Inorganica Chimica Acta, 160 (1989) 183–188

Synthesis and Spectroscopic Studies of the Complexes of Biuret with Alkaline Earth Metal Halides

MARGARET GOODGAME* and IZHAR HUSSAIN

Chemistry Department, Imperial College of Science & Technology, London SW7 2AY (U.K.)

(Received November 7, 1988)

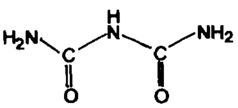
Abstract

The preparations are reported of the complexes $Mg(biuret)_2X_2$ (X = Cl or Br), $Mg[(biuret)_2(H_2O)_2]X_2$ (X = Cl or Br), $Ca(biuret)_2Cl_2$, $Ca(biuret)_4Br_2 \cdot 2H_2O$, $Ca(biuret)_4X_2$ (X = Cl or Br) and $Sr(biuret)_4Br_2$. The infrared spectra, between 4000–400 cm^{-1}, are recorded to distinguish the mode of coordination of biuret in these complexes. ESR spectra at both X- and Q-band are reported for manganese(II) ions doped in the lattices of these complexes, and the zero-field splitting parameters D and $\lambda(=E/D)$ are deduced. The D values observed for $Mg[(biuret)_2(H_2O)_2]X_2$ (X = Cl or Br) are consistent with the coordination of water molecules instead of halides. ESR spectra of the complexes, $Mg(biuret)_2X_2$ (X = Cl or Br) closely resemble those of analogous zinc complexes, which contain chelating biuret molecules. The IR spectrum shows monodentate coordination of biuret molecules in $Ca(biuret)_2Cl_2$ and the ESR spectrum is consistent with a *trans*-CaO_4Cl_2 chromophore, suggesting that the biuret is acting as a monodentate bridging ligand. For $Ca(biuret)_4X_2$ and $Sr(biuret)_4Br_2$ chelating ligands are present and the D values are very low, suggesting little distortion from cubic symmetry.

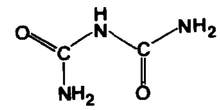
Introduction

Although the complexes formed by biuret with transition metals have been studied extensively [1–3], those of the main group metals have received little attention. Some predictions for the complex formation of biuret with alkali and alkaline earth metal ions, as derived from quantum chemical calculations within the LCGO-MO-SCF framework, have been reported [4] and the formation of these complexes in DMSO solutions has been studied by means of ^1H NMR spectroscopy and solubility data [5], but only one solid complex of biuret with strontium perchlorate has been reported [6].

The biuret molecule can adopt either the *cis*- or the *trans*-configuration (**IA** and **IB**). In the X-ray crystal structures of $Zn(biuret)_2Cl_2$ [7] and $Sr(biuret)_4(ClO_4)_2$ [6], biuret is bound to the metal as a bidentate ligand via two O atoms and is in the *cis*-configuration. The same type of coordination has been inferred from ESR spectroscopic data for Mn, Co and Ni complexes [2]. On the other hand, in the corresponding Cd and Hg complexes, biuret adopts the monodentate, *trans*-configuration with an intramolecular hydrogen bond and the same configuration has been found in the crystal of biuret hydrate [8].



1A



1B

Here, we report the preparation of several complexes of biuret with alkaline earth halides. The mode of coordination of biuret in these complexes has been established by IR, and their structures studied by the ESR spectra of Mn(II) doped complexes.

Experimental

Preparation of Complexes

Commercially available biuret was purified by recrystallization from ethanol. All other chemicals were of reagent grade and were used without further purification.

Bis(biuret)calcium(II) chloride and tetrakis(biuret)calcium(II) chloride

A warm solution of calcium chloride (0.555 g, 0.005 mol) in absolute ethanol (20 cm^3) was added to a warm solution of biuret (2.06 g, 0.02 mol) in ethanol (120 cm^3). The reaction mixture was refluxed for 3 h and the white precipitate thus formed was filtered off, washed with ethanol and dried *in vacuo* over P_2O_5. *Anal.* Found: C, 15.41; H, 3.16; N, 26.28. Calc. for $Ca(biuret)_2Cl_2$: C, 15.14; H, 3.15; N, 26.50%.

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

After filtering off the precipitated Ca(biuret)$_2$Cl$_2$, the filtrate was stored at room temperature. White crystals which formed were filtered off, washed with ethanol, and dried at 110 °C for 12 h. The crystals crumbled to a white powder. *Anal.* Found: C, 18.49; H, 4.20; N, 32.31; Cl, 13.54. Calc. for Ca(biuret)$_4$Cl$_2$: C, 18.36; H, 3.82; N, 32.12; Cl, 13.57%.

Drying at room temperature yielded a product with different, variable analysis, suggesting that the fresh crystals contain water or ethanol. The anhydrous product is extremely hygroscopic.

Tetrakis(biuret)calcium(II) bromide dihydrate

This complex was prepared by the method used for Ca(biuret)$_2$Cl$_2$. *Anal.* Found: C, 14.78; H, 3.45; N, 25.79. Calc. for Ca(biuret)$_4$Br$_2$·2H$_2$O: C, 14.82; H, 3.70; N, 25.92%.

Tetrakis(biuret)calcium(II) bromide

This complex was prepared by refluxing the hydrated complex in dry ethyl acetate for 24 h. *Anal.* Found: C, 15.63; H, 3.13; N, 27.25. Calc. for Ca(biuret)$_4$Br$_2$: C, 15.69; H, 3.27; N, 27.45%.

Bis(biuret)magnesium(II) chloride

Magnesium chloride hexahydrate (0.01 mol) was dehydrated in ethanol:2,2-dimethoxypropane and was mixed with a warm solution of biuret (0.02 mol) in ethanol. The reaction mixture was then refluxed for 24 h and the white precipitate thus formed was filtered off, washed with diethyl ether and dried *in vacuo* at room temperature.

This complex can also be prepared by heating the analogous hydrated complex at 120 °C for 24 h. *Anal.* Found: C, 15.63; H, 3.56; N, 27.03. Calc. for Mg(biuret)$_2$Cl$_2$: C, 15.93; H, 3.32; N, 27.88%.

Diaquobis(biuret)magnesium(II) chloride

A warm solution of MgCl$_2$·6H$_2$O (1.02 g, 0.005 mol) in absolute ethanol (20 cm^3) was added to a warm solution of biuret (2.06 g, 0.02 mol) in ethanol (120 cm^3). The reaction mixture was refluxed for 3 h, concentrated and allowed to cool overnight. The white precipitate thus formed was filtered off, washed with ethanol and dried over P$_2$O$_5$.

This complex can also be prepared by recrystallizing the anhydrous complex from water. *Anal.* Found: C, 14.55; H, 4.14; N, 24.87. Calc. for Mg[(biuret)$_2$(H$_2$O)$_2$]Cl$_2$: C, 14.23; H, 4.15; N, 24.90%.

Bis(biuret)magnesium(II) bromide

This complex was prepared by refluxing the stoichiometric quantities of MgBr$_2$·6H$_2$O and biuret in dry ethyl acetate for 72 h. The precipitate thus formed was washed thoroughly with diethyl ether and dried *in vacuo*. *Anal.* Found: C, 12.55; H, 2.66; N, 20.77. Calc. for Mg(biuret)$_2$Br$_2$: C, 12.30; H, 2.56; N, 21.52%.

Diaquobis(biuret)magnesium(II) bromide

This complex was prepared by the recrystallization of the anhydrous complex from water. *Anal.* Found: C, 11.08; H, 3.10; N, 18.83; Br, 37.35. Calc. for Mg[(biuret)$_2$(H$_2$O)$_2$]Br$_2$: C, 11.26; H, 3.28; N, 19.70; Br, 37.53%.

Tetrakis(biuret)strontium(II) bromide

Strontium bromide (1.24 g, 0.005 mol) and biuret (2.06 g, 0.02 mol) were dissolved in hot ethanol (120 cm^3), and the solution was refluxed for 3 h with constant stirring. It was then concentrated and allowed to stand overnight. The white precipitate thus formed was filtered off, washed with ethanol and dried *in vacuo* at 50 °C. *Anal.* Found: C, 14.76; H, 3.54; N, 25.24. Calc. for Sr(biuret)$_4$Br$_2$: C, 14.55; H, 3.03; N, 25.47%.

Analytical results were obtained by the Imperial College Microanalytical Laboratory.

Infrared spectra were obtained using a Perkin-Elmer 1720 Infrared Fourier Transform Spectrometer.

For the ESR study the normal doping level was 1% of manganese in all cases. ESR spectra were obtained as described previously [2], using polycrystalline samples at room temperature.

Results and Discussion

Infrared Spectra

Considerable differences can be expected between the infrared spectra of the *cis* and *trans* forms of biuret. The infrared spectra for both types of complex and their deuterated analogues have been reported and normal coordinate analyses have been carried out to assign the bands [3, 9]. For *cis*-biuret complexes, the presence of two carbonyl stretching absorptions very close together, along with the occurrence of the imide II band near 1500 cm^{-1}, clearly defines bidentate coordination. On the other hand, for the *trans*-biuret complexes, where biuret acts as a monodentate ligand, the presence of two well separated carbonyl stretching absorptions and the occurrence of the imide II band around 1580 cm^{-1} were observed and no band could be seen near 1500 cm^{-1}. The infrared spectra of monodentate biuret complexes are also closely parallel to that of uncomplexed biuret hydrate [10], which exists in the *trans*-configuration [8] shown to be present in these complexes.

The characteristic bands in the infrared spectra of all these complexes are given in Table 1, together with the frequencies reported for biuret hydrate, Cd(biuret)$_2$Cl$_2$ and Hg(biuret)$_2$Cl$_2$ [3, 10].

Most of these complexes contain biuret in the *cis*-configuration (IA). This can readily be seen by the presence of two carbonyl stretching bands close together, which is some cases appear as a single very

TABLE 1. Characteristic infrared spectral bands of biuret complexes

Compound	C=O stretching bands		Imide II band	Imide III band
Biuret hydrate	1745s	1718vs	1515m	1365s
$Cd(biuret)_2Cl_2$	1748s	1696vs	1579s	1352s
$Hg(biuret)_2Cl_2$	1739s	1693vs	1591s	1365s
$Ca(biuret)_2Cl_2$	1744s	1692vs	1585s	1348s
$Zn(biuret)_2Cl_2$		1699vs	1492s	1336s
$Mg(biuret)_2Cl_2$		1713vs	1505s	1338s
$Mg(biuret)_2Br_2$		1708vs	1501s	1339s
$Mg[(biuret)_2(H_2O)_2]Cl_2$	1744s	1713vs	1505s	1340s
$Mg[(biuret)_2(H_2O)_2]Br_2$	1707s	1694vs	1496s	1340s
$Ca(biuret)_4Cl_2$	1731s	1711s	1502s	1306s
$Ca(biuret)_4Br_2 \cdot 2H_2O$	1732s	1710sh	1501s	1305s
$Ca(biuret)_4Br_2$	1730s	1707s	1491s	1304s
$Sr(biuret)_4Br_2$	1725sh	1690vs	1495s	1327s

strong band, and the imide II band around 1500 cm^{-1}. On the other hand, the compound $Ca(biuret)_2Cl_2$ contains monodentate biuret which appears to be in the *trans*-configuration (**IB**). The appearance of two well separated carbonyl absorptions and imide II band around 1580 cm^{-1} in the spectrum of this complex is clearly consistent with this type of coordination. Further, the similarity of its spectrum to those of analogous Cd and Hg complexes [3] confirms that biuret in this complex exists in the *trans*-configuration, coordinating through one of the two carbonyl oxygens.

The criterion for the existence of bonding through oxygen in these complexes is the shifting of the carbonyl stretching frequencies, imide I_s(symmetric) and imide I_{as}(asymmetric) bands, towards the lower frequency side. All of these complexes show the decrease in the frequencies of carbonyl stretching bands confirming that the coordination of biuret with these metals is through carbonyl oxygens.

A band observed at 1740 cm^{-1} in the hydrated $MgCl_2$ complex disappeared on dehydration. An important feature, in the infrared spectra of $CaBr_2$ complexes, is the appearance of some extra bands, around 1540 and 1600 cm^{-1}, and the considerable decrease in the frequency of imide III band for which no explanation can be given.

Electron Spin Resonance Spectra

ESR spectra have been obtained at both X- and Q-band for manganese(II) ions doped at a nominal 1% into the lattices of compounds $Mg(biuret)_2X_2$ (X = Cl or Br), $Mg[(biuret)_2(H_2O)_2]X_2$ (X = Cl or Br), $Ca(biuret)_2Cl_2$ and $Ca(biuret)_4Br_2 \cdot 2H_2O$.

At X-band all the complexes gave very good quality but complicated spectra (Fig. 1) with considerable overlapping of transitions and detailed interpretation was difficult. Strong absorption near zero field was observed for the compounds $M(biuret)_2Cl_2$ (M = Mg or Ca), suggesting D values of about 0.1–0.2 cm^{-1}. The X-band spectrum of $Mg(biuret)_2Br_2$ was much simpler in form, with the main intensity near $g_{eff} = 6$, indicating a much higher value of D and a low but finite λ. The highest bands observed around 560 and 640 mT for $Mg[(biuret)_2(H_2O)_2]X_2$ (X = Cl or Br) respectively suggested D values of about 0.05–0.08 cm^{-1} for these complexes.

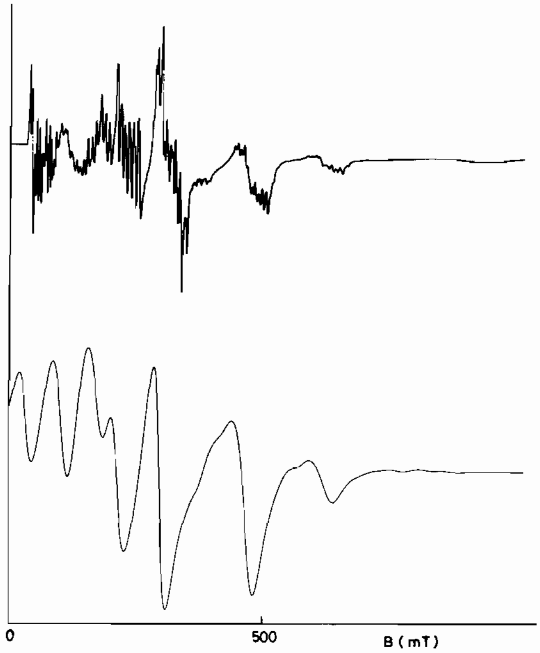


Fig. 1. X-band ESR spectrum of $Ca(Mn)(biuret)_2Cl_2$ and simulated spectrum for $D = 0.121$ cm^{-1}, $\lambda = 0.023$.

The better resolved Q-band spectra (Fig. 2) were, therefore, used to calculate the precise values of zero field splitting parameters D and $\lambda(=E/D)$, for the

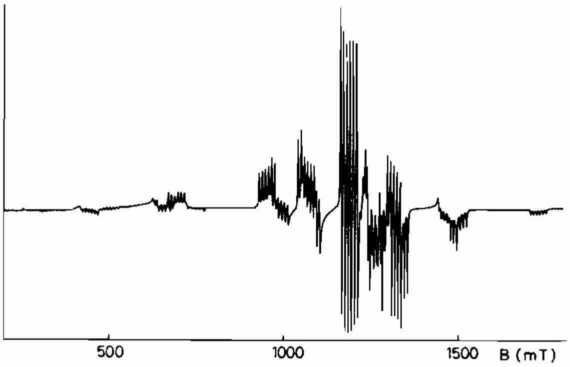


Fig. 2. Q-band ESR spectrum of Ca(Mn)(biuret)$_2$Cl$_2$.

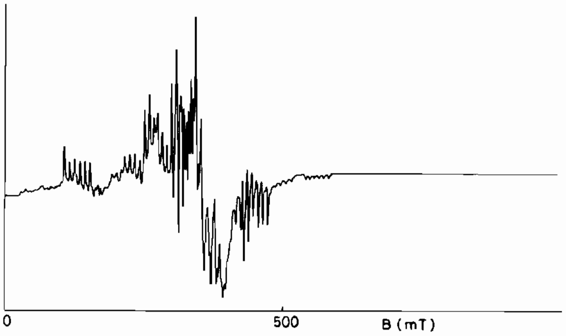


Fig. 3. X-band ESR spectrum of Mg(Mn)[(biuret)$_2$(H$_2$O)$_2$]-Cl$_2$.

individual compounds, in the spin Hamiltonian (1). Experimental resonance fields agreed well with those calculated, using the program ESRS [11], by exact diagonalization of the matrix derived from (1) with g_{iso} = 2.00. The results are given in Tables 2–4.

$$\mathcal{H} = g\beta BS + D(Sz^2 - 1/3S(S+1)) + E(Sx^2 - Sy^2) \quad (1)$$

Only for the complex Mg[(biuret)$_2$(H$_2$O)$_2$]Cl$_2$, was the D value small enough and the hyperfine splitting sufficiently well resolved, at X-band (Fig. 3), that the sign of D could be determined. The average spacing of the hyperfine components was greater for the lowest-field allowed transition than for the highest-field observed band and hence D is found to have negative sign. The intensity of the lowest-field allowed transition was considerably higher and it seems that this band has been mixed with spin-forbidden bands, mainly the 5–2 transition in the xz and yz planes, which always appears in this region.

The parameters obtained from the Q-band spectra were then used to simulate the X-band spectra using the program SHAPE 9 [12]. The agreement with experiment was good (Fig. 1).

Values of D and λ for all these complexes are listed in Table 5. The D values observed for Mg(Mn)-[(biuret)$_2$(H$_2$O)$_2$]X$_2$ (X = Cl or Br) are close to one

TABLE 2. Q-band ESR spectrum (mT) of Ca(Mn)(biuret)$_2$Cl$_2$

Observed (ν = 33.880 GHz)	Calculated for D = 0.121 cm^{-1}, λ = 0.023			
	B	*TP*	Field direction	Levels
274.9w				
281.8w				
441.9w	441.2	0.05	θ = 18°, ϕ = 00°	5--2
446.3w	446.7	0.07	θ = 19°, ϕ = 90°	5--2
503.0w				
Overlap	650.0	0.51	θ = 62°, ϕ = 00°	4--2
626–685w	664.8	0.51	θ = 63°, ϕ = 90°	4--2
692.6w/m	692.0	5.06	z	2--1
Region	746.3	0.32	θ = 16°, ϕ = 00°	5--3
725–774w	749.7	0.36	θ = 17°, ϕ = 90°	5--3
950.8m/s	950.9	4.00	y	6--5
	951.1	8.05	z	3--2
986.5m	987.5	3.96	x	6--5
1060.6m/s	1060.2	7.00	y	5--4
1077.3m/s	1076.1	6.97	x	5--4
1182.2s	1181.9	8.70	x	4--3
1183.6s	1184.6	8.69	y	4--3
	1210.2	9.02	z	4--3
1309.0s	1308.8	8.65	x	3--2
1328.3s	1328.2	8.60	y	3--2
1463.5w	1462.4	6.11	x	2--1
1469.8m	1469.4	7.97	z	5--4
1497.1m	1496.9	6.05	y	2--1
1728.2w	1728.6	4.96	z	6--5

TABLE 3. Q-band ESR spectrum (mT) of $Mg(Mn)[(biuret)_2(H_2O)_2]Cl_2$

Observed (ν = 33.995 GHz)	Calculated for D = 0.054 cm^{-1}, λ = 0.105			
	B	*TP*	Field direction	Levels
420w	420.5	0.02	$\theta = 40°, \phi = 90°$	5--2
	615.5	0.01	$\theta = 82°, \phi = 00°$	4--2
637w	638.0	0.04	$\theta = 77°, \phi = 90°$	4--2
664w				
985w/m	983.2	5.11	z	6--5
1065w	1064.9	4.58	y	2--1
1102m	1098.6	8.09	z	5--4
	1136.0	7.62	y	3--2
1139m/s	1138.8	4.49	x	2--1
1170m/s	1170.9	7.55	x	3--2
1208s	1207.7	8.94	x	4--3
1210s	1210.0	8.94	y	4--3
1215s	1214.1	9.02	z	4--3
1250m	1249.5	8.39	x	5--4
1286m	1287.3	8.30	y	5--4
	1296.7	5.54	x	6--5
1329m	1329.8	7.93	z	3--2
1370w	1368.3	5.43	y	6--5
1445w	1445.8	4.91	z	2--1

TABLE 4. Q-band ESR spectrum (mT) of $Mg(Mn)(biuret)_2Cl_2$

Observed (ν = 33.870 GHz)	Calculated for D = 0.194 cm^{-1}, λ = 0.079			
	B	*TP*	Field direction	Levels
245.4w				
249.6w				
Region of overlap	381.6	5.33	z	2--1
	425.5	0.51	$\theta = 23°, \phi = 00°$	5--2
470.6w/m	470.4	0.69	$\theta = 28°, \phi = 90°$	5--2
660.9w	661.4	1.47	$\theta = 55°, \phi = 00°$	4--2
747.4m	746.6	3.51	y	6--5
	754.1	1.28	$\theta = 61°, \phi = 90°$	4--2
796.9w	795.1	8.35	z	3--2
943.4m/s	939.9	6.33	y	5--4
	946.3	3.37	x	6--5
1016.5m/s	1016.5	6.25	x	5--4
1129.6s	1130.7	8.28	x	4--3
1156.7s	1157.3	8.19	y	4--3
1209.8s	1208.8	9.16	z	4--3
1299.0s	1299.9	8.86	x	3--2
1412.4m/s	1412.5	8.59	y	3--2
	1554.6	6.90	x	2--1
1623.6m	1623.7	7.91	z	5--4
1740.2w	1740.7	6.55	y	2--1
	2041.3	4.77	z	6--5

another, but very different from those of the analogous anhydrous complexes. The low values of D for these hydrated complexes are consistent with a coordination sphere of six oxygens and suggest the formulation of these compounds as dihydrates, with water molecules replacing the halide ions in the coordination sphere.

The negative sign for D suggests the presence of a compressed octahedron around the metal ion. This is consistent with the previously observed [1] weakness of biuret as a ligand.

Further, for $Mg(Mn)(biuret)_2X_2$ (X = Cl or Br) the values of zero field splitting parameters D and λ are similar to the values previously found for manganese-

TABLE 5. ZFS parameter of Mn(II) in biuret complexes

Complex	D (cm^{-1})	λ
Mg(biuret)$_2$Cl$_2$	0.194	0.079
Mg(biuret)$_2$Br$_2$	0.491	0.015
Mg[(biuret)$_2$(H$_2$O)$_2$]Cl$_2$	−0.054	0.105
Mg[(biuret)$_2$(H$_2$O)$_2$]Br$_2$	−0.074[a]	0.180
Ca(biuret)$_2$Cl$_2$	0.121	0.023
Ca(biuret)$_4$Cl$_2$	0.042	0.240
Ca(biuret)$_4$Br$_2$·2H$_2$O	0.035	0.290
Sr(biuret)$_4$Br$_2$	<0.020[b]	

[a]Negative sign assumed by analogy with chloride. [b]Too small to evaluate.

(II) ions in the analogous zinc complexes [2]. It suggests that, as with zinc, these complexes have a distorted octahedral structure, with each metal ion surrounded by four oxygen atoms, from two chelating biuret molecules, and halides occupying the *trans* positions.

The observed D and λ values for Ca(Mn)(biuret)$_2$-Cl$_2$ are consistent with a *trans*-CaO$_4$Cl$_2$ chromophore. The lower D value, compared with that of Mg(Mn)-(biuret)$_2$Cl$_2$, is in line with the usual observation that D decreases as the size of the host ion increases. If the complex contained a CaO$_2$Cl$_4$ chromophore, with bridging chlorides, a D value lower than about 0.08 cm^{-1}, as found for Cd(biuret)$_2$Cl$_2$, would be expected. In view of the infrared results (*vide supra*) it seems that in this complex, as in the analogous mercury complex, biuret may be acting as a monodentate bridging ligand and coordinating, through one of the two carbonyl oxygens, with two Ca atoms.

In contrast to magnesium, calcium and strontium form complexes of the type M(biuret)$_4$X$_2$. Manganese(II) ions in these complexes give very low D values but high λ. Since the infrared spectra show chelating biuret, it seems likely that the structures are similar to that of Sr(biuret)$_4$(ClO$_4$)$_2$, which has an eight-coordinate structure with little distortion.

Acknowledgements

We thank the Government of Pakistan for a Scholarship and the University of Baluchistan for leave of absence (to I.H.). We thank Dr J. F. Gibson for the use of computer programs.

References

1 A. W. McLellan and G. A. Melson, *J. Chem. Soc. A*, (1967) 137.
2 M. Goodgame, I. Hussain and J. N. Okey, *Polyhedron*, *7* (1988) 1869.
3 Y. Saito, K. Machida and T. Uno, *Spectrochim. Acta, 26*, (1970) 2089.
4 B. M. Rode and K. H. Gstrein, *J. Chem. Soc., Faraday Trans. II*, (1978) 889.
5 K. H. Gstrein and B. M. Rode, *Inorg. Chim. Acta, 33*, (1978) 1.
6 S. Haddad and P. S. Gentile, *Inorg. Chim. Acta, 12* (1975) 131.
7 M. Nardelli, G. Fava and G. Giraldi, *Acta Crystallogr., 16* (1963) 343.
8 E. W. Hughes, H. L. Yakel and H. C. Freeman, *Acta Crystallogr., 14* (1961) 345.
9 B. B. Kedzia, P. X. Armendarez and K. Nakamoto, *J. Inorg. Nucl. Chem., 30* (1968) 849.
10 T. Uno, K. Machida and Y. Saito, *Bull. Chem. Soc. Jpn., 42* (1969) 1539.
11 D. Vivian and J. F. Gibson, *J. Chem. Soc., Faraday Trans. II*, (1975) 1640.
12 J. F. Gibson and G. M. Lack, unpublished work.