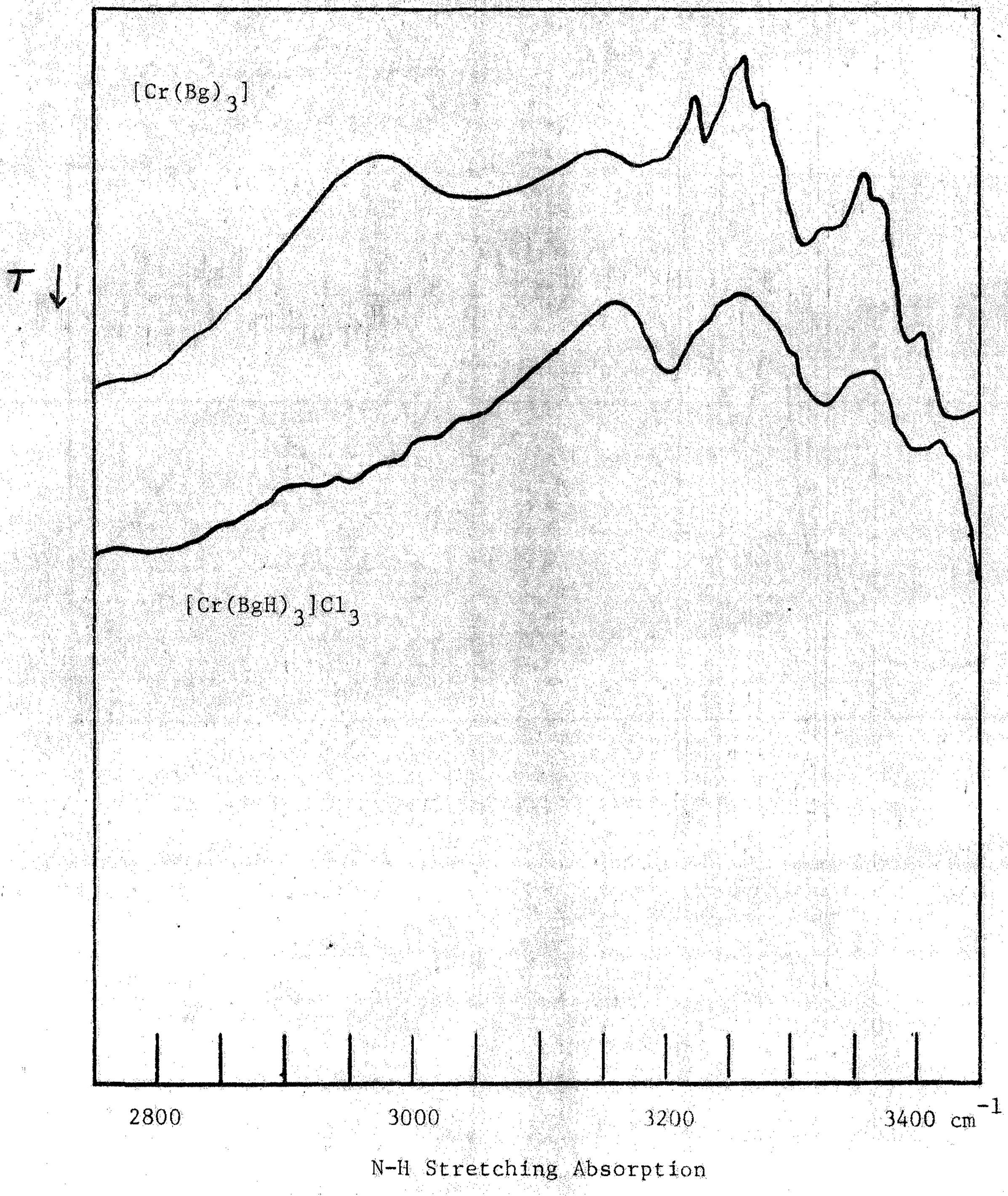

[Cr(Bg)$_3$]
T ↓
[Cr(BgH)$_3$]Cl$_3$
2800
3000
3200
3400 cm^{-1}
N-H Stretching Absorption

Figure 4.1

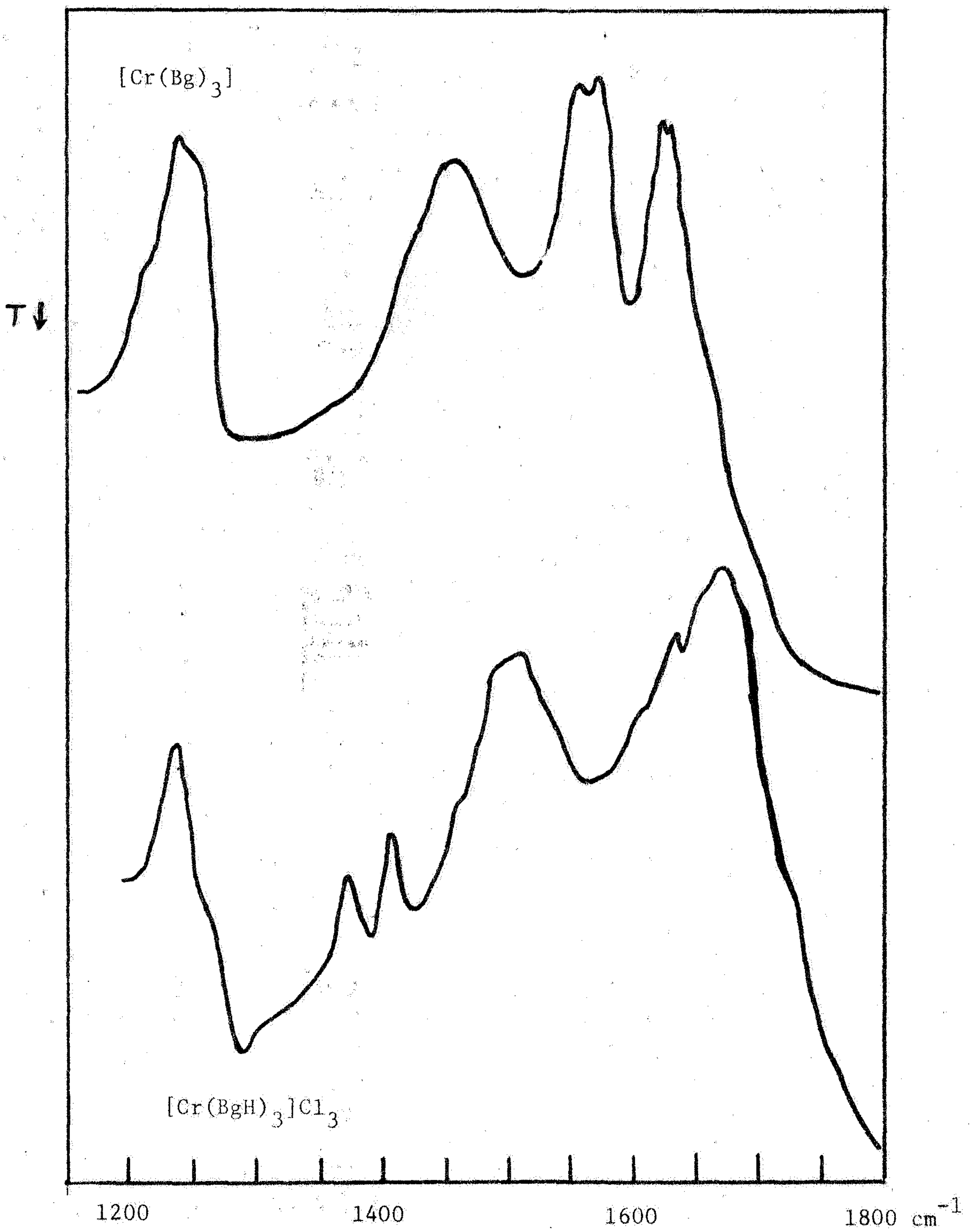


Figure 4.3

partial deuteration while new bands appear at 1220 and 923 cm^{-1}. In the spectrum of the undeuterated compound the 1600 - 1625 cm^{-1} band is assigned as the NH_2 bending mode and the 1200 cm^{-1} band to the NH_2 rocking vibration. The new bands, appearing at 1220 and 923 cm^{-1} after deuteration are therefore assigned to the ND_2 bending and rocking modes. These assignments give very satisfactory values for the isotopic shift, (1.33 and 1.30 respectively). Deuteration does not affect bands at 1509 and 1401 cm^{-1} and these are assigned as N - C - N stretching modes. Even the 1509 cm^{-1} band is well below the usual range for C = N stretching vibrations, and it is postulated therefore that, as in the case of the biguanide cation (see page 81), a resonance effect gives rise to an equivalence of all the C - N bond orders.

Below 1200 cm^{-1} the spectrum appears to be affected only slightly by deuteration, and the bands in the region 1200 - 700 cm^{-1} are therefore assigned to skeletal modes.

(b) Tris(biguanide) chromium(III)

The spectrum of the chromium biguanide complex in the 1200 - 1700 cm^{-1} is much better resolved than that of the free ligand so that assignments, based on studies with the deuterated complex, are more easily made. The disappearance of the band at 1624 - 1630 cm^{-1} upon deuteration means that it can be assigned definitely to the NH_2 bending mode, while the lack of any significant shift in the 1560 - 1580 cm^{-1} band indicates that this is very largely an N - C - N stretching absorption. The broad band at 1458 cm^{-1} becomes resolved, after deuteration, into a strong broad

Table 4.1

Infrared Spectra of Biguanide Base and Deuterated Biguanide Base[*]

Biguanide	Deutero-Biguanide	Assignment
(1625 vs[**] (1600 vs	ca. 1620 sh))	NH_2 Bending
(1560 sh (1509 vs (1411 vs	1600) 1500 sv br) 1405 s)	N - C - N Stretching
	1220 m	ND_2 Bending
1200 s	1200 w	NH_2 Rocking
1109 w 1032 m	1135 w) 960 m)	Skeletal modes
	923 m	ND_2 Rocking
914 w 850 w	905 m) 818 m) 762 m)	Skeletal modes

[*] All data given in wave-numbers (cm^{-1})

[**] v = very, s = strong, m = medium, w = weak, br = broad.

Table 4.2

Infrared Spectra of $[Cr(Biguanide)_3]$ and deuterated $[Cr(Biguanide)_3]$

$CrBg_3$	Deuterated $CrBg_3$	Assignment
1630 vs	1630 w sh	NH_2 bending
1624 vs		
1580 vs)	1561 vs))	
1560 vs)	1546 vs))	Mainly N – C – N stretching
	1485 vs))	
1458 vs br	1415 s))	
1260 sh		NH_2 rocking
1240 vs		
	1227 m br	ND_2 bending
1098 m	1091 w	
1054 m	1026 w	
	1004 w	ND_2 rocking (?)
944 vw	925 vw	
	852 vw	
	830 vw	
770 w		
	764 m	

maximum at 1415 cm^{-1} and a weaker one at 1485 cm^{-1}. Thus overall there appears to be no real shift in this absorption, and it too is assigned as an N - C - N stretching mode.

It is interesting to note that there appears to be very little coupling between the N - H bending and N - C - N stretching modes in biguanide complexes. This is in contrast to the case of 1,3-diimine complexes for which infrared spectra have been measured recently. For these complexes, bands at 1580 and 1620 cm^{-1} were both shifted significantly upon deuteration, indicating that the N - H bending mode made a considerable contribution to both bands.

Deuteration of $Cr(Bg)_3$ causes the disappearance of the 1240 cm^{-1} band. As in the case of the free ligand, this band is assigned to the NH_2 rocking mode. The band which remains in this region at 1227 cm^{-1} is assigned to the ND_2 bending mode (giving an isotopic shift, $\nu H/\nu D = 1.33$). It is not possible to make a definite assignment for the ND_2 rocking mode which is expected to appear at around 930 cm^{-1} (assuming an isotopic shift of 1.33), although it could be assigned to a new band which appears at 1004 cm^{-1}. This assignment gives an isotopic shift of 1.25 which is low for a pure NH_2 rocking mode but this could result from coupling of the NH_2 rocking mode with some other mode of the same symmetry.

Below 1200 cm^{-1} the spectrum is almost unaffected by deuteration and only some minor shifts, generally to lower frequencies, are found together with some small changes in intensity. Absorption in this region is most probably due to various skeletal modes.

Table 4.3

Infrared Spectra of Biguanide Complexes

[$CoBg_2$]	[$Co(BgH)_2$]SO_4	[$CuBg_2$]	[$Cu(BgH)_2$] Cl_2	Assignment
1608 vs	1661 vs	1625 vs	1686 vs)	
			1630 w)	NH deformation
	1631 sh	1605 vs	1610 w)	
1567 vs	1513 vs	1566 vs	(1545 s)	
			(1515 sh)	
			)	N - C - N
(1493 vs	1391 w	(1490 sh	)	
(1462 w		(1460 vs	1435 w)	stretch
		(1449 vs	)	
1295 vs	1304 s	1280 vs	1284 m)	NH_2 rock
		1218 w	1259 m)	
		1158 vw	1160 vw	
1116 w br	obscured by	1114 vw	1104 vw	
	$SO_4^=$			
1062		1057	1043	
1016 w sh		970 vw		
952 vw	967 vw	937 w	963 vw	
787 w br	808 w	800 s		
762 w br	754 w	757 w	754 sh	
		738 w	720 s	
672 m		678 m		

Table 4.3 (Cont'd)

$[CrBg_3]$	$[Cr(BgH)_3]Cl_3$	Assignment
(1630 vs	(1673 vs br)	NH_2 deformation
(1624 vs	(1624 m sh)	
(1580 vs	)	
(1560 vs	1509 s br)	N – C – N stretch
(1458 vs	1406 w)	
	1372 w)	
1260 sh	1267 sh)	NH_2 rock
1240 vs	1240 vs)	
1148 sh	1148 sh	
1098 m	1128 w	
1054 m	1093 vw	
944 w	951 vw	
	(784 sh	
770 w	(764 w	

$[CoBg_3].nH_2O$	$[Co(BgH)_3]Cl_3$	Assignment
(1630 vs)	(1665) vs br	NH_2 bending
(1610 vs)	(1690)	
	(1600 sh	
1575 vs br	1510 s br	
1450 vs br		N–C–N stretching
	1395 s	
1255 sh		NH_2 rock
1235 vs	1240 m	
1107 w	1129 w	
1055 w		
	1086 vw	
949 w	954 vw	
	(760 sh	
	(733 m	

(c) Spectra of Biguanide Complexes in General

The assignments made for the spectra of biguanide and tris(biguanide) chromium(III) have been used in making similar assignments for the spectra listed in table 4.3. The region of greatest interest in these spectra is that between 1350 and 1700 cm^{-1} in which the N - C - N stretching and N-H bending modes are found. In order to facilitate a more detailed examination of the spectra in this region, they were plotted for comparison in figure 4.4. Here, the systematic differences between the spectra of the cationic and neutral complexes are highlighted and it may be observed that for a particular metal ion, the N-H bending frequency is higher and the N - C - N stretching frequencies are lower, in the cationic complex.

These observations are perhaps most satisfactorily explained by making use of the work of Bellamy and Williams (10) who provided an explanation for the pattern of C - H stretching and deformation frequencies in a number of CH_3 - X compounds. In the case of the methylhalides they postulated that as the series is traversed from CH_3F the p character of the C - X bond increases and as a result the s character of the C - H bond increases along the same series. Since p orbitals are more diffuse, yet have greater directional properties than s orbitals, an increase in the s character of the C - H bonds would be expected to give rise to shorter bond lengths and higher C - H stretching frequencies, while the decreasing directional character of the bonds should be reflected in a lowering of the C - H bending frequencies. These expectations are borne out by experiment.

Hadzi (47) has extended these arguments to explain the differences in N - H stretching and bending frequencies between aliphatic and aromatic

I.R. Spectra of Biguanide Complexes Between 1350 and 1700 cm^{-1}.

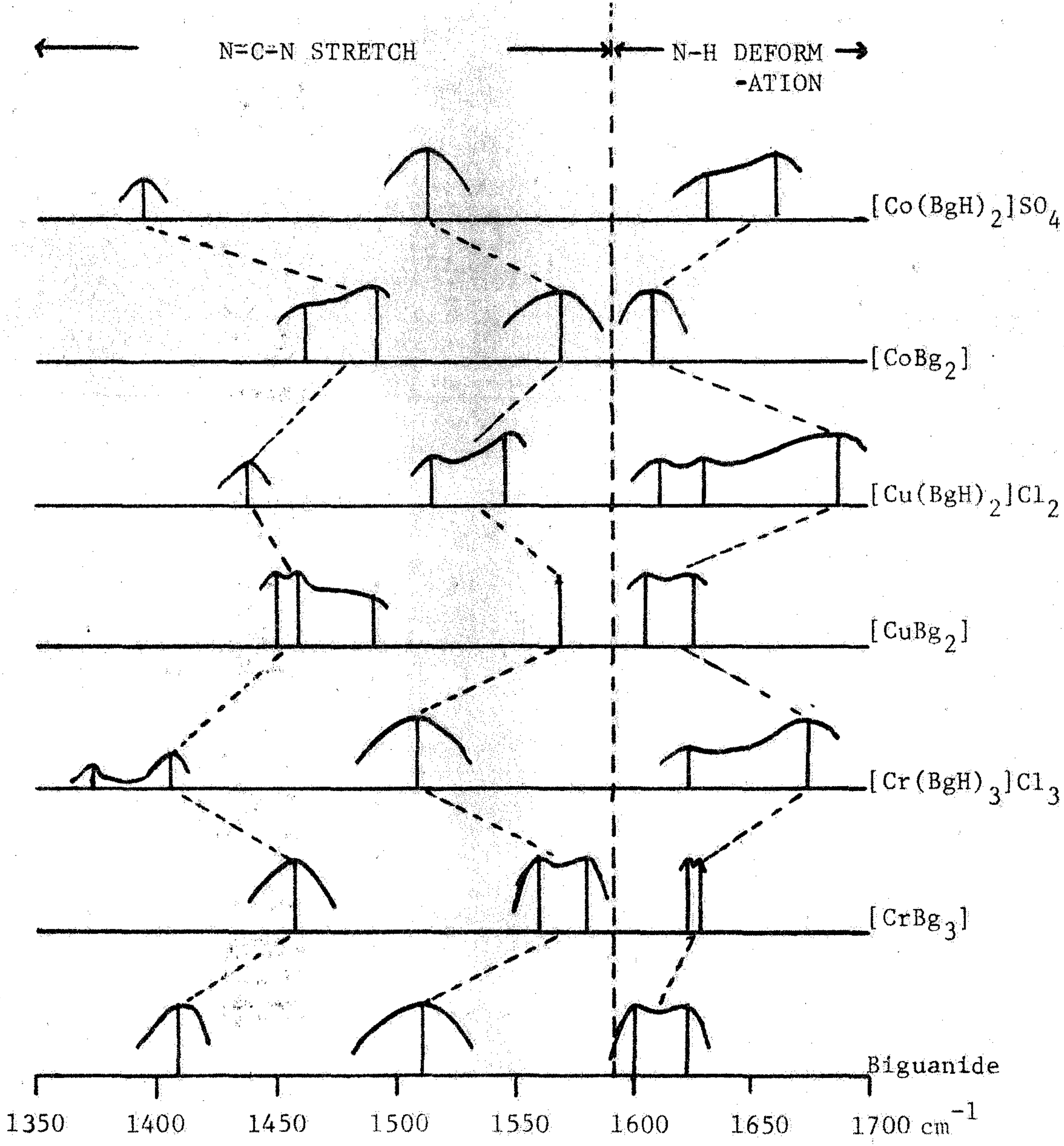
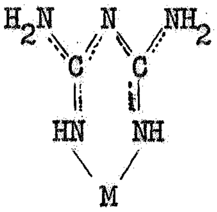


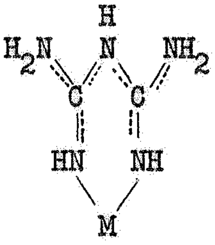
Figure 4.4

amines. He suggested that in the aromatic amines there is conjugation of the nitrogen lone pair electrons with the aromatic ring and this is facilitated if the lone pair orbital has more p character. The increase in the p character of the lone pair orbital requires a corresponding increase in the s character of the N - H bonds which in turn gives rise to increased N - H stretching frequencies and decrease N - H bending frequencies. Hadzi also made similar observations on the spectra of phenols and aliphatic alcohols.

Arguments such as these may well be applicable in the case of the biguanide complexes. It has been postulated in an earlier chapter that the structures of the cationic and neutral complexes can be represented by XLVII and XLVIII below, in which there are two amino groups conjugated with the chelate ring.



XLVII



XLVIII

This situation bears some resemblance to the case of the aromatic amines. Protonation of the chelate ring (probably at N^3) decreases the effectiveness of the conjugation in the system, weakens the C - N bonds and gives rise to lower N - C - N stretching frequencies. The decreased degree of conjugation will have the added effect of lowering the p character of the nitrogen lone pair orbitals and, hence, of increasing the p character of the N - H bonds. This should result in higher N - H deformation frequencies in the protonated (cationic) complexes, as observed, and lower N - H stretching frequencies. While no significant differences in the N - H stretching frequencies have been observed between the two types of complex, this does not mean that the above explanation is faulty, since hydrogen bonding tends to overshadow all other effects in this region of the spectrum.

4.3. EXPERIMENTAL

Infrared spectra were measured on a Perkin Elmer model 221 or a Grubb Parsons "Spectromaster" spectrophotometer. Samples were prepared by mulling compounds in liquid paraffin (nujol) or hexachlorobutadiene and mounting between alkali halide plates.

CHAPTER 5

Some Complexes of Sulphur-Containing Ligands

Guanylurea, biuret, guanylthiourea and dithiobiuret all have structures which are similar, in many respects, to that of biguanide. However, the presence of oxygen or sulphur, as well as nitrogen, in these compounds should allow the formation, in each case, of at least two types of chelate complex with transition metal ions. Thus it has been shown (see references in chapter 1) that biuret is coordinated through nitrogen alone in some of its complexes and through oxygen alone in others. Similarly it has been suggested (78) that guanylthiourea forms two kinds of complex; those in which the ligand coordinates solely through nitrogen, and those in which coordination is through both nitrogen and sulphur. Guanylurea appears to be coordinated through nitrogen in all of its complexes (78). Too few complexes of dithiobiuret have been studied for any conclusions to be drawn, regarding the means of coordination of this ligand.

A study of the coordination chemistry of some of these compounds is a natural extension of an investigation of biguanide complexes. The structural similarity between biguanide and the oxygen- or sulphur-containing ligands could well mean that information derived from an examination of one group of compounds will be useful in the study of another group.

It was decided to concentrate here on the sulphur-containing ligands, guanylthiourea and dithiobiuret, since complexes of biuret and guanylurea have been studied quite extensively elsewhere. Accordingly, work has been directed at both extending the range of known complexes of these ligands and checking some of the earlier reports of their complexes.

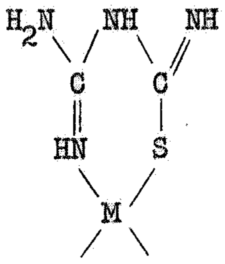
5.1 Guanylthiourea Complexes

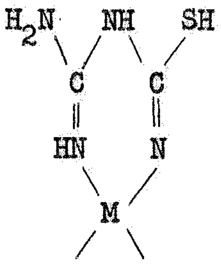
From the limited data available (69,73,80) it appears that the type of bonding in complexes of guanylthioureas may depend both upon the metal ion involved and the substituents on the ligand. It has been postulated (69,73,80) that in the known complexes of guanylthiourea and S-ethylguanylthiourea the type of coordination with the different metal ions is as shown in table 5.1.

Table 5.1*

Ligand	Co^{III}	Co^{II}	Ni^{II}	Cu^{II}	Pd^{II}	Ref.
guanylthiourea	N-S	N-S	N-N	N-S	N-S	(73,80)
S-ethylguanylthiourea		N-S	N-N	N-N		(69)

* N-S refers to coordination via nitrogen and sulphur, e.g. as in XXXIV
N-N refers to coordination via nitrogen alone, e.g. as in XXXV.


XXXIV


XXV

It is interesting to note that the thioamide group provides similar alternative bonding schemes to those found in thiocyanate complexes.

Lewis, Nyholm and Smith (56) have pointed out that the type of coordination in thiocyanate complexes may be correlated with the classification of metal ions proposed by Arhland, Chatt and Davies (1). They noted that class (a) metals (see figure 5.1) form isothiocyanates (N-bonded), while class (b) metals form thiocyanates, (S-bonded).

In view of the similarity between the thiocyanate and thioamide groups it might be expected that the same factors will govern the nature of the coordination of the two groups with the various transition metal ions. Thus it would be expected that only metal-nitrogen bonds would be formed in guanylthiourea complexes with class (a) acceptors while both metal-nitrogen and metal-sulphur bonds would be formed in the complexes with class (b) acceptors.

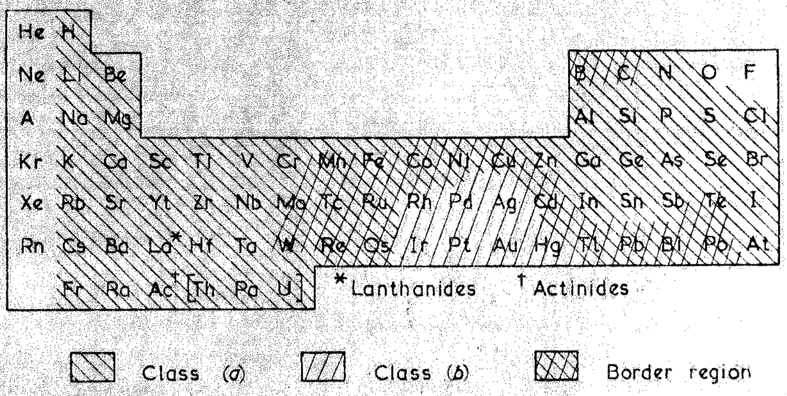
The data in table 5.1 are not entirely compatible with these expectations, since cobalt-sulphur bonding has been inferred both for the cobalt(II) and cobalt(III) guanylthiourea complexes. This is in contrast to the situation in the thiocyanate complexes of cobalt, where metal-nitrogen bonding is known to exist.

However, cobalt(II), copper(II), nickel(II) and, possibly, cobalt(III) are in the border region between (a) and (b) class ions, and it is probable that the weak (a)- character is, in some cases, overridden by other factors. The palladium(II) ion is definitely in class (b) and, as expected, metal-sulphur bonds appear to be present in the guanylthiourea complex (73).

It has been observed (80) that the reactions of guanylthiourea with cupric salts afford brownish-yellow products, containing copper and ligand

Figure 5.1 (Taken from Ref. 1)

Classification of acceptor atoms in their normal-valent states



in an approximately 1 to 1 mole ratio. The room temperature magnetic moments of these products are anomalously low and chemical evidence suggests that they contain metal to sulphur bonds. There has been no attempt made to explain these observations and the unusual properties of these compounds should therefore provide an interesting study. It is interesting to note, too, that copper is an element in the border-region of the classification of Ahrland et. al. (1). Copper(II) generally exhibits class (a) character while copper(I) is considered as belonging in class (b).

The work of Ray and Chaudhury (80) on these copper derivatives has been repeated and extended here, and some interesting results have been obtained.

To date there have been no reports of guanylthiourea complexes of metal ions with definite class (a) behaviour. Accordingly, the reaction between guanylthiourea and the chromium(III) ion has been studied here.

5.2 Copper Complexes of Guanylthiourea

The reactions between cupric salts and guanylthiourea have been investigated briefly, both by Trimble (104) and Ray and Chaudhury (80). It was observed that in all cases these reactions yielded products which contained copper and guanylthiourea in an approximately 1 to 1 mole ratio. The magnetic moments of these compounds were found (80) to be lower than expected for magnetically dilute d^9 complexes, and this was attributed to "an unusually high temperature effect." It is not at all clear what was meant by this statement since it was not elaborated upon.

Although Ray and coworkers (80,73) have found that nickel(II) and cobalt(II) form bis-guanylthiourea complexes, and cobalt(III) forms a tris-guanylthiourea complex, they did not comment upon, or suggest a reason for, the fact that cupric salts afford only monoguanylthiourea complexes. Furthermore, it is interesting to note that Paigankar and Haldar (69) have recently prepared a copper(II) complex of S-ethylguanylthiourea which has a metal ligand ratio of 2 to 1. It is a normal, paramagnetic complex with a magnetic moment of 1.82 B.M. and its magnetic susceptibility obeys a Curie-Weiss law with a Θ-value of 4°K. These authors did not comment upon the fact that the introduction of an S-ethyl-substituent into the ligand allowed the formation of a bis-complex with markedly different properties to the complexes of the parent ligand, obtained by Ray and Chaudhury (80).

Because the differences between guanylthiourea and the S-ethylguanylthiourea appear to be very significant, a detailed investigation of the reactions of the former compound with cupric salts has been undertaken here.

It has not been possible in this study to obtain stoichiometric compounds by the reaction of cupric salts with guanylthiourea. Two different preparations under the same conditions, gave copper-ligand ratios of 1 to 1.1 and 1 to 1.25 respectively. Similar difficulties were experienced by Trimble (104), who obtained a product with a 1 to 0.9 copper-ligand ratio, when he caused cupric acetate and guanylthiourea to react. Ray and Chaudhury (80), however, claim to have prepared pure samples of the compounds $[Cu(C_2H_5N_4S)(H_2O)_2]SO_4.4H_2O$ and $[Cu(C_2H_5N_4S)(OH)(H_2O)].H_2O$.

Products obtained in this work have been assigned formulae such as $[Cu_2(C_2H_5N_4S)_2\ Cl.\ x\ (C_2H_6N_4S)$, where $x = 0$ to $0.5]$. The material from one preparation, with $x = 0.5$, was studied in some detail. In agreement with the results of Ray and Chaudhury (80) the material had a lower magnetic moment than expected for a copper(II) compound. However, an investigation of the temperature dependence of the magnetic susceptibility showed that the Curie-Weiss law was obeyed, with $\theta = 4^{o}K$. (See table 5.2 and figure 5.2). Thus the possibility that magnetic interaction between two copper(II) ions in a dimeric molecule had reduced the magnetic moment, could be eliminated.

It was noted, however, that if the magnetic susceptibility of a dimeric molecule were attributed to only one of the copper atoms, the other being diamagnetic, then the paramagnetic copper atom would have a magnetic moment of approximately 1.9 B.M. Such a situation would require that the complex be formulated as $Cu^{II}.\ Cu^{I}\ (C_2H_5N_4S)_2\ Cl.\frac{1}{2}(C_2H_6N_4S)$; i.e. the complex would contain both cupric and cuprous ions.

Similar formulations for the compounds prepared by Ray and Chaudhury (80) would be:

$Cu^{II}.\ Cu^{I}\ (C_2H_5N_4S)_2.HSO_4.6H_2O$ and $Cu^{II}.\ Cu^{I}\ (C_2H_5N_4S)_2(OH).2H_2O$.
Magnetic moments based on these formulae are 2.08 B.M. and 2.03 B.M. respectively. There appears to be no satisfactory alternative means of explaining the magnetic properties of these compounds. Furthermore,

Table 5.2

Magnetic Properties of Copper Guanylthiourea Compound***

$T^{o}K$	χ_g	χ_M*	χ_A**	μ_{eff} (B.M.)	$\frac{1}{\chi_A}$
284.5	3.78	1506	1626	1.93	616
250.8	3.63	1717	1837	1.93	544
217.3	4.22	1996	2116	1.93	473
183.0	5.01	2370	2490	1.92	402
150.1	6.18	2923	3043	1.93	329
116.5	8.04	3803	3923	1.92	255

* Molecular weight, based on the copper analysis, is taken as 473.0

** Diamagnetic correction taken as 120×10^{-6} c.g.s.

*** Data in c.g.s. units.

there is a certain amount of indirect evidence which favours the hypothesis:

(i) It is well known that compounds with the thiol (-SH) group are reducing agents, the reducing properties being due to the fact that the following reaction, the formation of a disulphide, can occur:

$$2\ R\text{-}SH + [O] \longrightarrow R\text{-}S\text{-}S\text{-}R + H_2O.$$

Guanylthiourea should therefore be capable of acting as a reducing agent, accounting for the reduction of copper(II) to copper(I).

(ii) It is now possible to explain the differing coordination properties of guanylthiourea and S-ethylguanylthiourea. The ethyl-group

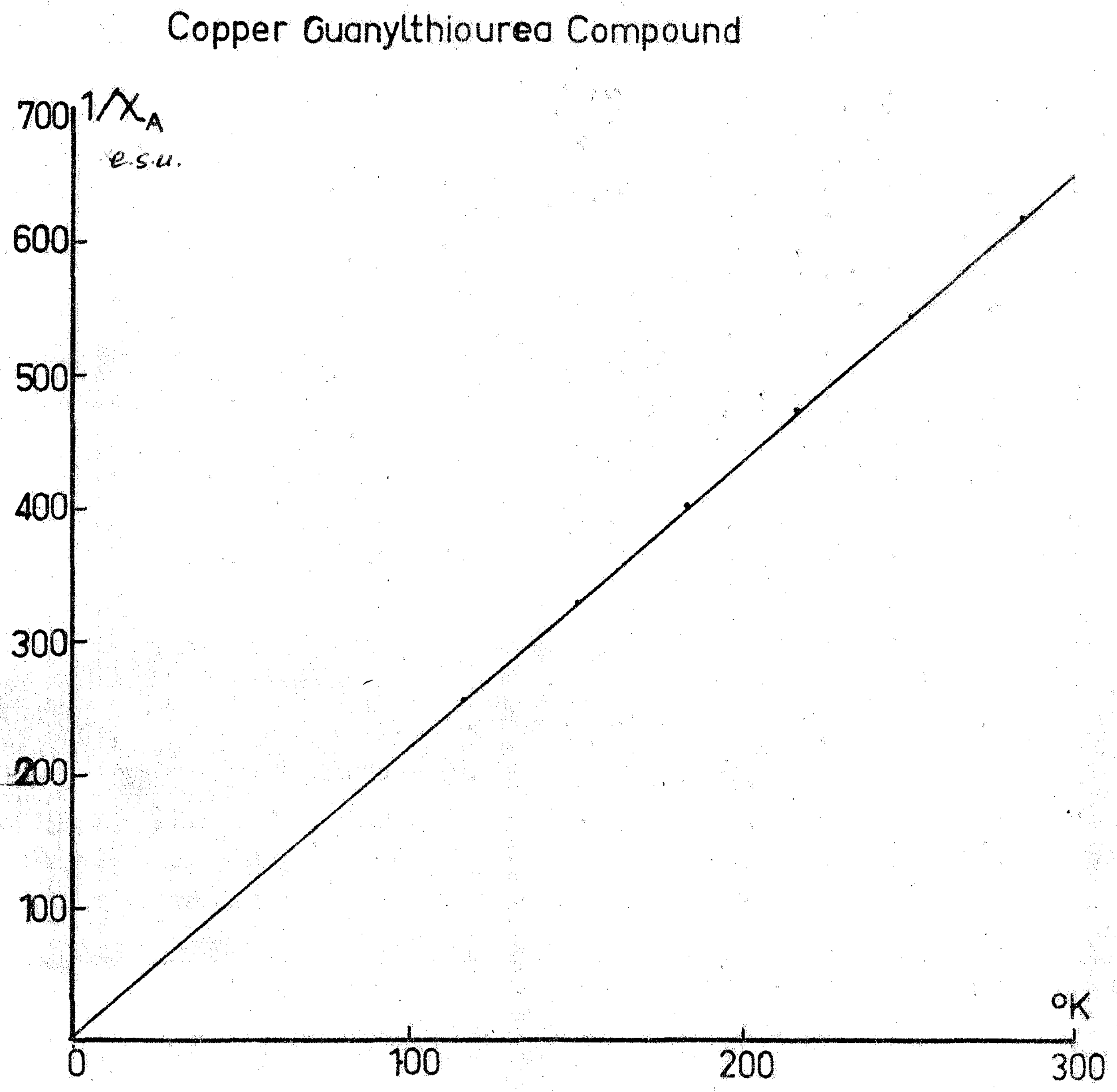

Copper Guanylthiourea Compound
1/χA
e.s.u.
700
600
500
400
300
200
100
0
100
200
300
°K

Figure 5.2

in the latter compound destroys the reducing property of the guanylthiourea by blocking the formation of the disulphide. Thus, S-ethylguanylthiourea is a normal chelating agent, and forms the expected bis-complex with copper(II).

(iii) Furthermore the presence of metal-sulphur bonds in the copper-guanylthiourea compound, inferred elsewhere (80) from its chemical properties, can be understood if it is agreed that cuprous ions are present. Copper(I) is known to belong in class (b) of the Ahrland classification (1) and should readily form metal-sulphur bonds. In the S-ethylguanylthiourea-copper complex reported by Paiganka and Haldar (69), only cupric ions, known to have class (a) character, are present and, as expected, only metal-nitrogen bonds are found.

(iv) The reaction of dithiobiuret with cupric salts is also pertinent here. It has been shown in this study (page116) that the yellow compound, previously supposed (4) to be a dithiobiuret complex of copper(II) is actually a cuprous complex. In this case, copper(II) is completely reduced to copper(I) whereas in the reaction with guanylthiourea, only half of the copper(II) is reduced.

At this stage it is only possible to speculate on possible structures for the copper-guanylthiourea compound. All that can be said is that it is most probably a mixed-valence compound containing both copper(II) and copper(I) ions in 1:1 mole ratio. It is interesting to compare the properties of the copper-guanylthiourea complexes with those of other mixed-valence compounds reported previously.

For mixed-valence compounds there exists the possibility that electron transfer may occur between two metal ions of different valence. This electron transfer can, under some circumstances, give rise to unusual magnetic, spectral and electrical properties. Measurement of these properties for a particular compound may afford useful structural information. Robin and Day (25a) have proposed a method of classifying mixed-valence compounds based on physical properties, as set out in table 5.3.

Both the electronic spectrum and magnetic properties of the copper-guanylthiourea complexes described above have been measured. The magnetic properties (Table 5.2, figure 5.2) obey the Curie-Weiss law, implying that the compound is magnetically dilute and could belong to either class I or class III-A. The electronic spectrum (figure 5.3) contains intense absorption which could be attributed to either mixed-valence or metal-ligand charge transfer. The latter might be expected for metal-sulphur bonds.

5.3 Reactions of Chromium(III) with Guanylthiourea

Accordingly, the reaction between guanylthiourea and the chromium(III) ion has been studied here in an attempt to determine whether complexes can be obtained, and, if so, to determine the type of coordination involved.

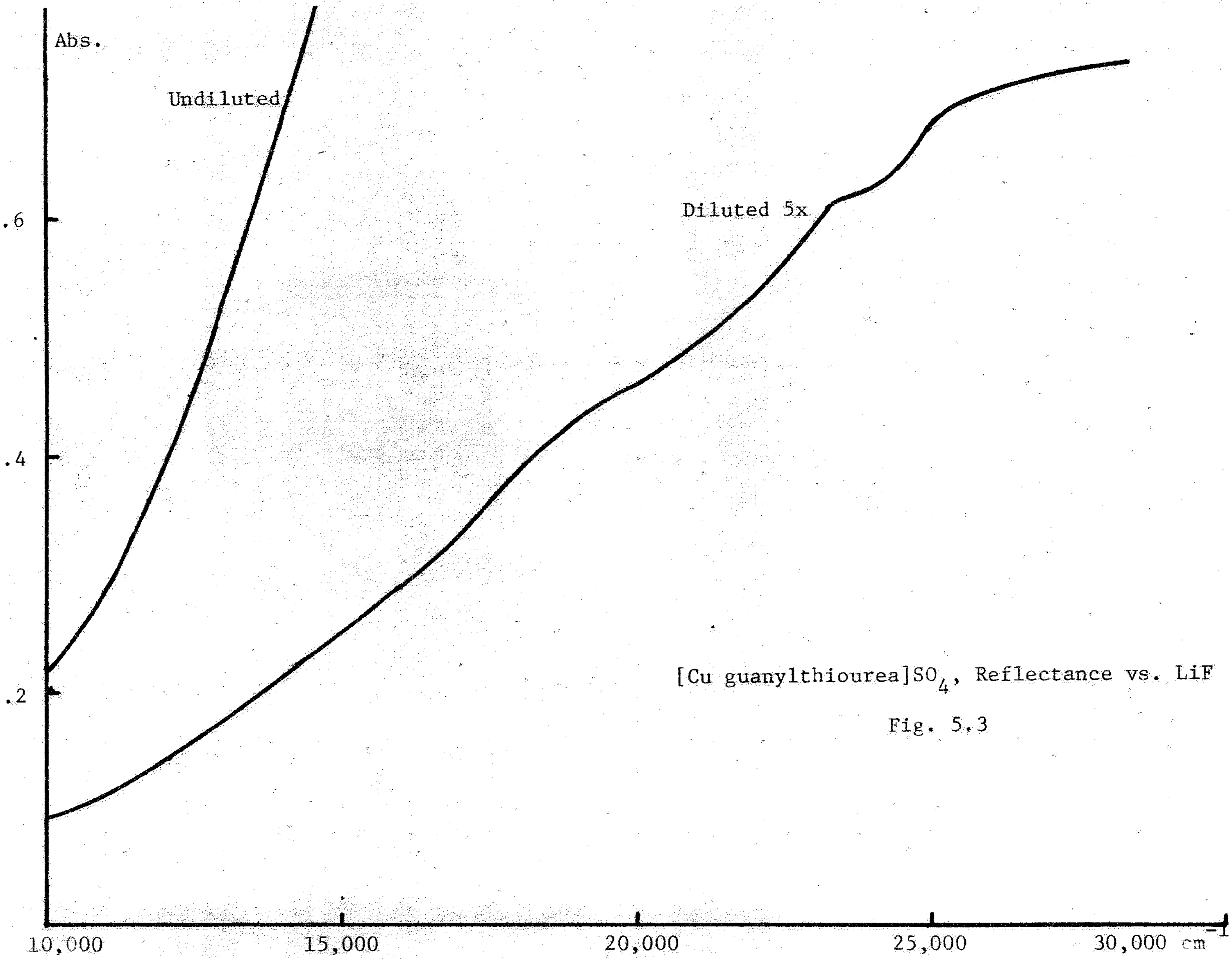
No guanylthiourea complexes of metal ions with definite class a character (see figure 5.1 page) have yet been reported. As mentioned earlier, guanylthiourea would be expected to coordinate through nitrogen alone in these complexes, whereas coordination via sulphur and nitrogen would be expected in complexes with class b metals.

While attempts to prepare a complex from aqueous solutions were not

Table 5.3

CHARACTERISTICS OF THE FOUR CLASSES OF MIXED VALENCE COMPOUNDS

Class I	Class II	Class III-A	Class III-B
(1) Metal ions in ligand fields of very different symmetry and/or strength, i.e., tetrahedral vs. octahedral	(1) Metal ions in ligand fields of nearly identical symmetry, differing from one another by distortions of only a few tenths Å	(1) Metal ions indistinguishable but grouped into polynuclear clusters	(1) All metal ions indistinguishable
(2) $\alpha = 0$; valences very firmly trapped	(2) $\alpha > 0$; valences distinguishable, but with slight delocalization	(2) α maximal locally	(2) α maximal; complete delocalization over the cation sublattice
(3) Insulator; resistivity of 10^{10} ohm cm or greater	(3) Semiconductor; resistivity in the range 10–10^{7} ohm cm	(3) Probably insulating	(3) Metallic conductivity; resistivity in the range 10^{-2}–10^{-6} ohm cm
(4) No mixed valence transitions in the visible region	(4) One or more mixed valence transitions in the visible region	(4) One or more mixed valence transitions in the visible region	(4) Absorption edge in the infrared, opaque with metallic reflectivity in the visible region
(5) Clearly shows spectra of constituent ions, IR, UV, Mössbauer	(5) Shows spectra of constituent ions at very nearly their normal frequencies	(5) Spectra of constituent ions not discernible	(5) Spectra of constituent ions not discernible
(6) Magnetically dilute, paramagnetic or diamagnetic to very low temperatures	(6) Magnetically dilute, with both ferromagnetic and antiferromagnetic interactions at low temperatures	(6) Magnetically dilute	(6) Either ferromagnetic with a high Curie temperature or diamagnetic, depending upon the presence or absence of local moments



[Cu guanylthiourea]SO_4, Reflectance vs. LiF

Fig. 5.3

successful, it was found that an alcoholic solution containing chromic chloride and guanylthiourea slowly turned pink-violet, suggesting that some reaction was occurring. In order to determine the nature of the species formed, a series of solutions containing a fixed concentration of chromic chloride with varying amounts of ligand were made up as set out in table 5.4.

Table 5.4

Solution No.	1	2	3	4	5	6	7	8
Mole ratio:								
guanylthiourea/$CrCl_3$	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Colour at $\text{equ}\backslash^{\text{ium}}$	←——green——→				grey		←pink-violet→	
Absorbance at 515 mμ	0.23	0.23	0.26	0.36	0.53	0.73	1.04	1.02

All of the solutions were originally green and the electronic spectra contained two bands, at 15,400 and 21,400 cm^{-1}, characteristic of the octahedral $[CrCl_2(H_2O)_4]^+$ ion. Within a matter of minutes solutions (7) and (8) began to darken and within one day they had become pink-violet; at the same time solution (6) had become greyish. In all solutions the two spin allowed bands observed previously had shifted to higher energies, the larger shifts being observed in those solutions containing ligand in greater concentrations. After fourteen days pink precipitates had formed from solutions (7) and (8) and the spectra of these two solutions, and of (6), had become very similar, each giving rise to bands at about 19,400 cm^{-1} and 24,500 cm^{-1}. These band positions remained constant thereafter. The solutions of lower ligand concentration had also come to equilibrium at this stage and the spectra of these solutions contained bands at frequencies intermediate between those exhibited by the original green solutions and those of the pink solutions (6), (7) and (8).

It is significant that the pink colour developed only in those solutions where the ligand to chromium(III) mole-ratio was equal to or greater than three. In solutions with greater ligand concentrations there appeared to be no increase in the hypsochromic shift of the absorption maxima. This suggests that the tris-(guanylthiourea) chromium(III) species is formed in solution. Furthermore, the fact that no isosbestic point has been found indicates that more than one complex species is formed by the reaction of $CrCl_3$ and guanylthiourea, most probably the mono - and bis- complexes.

The positions of the two bands observed for the pink solutions, at 19,400 and 24,500 cm^{-1}, are in the region associated with the chromium(III) octahedrally coordinated by six nitrogen atoms. These band positions are compared with those for chromium(III) complexes of nitrogen containing ligands, in Table 5.5.

Table 5.5

Complex	$^4A_2(F) \leftarrow {}^4T_2(F)$	$^4A_2(F) \rightarrow {}^4T_1(F)$
$Cr(guanylthiourea)_3$	19,400	24,500
$Cr(Bg)_3$	20,000	26,300
$Cr\ en_3$	21,680	28,490
$Cr(NH_3)_6$*	21,500	28,500

* Values given in Jorgensen C.K. : Absorption Spectra and Chemical Bonding in Complexes. Pergamon p. 290.

Thus, as expected, metal nitrogen bonds only, appear to be formed between guanylthiourea and chromium(III).

Attempts were made to isolate sufficient of the solid complex for purposes of characterisation and details of these experiments will be found in the experimental section at the end of this chapter. All solid products from solutions of guanylthiourea and chromic ion showed evidence of partial decomposition of the ligand to dicyandiamide (which gives rise to two bands in the $C\equiv N$ stretching region of the infrared spectrum of these products). One particular sample was analysed completely and characterised by spectral and magnetic measurements. The analysis corresponded to the formula $Cr_2(C_2H_5N_4S)_3\ (C_2H_4N_4)\ Cl_3.xCH_3OH.5H_2O$ where x is approximately 6, $C_2H_5N_4S$ is guanylthiourea and $C_2H_4N_4$ is dicyandiamide. The presence of methanol in the product is suggested by the analyses and by the appearance of bands at 2816 and 2922 cm^{-1} in the C-H stretching region, of the infrared spectrum. Other bands expected for methanol, the O-H stretching and CH bending, are masked by N-H bending and stretching and C-N stretching modes, respectively, of the guanylthiourea and dicyandiamide molecules. The infrared spectrum is listed in table 5.6.

Room temperature (293.0°K) magnetic measurements for the compound gave a gram susceptibility (χ_g) of 11.28 c.g.s. This corresponds to a magnetic moment per chromium atom, based on the chromium analysis, of approximately 3.5 B.M., which is lower than expected for a magnetically dilute d^3 complex.

The electronic spectrum of the compound was measured both by diffuse reflectance (see figure 5.4) and in aqueous solution. There is no doubt that the chromium ion is surrounded by a pseudo-octahedral ligand field of fairly low symmetry. The two strong bands observed at 18,700 and 25,000 cm^{-1}

can be assigned as the $^{4}T_{2g}(F) \leftarrow {}^{4}A_{2g}$ transitions in octahedral symmetry. The small shoulded observed at 13,700 cm^{-1} is assigned as the spin-forbidden, $^{2}E_{g} \leftarrow {}^{4}A_{2g}$ transition, in octahedral symmetry. Both spin allowed bands show evidence of marked splitting. This is to be expected, since the formula for the compound does not allow for a highly symmetrical ligand field.

Table 5.6

Infrared Spectra below 2000 cm^{-1} of Guanylthiourea Compounds

Guanylthiourea	Chromium Guanylthiourea Compound	Copper Guanylthiourea Compound	Assignment*
1635 sh	1590–	1645 vs br	
1612 vs	1670 vs br		NH_2 bending
		1572 vs)	
		1565 vs)	
1508 vs br	1512 vs	1505 vs)	N–C–N stretching
1483 vs		1480 sh)	
	1458) m		νC–N + νC–S
	1448)		
1415 vs		1430 vs	
1325 s	1340 s	1320 s	
	1240 s	1250 s	
1188 s			
1165 sh	1152 s	1155 s	
1068 m	1050 s		
		962 w	
943 s			
	895 m	905 m	
		890 sh	
758 sh	760 sh	773 s	
740 s	715 s	715 s	

*Assignments are based on empirical correlations with earlier work on thiourea ( ) and dithiobiuret (101), together with work carried out in this project on biguanides.

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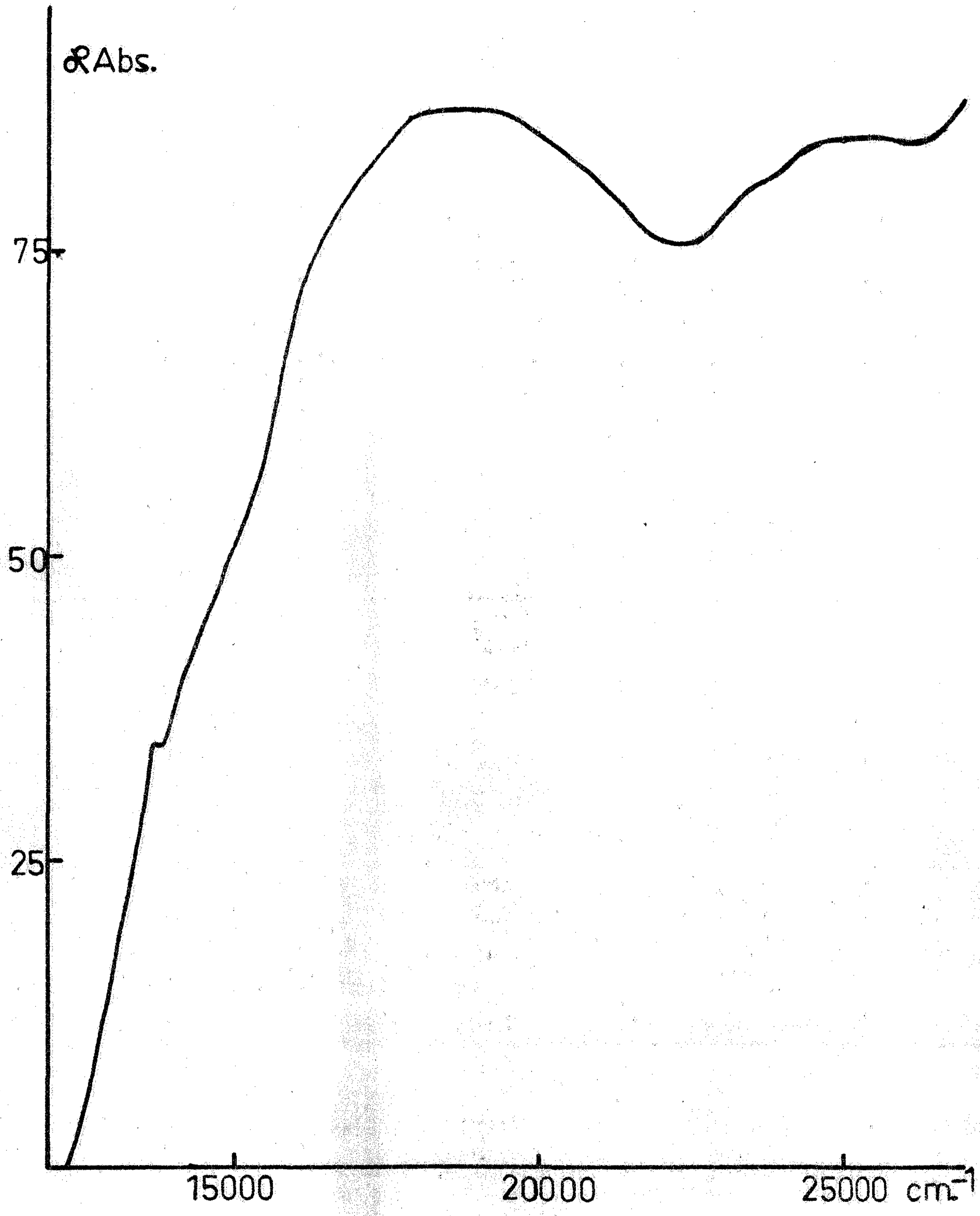

Diffuse Reflectance Spectrum of Chromium(III)-Guanylthiourea Adduct

Figure 5.4

It can be concluded from these results that the chromic ion and guanylthiourea apparently react in solution to form a tris-(guanylthiourea) chromium complex species of some kind. The species does not precipitate from solution, but instead precipitates are formed which contain both guanylthiourea and the decomposition product dicyandiamide.

5.4 Reactions of Dithiobiuret with Transition Metals

Only the silver(I) complex $[Ag_2(C_2H_5N_3S_2)_3](NO_3)_2$ has been characterised previously (101). The two copper compounds which have been reported, the products of the reactions between dithiobiuret and the cupric (4) and cuprous (3) ions respectively, were both described as yellow, but were not further characterised in any way.

In order to obtain a comparison between the coordinating properties of dithiobiuret, guanylthiourea and the other ligands mentioned earlier, its reactions with cupric salts have been investigated.

5.4 a) Copper Dithiobiuret Complex

The bright yellow product obtained when an aqueous solution of cupric sulphate was added to an aqueous solution of dithiobiuret, was found to be diamagnetic at room temperature. Furthermore, no maxima were observed in its diffuse reflectance spectrum between 300 and 1000 millimicrons. These data, together with a complete elemental analysis of the compound indicate that it should be formulated as the copper(I) complex, $[Cu_2(C_2H_5N_3S_2)_3]SO_4$.

This result is readily explained by the fact that dithiobiuret is known to be a fairly strong reducing agent (54). It seems certain that the cupric ions have been reduced by the ligand.

The close similarity of the formula of the cuprous complex with that of the silver(I) complex mentioned above, was suggestive that the two compounds might have similar structures. Accordingly the infrared spectrum of the copper(I) complex was measured for comparison with the spectrum of the silver complex, reported by Stephen and Townshend (101). The two spectra, listed in table 5.7, are in good agreement and it seems certain that the structures of the two complexes are also very much alike.

Stephen and Townshend suggested that the silver dithiobiuret complex had the same structure as the thiourea complex, $[Ag_2tu_3](NO_3)_2$, which they also studied. It was proposed that the dithiobiuret would be monodentate and coordinated through a sulphur donor atom.

5.5 Conclusions

This section of the project, the study of the sulphur containing ligands guanylthiourea and dithiobiuret, was undertaken because of the structural similarities between these compounds, the oxyanalogues, and biguanide. The result, however, has been rather to emphasise the differences in properties between the two groups of compounds.

It has been demonstrated that both guanylthiourea and dithiobiuret, in reacting with cupric salts, reduce them at least partly to the cuprous state. The reducing properties of these ligands are attributable to thiol groups which are readily oxidised to inter- or intra-molecular disulphide linkages.

An interesting extension of this work would be the study of the

Table 5.7

Infrared Spectra of dithiobiuret and its complexes*

Stephen & Townshend		This Work		Assignment (101)
Dithiobiuret	Ag^{I} Complex	Dithiobiuret	Cu^{I} Complex	
3000 s br	3230 s 3100 s	3350 to 3000 s br	3050 -3350 s br	(NH) stretching
1633 w 1613 p	1636 w sh 1603 m	1631 w 1612 s	1610 s br	NH_2 bending
1552 s br 1500 sh	1556 s 1527 w sh	1546 s	1572 s	(C=N) stretching
1492 s 1405 s	1480 m 1400 w sh	1480 m sh 1393 s 1333 vs	1471 vw 1399 m 1319 vs	(C=S) str.
1113 s	1113 s	1113 s	obscured by $SO_4^{=}$ ($\nu 3$)	(NH_2) rocking
		998 w	962 w	
		831 m		
786 m 744 s			799 w	Mostly C=S Some C=N
717 w	706 w	725 m	718 m	

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* s = strong, w = weak, m = medium, br = broad, sh = shoulder.

S-substituted compounds in which the reducing properties should be blocked. Some complexes of S-ethylguanylthiourea have been studied by Paigankar and Haldar (69) who found that it acted as a normal bidentate chelating agent with cobalt(II), nickel(II) and copper(II).

The fact that the reaction of guanylthiourea and chromium(III) results in the decomposition of a portion of the former without the formation of any stoichiometric complex, may be due at least partly to the instability of the unsubstituted thiol group. Thus a study of the reaction of an S-substituted guanylthiourea with chromium(III), and other metal ions, may be worthwhile.

5.6 EXPERIMENTAL

a. Preparation of the ligands

Guanylthiourea and dithiobiuret were prepared by the literature method (55). H_2S was passed into a hot aqueous solution of dicyandiamide for several hours. The required products were obtained from the resultant solution.

b. Preparation of Copper-Guanylthiourea Compound

An aqueous solution containing 2.5 gm. of cupric chloride hexahydrate was added to a vigorously stirred aqueous solution of 3.5 gm. of guanylthiourea. A brown gelatinous precipitate formed immediately. This was centrifuged, washed once with water then twice with alcohol and dried at room temperature. The dark brown residue which formed, was crushed to a yellowish-brown powder. The yield was approximately 1.5 gm. or 44%, based on the amount of cupric chloride.

The compound was analysed for copper, nitrogen and chlorine.

Found: Cu, 26.9, 26.7%; N, 30.8, 30.8%; Cl, 8.2%.

Calculated for: $Cu_2(C_2H_5N_4S)_2Cl.\frac{1}{2}C_2H_6N_4S$.

Cu, 27.8%; N, 30.7%; Cl, 7.8%.

Another preparation of the compound gave the following analyses: Cu, 27.0, 27.2%; N, 26.6, 26.8%.

The magnetic properties of the compound have been summarised in table 5.2 and the infrared spectrum is listed in table 5.6.

c. Preparation of Chromium-Guanylthiourea Adducts

The solid residue described in section 5 was prepared as follows: A solution of 0.9 gms. guanylthiourea and 0.3 gms. of $CrCl_3$ in 30 mls. of methanol was allowed to stand in a stoppered flask for three months. The pink-violet solution was then poured into 30 mls. of dioxan and a pink precipitate was immediately obtained. This was filtered, washed with dioxan and dried in the air at room temperature.

Analyses: Cr, 11.4%; C, 18.26%; H, 5.03%; N, 25.21%;
S, 9.80%; Cl, 10.52%.

As stated earlier, the material was formulated as $Cr_2(C_2H_5N_4S)_3(C_2H_4N_4)Cl_3.xCH_3OH$, ($x \approx 6$), $5H_2O$

d. Copper Dithiobiuret Complex

The complex was prepared by adding solution containing 0.83 gms. of cupric sulphate pentahydrate in 10 mls. of water to a solution of 0.90 gms. of dithiobiuret in 50 mls. of hot water. A yellow precipitate was obtained immediately. This was washed with water and dried in vacuo over silica gel.

Analyses: Found: Cu, 20.7, 20.9%; C, 11.53%; H, 2.74%; N, 19.86, 19.82%; S, 35.3% (total S).

Calculated for $Cu_2(C_2H_5N_3S_2)_3SO_4$: Cu, 20.2%; C, 11.47%; H, 2.40%; N, 20.04%; S, 36.4%.

$\chi_g = -0.45$ c.g.s. (Room Temperature).

Analyses:

The chromium-guanylthiourea compound was analysed by the Alfred Bernhardt Micronalytical Service at the Max Planck Institute, Mülheim, West Germany. All C and H analyses were also carried out by this service.

Copper: was determined by first decomposing the complexes with a 1:1 mixture of concentrated nitric and sulphuric acids then plating out the copper on a tared platinum cathode, by the usual method (Ref. 105, page 608).

Sulphur: Total sulphur was determined by oxidation of any organic sulphur to sulphate, with bromine and nitric acid. The sulphate was then determined gravimetrically (Ref. 105, page 467).

Physical Measurements were carried out as described in earlier chapters.

References

1. Ahrland, Chatt and Davies, Quart. Rev., 12, 265, (1958).
2. Angell, C.L. and Sheppard, N., Trans. Farad. Soc., 53, 589, (1957).
3. Baldwin, M.M., U.S. Pat., 2959515 (1960); C.A. 55, 16,900^{a} (1961).
4. Bandyapodhayay, D., J. Indian. Chem. Soc., 32, 651, (1955).
5. Banerjee, R.S. and Basu, S., J. Inorg. & Nuclear Chem., 27, 2452, (1965).
6. Banerjee, R.S. and Basu, S., ibid. 27, 353, (1965).
7. Banerjea, D., J. Indian Chem. Soc., 38, 642, (1961).
8. Banerjea, D. and Chakravarty, B., J. Inorg. & Nuclear Chem., 26, 1233, (1964).
9. Belcher, R. and Godbert, A.L., Semi-Micro Quantitative Organic Analysis, Longmans, Green and Co., page, 87, 1945.
10. Bellamy, L.J. and Williams, R.L., J. Chem. Soc., 1956, 2573.
11. Bertrand, J.A. and Carpenter, D.A., Inorg. Chem., 5, 514 (1966).
12. Biechler, Compt., Rend., 200, 141, (1935).
13. van Bronswyk, W. and Sheldon, J.C., Aust. J. Sci., 29, 475, (1967).
14. Carlin, R.L., in Transition Metal Chemistry, Vol. 1, R.L. Carlin ed., Edward Arnold Ltd., London, 1968 pp. 1-31.
15. Chakravorty, A. and Basu, S., J. Inorg. and Nuclear Chem., 17, 55, (1961).
16. Charles, R.G., J. Org. Chem. 22, 677, (1957).
17. Chatterjee, K.K., and Porter G.B., Inorg. Chem., 5, 860, (1966).
18. Colthup, N.B., Daly, L.H. and Wiberly, S.C., Introduction to Infrared Spectroscopy, Academic Press, N.Y., and London, 1964.
19. Cotton, F.A., Goodgame, D.M.L. and Goodgame, M., J. Am., Chem. Soc., 83, 4690, (1961).
20. Cotton, F.A. and Soderberg, R.H., ibid, 84, 872, (1962).

21. Cotton, F.A. and Soderberg, R.H., Inorg. Chem., 3, 5, (1964).

22. Cotton, F.A. and Wood, J.S., ibid, 3, 245, (1964).

23. Cramer, N., Ber., 34, 2594 (1901).

24. Curd, F.H.S., Crowther, A.F., Richardson, D.N. and Rose, F.L., J. Chem. Soc., 1948, 1630.

25. Curd, F.H.S., and Rose, F.L., Nature 158, 707, (1946).

25a. Day, P. and Robin, M.B., Advances in Inorganic Chem., and Radiochem., 10, 247, (1967).

26. Diamantis, A.A., Weigold, H. and West, B.O., J. Chem. Soc., 1967A, 1281.

27. Diana, G.D., Zalay, E.S. and Cutler, R.A., J. Org. Chem., 30, 298 (1965).

28. Dunn, T., in Modern Coordination Chemistry; Lewis, G. and Wilkins, R.G., ed., Interscience, page 289, 1960.

29. Dutta, R.L., J. Indian Chem. Soc., 37, 499, (1960).

30. Dutta, R.L., Sur, B., and Sengupta, N.R., ibid, 37, 565, 573, (1960).

31. Dutta, R.L. and Lahiry, S., ibid, 38, 689, (1961).

32. Dutta, R.L. and Lahiry, S., ibid, 40, 863, (1963).

33. Einstein, F.W. and Rodley, G.A., J. Inorg. and Nuclear Chem., 29, 347, (1967).

34. Everett, G.W. and Holm, R.H., J. Am. Chem. Soc., 87, 2117, (1965).

35. Everett, G.W. and Holm, R.H., ibid, 88, 2442, (1966).

36. Ferguson, J., J. Chem. Phys., 39, 116, (1963).

37. Figgis, B.N., Introduction to Ligand Fields; Interscience, 1966.

38. Figgis, B.N., Trans. Farad. Soc., 56, 1553, (1960).

39. Figgis, B.N. and Lewis, J., Progress in Inorg. Chem., 6, 192, (1964).

40. Figgis, B.N. and Nyholm, R.S., J. Chem. Soc., 1959, 331.

41. Figgis, B.N. and Nyholm, R.S., J. Chem. Soc., 1959, 338.

42. Foye, W.O., O'Laughlin, R.L. and Duvall, R.N., J. Pharm. Sci., 50, 641, (1961).

43. Freeman, H.C., Smith, J. and Taylor, J., Nature, 184, 707, (1959).

44. Freeman, H.C., Smith, J. and Taylor, J., Acta. Cryst., 14, 407, (1961).

45. Ghosh, S.P. and Chatterjee, A.K., J. Indian Chem. Soc., 32, 222, (1955).

46. Goodgame, D.M.L. and Goodgame, M., Inorg. Chem., 4, 139, (1965).

47. Hadzi, D., in Infrared Spectroscopy, Mansel Davies ed., Elsevier, page 244, 1963.

48. Hall, D. and Waters, T.N., J. Chem. Soc., 1960, 2644.

49. Hechenbleikner, J. and Kaiser, D.W., U.S. Pat. 2768205 (1956) C.A. 51, P16544h (1957).

50. Holm, R.H., J. Am. Chem. Soc., 83, 4683, (1961).

51. Holmes, O.G. and McClure, D.S., J. Chem. Phys., 26, 1686, (1957).

52. Jeffrey, Nature, 159, 1620, (1947).

53. Karipides, D. and Fernelius, W.C., Inorg. Syntheses, 7, 56, (1963).

54. Kurzer, F., Chem. Rev., 56, 95, (1956).

55. Kurzer, F., Organic Syntheses, 35, 70, (1955).

56. Lewis, J., Nyholm, R.S. and Smith, P.W., J. Chem. Soc., 1961, 4590.

57. Melson, G.A., ibid, 1967A, 669.

58. Melson, G.A. and McClellan, A.W., ibid, 1967A, 137.

59. Michelsen, K., Acta, Chem. Scand., 19, 1175, (1965).

60. Nakamoto, K., Fujita, J., Tanaka, S. and Kobayashi, M., J. Am. Chem. Soc., 79, 4904, (1957).

61. Nardelli, M., Cavalca and Fava, G., Acta. Cryst., 13, 594, (1960).

62. Nardelli, M. and Chierci, I., J. Chem. Soc., 1960, 1952.

63. Nardelli, M., Gava, G. and Giraldi, G., Acta. Cryst., 16, 343, (1963).

64. Nishikawa, H. and Yamada, S., Bull. Chem. Soc., Japan, 37, 8, (1964).

65. Nishikawa, H., Yamada, S. and Tsuchida, R., Z. Naturforsch, 17b, 78, (1962).

66. Orgel, L.E., J. Chem. Phys., 23, 1004, (1955).

67. Oxley, P. and Short, W.F., J. Chem. Soc., 1951, 1252.

68. Pachler, K. and Stackelberg, M., Z. anorg. u. allgem. Chem. 305, 286, (1960).

69. Paigankar, A. and Haldar, B.C., J. Indian Chem. Soc., 44, 175, (1967).

70. Pavkovic, S.F. and Meek, D.W., Inorg. Chem., 4, 20, (1965).

71. Penland, R.B., Mizushima, S., Curran, C. and Quagliano, J.V., J. Am. Chem. Soc., 79, 1575, (1957).

72. Pimentell, G.C. and McClellan, A.L., The Hydrogen Bond. Freeman and Co., page 67, 1960.

73. Poddar, S.N. and Ray, P., J. Indian Chem. Soc., 29, 279, (1952).

74. Powell, D.B. and Sheppard, N., Spectrochim. Acta., 17, 68, (1961).

75. Pratt, J.M. and Silverman, P.R., J. Chem. Soc., 1967A, 1286.

76. Rathke, Ber. 11, 967, (1878); 12, 774, (1879).

77. Ray, P., J. Indian Chem. Soc., 32, 141, (1955).

77a. Ray, P., Inorg. Syntheses, 6, 68, (1960).

78. Ray, P., Chem. Rev., 61, 313, (1961).

79. Ray, P. and Bandyopadhayay, G., J. Indian Chem. Soc., 29, 865, (1952).

80. Ray, P. and Chaudhury, A.K., ibid, 27, 673, (1950).

81. Ray, P. and Das Sarma, B., ibid, 26, 137, (1949).

82. Ray, P. and Dutta, R.L., ibid, 36, 499, (1959).

83. Ray, P. and Dutt, N.K., ibid, 20, 91, (1943).

84. Ray, P. and Ghosh, S.P., ibid, 20, 323, (1943).

85. Ray, P. and Ghosh, S.P., ibid, 20, 295, (1943).

86. Ray, P. and Saha, H., ibid, 14, 670, (1937).

87. Rodley, G.A. and Smith, P.W., J. Chem. Soc., 1967A, 1580.

88. Sacconi, L., Campidini, M., Maggio, F. and Cavasino, F.P., J. Am. Chem. Soc., 84, 3246, (1962).

89. Sen, D., Science and Culture (Calcutta), 28, 84, (1962).

90. Sen, D., ibid, 27, 502, (1961).

91. Sen, D., ibid, 27, 501, (1961).

92. Sen, D., ibid, 27, 548, (1961).

93. Sen, D., ibid, 28, 292, (1962).

94. Shepherd, N., in Hydrogen Bonding, ed., Hadzi, D., Pergamon Press, page 85, 1960.

95. Shirai, K. and Sugiro, K., J. Org. Chem., 25, 1045, (1960).

96. Sinha, A.I.P. and Ghosh, S.P., J. Indian Chem. Soc., 38, 179, (1961).

97. Sinha, A.I.P. and Ghosh, S.P., Science and Culture (Calcutta) 27, 313, (1961).

98. Slotta, K.H. and Tschesche, R., Ber. 62, 1390, (1929).

99. Smith, P.W. and Wedd, A.G., J. Chem. Soc., 1968A, in press.

100. Smolka, A. and Friedrich, A., Monatsh. Chem., 9, 227, (1888).

101. Stephen, W.I. and Townshend, A., J. Chem. Soc., 1966A, 166.

102. Svatos, G.F., Curran, C. and Quagliano, J.V., J. Am. Chem. Soc., 77, 6159, (1955).

103. Tanabe, Y. and Sugano, S., J. Phys. Soc. Japan, 9, 753, 766, (1954).

104. Trimble, R.H., Anal. Chem., 34, 1633, (1962).

105. Vogel, A.I., Text-Book of Quantitative Inorganic Analysis. 3rd Ed., Longmans, 1961.

106. Wallach, O., Ber. 32, 1872, (1899).

107. Watt, G.W. and Alexander, P.W., J. Am. Chem. Soc., 89, 1814, (1967).

108. Wedd, A.G., Honours Thesis, University of Tasmania, Page 123, 1964.

109. Weinberg, Ed., Cherwin, R. and Billman, J.H., J. Am. Pharm. Assoc., 49, 441, (1960).

110. Wellman, K.M. and Harris, D.L. Chem. Comm., 1967, 568.

111. West, B.O., J. Chem. Soc., 1962, 1374.