Inorganica Chimica Acta, *73* (1983) 153–158

Copper(II) Complexes with Some 3-Amino-1-propanols

T. LINDGREN, R. SILLANPÄÄ, T. NORTIA and K. PIHLAJA

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50, Finland

Received February 23, 1983

Eight copper(II) chloride and bromide complexes with 3-amino-1-propanol and its methyl derivatives were prepared and characterized. In all cases the molar ratio of copper to aminoalcohol was 1:1. 3-Amino-1-propanol, 3-amino-2-methyl-1-propanol and erythro- and threo-4-amino-2-pentanol were used for complexation. The UV and VIS (50000–10 000 cm^{-1}) and IR spectra (4000–100 cm^{-1}) of the copper(II) complexes were measured.

The elemental analyses and spectral data suggest that aminoalcohols act as monoanionic, bidentate ligands. Furthermore, the complexes seem to be alkoxobridged square-planar dimers with terminal halogen atoms.

Introduction

The coordination chemistry of aminoalcohols and metal cations has received increasing attention recently. The chelates of aminoalcohols play important roles in nature, for example in the hormones adrenaline and noradrenaline and in the aminopolysaccharides [1].

In this study some 3-amino-1-propanols have been chosen as ligands and copper(II) in the form of chloride or bromide salt as the metal ion. In the literature there is not much information about the copper(II) complexes of 3-amino-1-propanols [2–4]. Much more widely studied are the corresponding complexes of 2-amino-1-propanols which gives us the possibility to compare the ethanolamine copper(II) complexes with those of propanolamine. The X-ray diffraction studies of the ethanolamine complexes reveal that they form an oxygen-bridged structure [2, 5–14]. The complexes are of the $[Cu(OCH_2CH_2NR_2)X]_n$ type, where X = Cl, Br, I, NCS or NCO and R = H, Me, Et, noPr or n-Bu. The complexes are dimers (n = 2) [2, 5, 7–10], tetramers (n = 4) [5, 9, 11–13] and polymers (n = ∞) [5, 6, 14]. The 2-amino-1-propanols and copper(II) ions form five-membered chelate rings whereas the 3-amino-1-propanols form six-membered chelate rings with copper(II) ion [2].

Experimental

Preparation of Ligands

3-Amino-1-propanol was a commercial product from Fluka A.G. (*purum*). 3-Amino-2-methyl-1-propanol was prepared from the ethyl ester of 2-cyanopropionic acid [15] by lithiumaluminiumhydride reduction. This aminoalcohol was boiling at 353 K/1.2 kPa. 4-Amino-2-pentanol was prepared by known methods [16, 17] and its diastereomers were separated by distillation [18].

Preparation of Complexes

The complexes were prepared by a modification of the method of Hein and Beerstecher [19] as follows: the ligand (0.002–0.005 mol) was dissolved in 40 ml absolute ethanol and 1 ml of trimethyl orthoformate was added to remove any water. The mixture was heated to 323 K. To this solution 20 ml warm ethanolic solution of copper(II) chloride or bromide containing 1 ml of trimethyl orthoformate was added dropwise during 30–60 minutes with continous stirring. The final copper–ligand ratio in the solution was 1:2.

The complex was precipitated during the addition of the copper salt. The mixture was allowed to cool to room temperature and the complex was separated by filtration, washed with dry ether, and allowed to dry in desiccator. The complexes of erythro-4-amino-2-pentanol were bluish; all the other complexes were green in colour.

From the literature [19] and from our own experience the complexes are formed according to eqn. 1:

$$2CuX_2 + 4aOH \longrightarrow [Cu(aO)X]_2\downarrow + 2aOH{\cdot}HX \qquad (1)$$

where X = Br, Cl and aOH = aminoalcohol

In the special case of a diastereomeric mixture of erythro- and threo-4-amino-2-pentanols we found that Cu(II) halide reacts preferably with threo-4-amino-2-pentanol. Eqn. 1 can so be written as eqn. 2:

0020-1693/83/$3.00

TABLE I. Elemental Analyses of the Prepared Copper(II) Complexes.[a]

Complexes	Cu %		Cl, Br %	
	found	calc.	found	calc.
$[Cu(ap)Cl]_2$	36.9	36.7	20.7	20.5
$[Cu(ap)Br]_2$	29.0	29.2	36.4	36.7
$[Cu(2\text{-}Me\text{-}ap)Cl]_2$	34.0	34.0	18.6	18.9
$[Cu(2\text{-}Me\text{-}ap)Br]_2$	27.2	27.4	34.2	34.5
$[Cu(1,3\text{-}diMe\text{-}ap)Cl]_2$[b]	31.6	31.6	17.2	17.6
$[Cu(1,3\text{-}diMe\text{-}ap)Br]_2$[b]	25.7	25.9	32.2	32.5
$[Cu(erythro\text{-}1,3\text{-}diMe\text{-}ap)Cl]_2$	31.4	31.6	17.2	17.6
$[Cu(erythro\text{-}1,3\text{-}diMe\text{-}ap)Br]_2$	26.0	25.9	32.6	32.5
$[Cu(threo\text{-}1,3\text{-}diMe\text{-}ap)Cl]_2$	31.6	31.6	17.6	17.6
$[Cu(threo\text{-}1,3\text{-}diMe\text{-}ap)Br]_2$	26.1	25.9	32.4	32.5

[a] ap = OH-deprotonated 3-amino-1-propanol. [b] Made from a mixture of the diastereomeric diols.

TABLE II. The UV–VIS Absorption Spectral Data of the Prepared Copper(II) Complexes.

Complexes	Band maxima/nm (cm^{-1})	
	solid state	in CH_2Cl_2
$[Cu(ap)Cl]_2$	263 (38000)	260 (38500)
		318 (31500)
	390 (25600)	375 (26700)
	623 (16000)	630 (15900)
$[Cu(ap)Br]_2$	263 (38000)	274 (36500)
		330 (30300)
	397 (25200)	392 (25500)
	624 (16000)	630 (15900)
$[Cu(2\text{-}Me\text{-}ap)Cl]_2$	265 (37700)	263 (38000)
		312 (32000)
	389 (25700)	377 (26500)
	637 (15700)	650 (15400)
$[Cu(2\text{-}Me\text{-}ap)Br]_2$	265 (37700)	274 (36500)
		328 (30500)
	397 (25200)	392 (25500)
	643 (15600)	625 (16000)
$[Cu(threo\text{-}1,3\text{-}diMe\text{-}ap)Cl]_2$	272 (36800)	264 (37900)
		312 (32000)
	401 (24900)	408 (24500)
	643 (15600)	637 (15700)
$[Cu(threo\text{-}1,3\text{-}diMe\text{-}ap)Br]_2$	268 (37300)	280 (35700)
		330 (30300)
	395 (25300)	400 (25000)
	645 (15500)	641 (15600)
$[Cu(erythro\text{-}1,3\text{-}diMe\text{-}ap)Cl]_2$	261 (38300)	260 (38400)

(continued on facing page)

TABLE II. *(continued)*

Complexes	Band maxima/nm (cm^{-1})	
	solid state	in CH_2Cl_2
		317 (31500)
	370 (27000)	377 (26500)
	672 (14900)	680 (14700)
$[Cu(erythro\text{-}1,3\text{-}diMe\text{-}ap)Br]_2$	264 (37900)	276 (36200)
		334 (29900)
	390 (25600)	398 (25100)
	682 (14700)	649 (15400)

$$2CuX_2 + 2e\text{-}aOH + 2t\text{-}aOH \longrightarrow [Cu(t\text{-}aO)X]_2\downarrow + 2e\text{-}aOH\cdot HX \qquad (2)$$

where X = Br, Cl and e-aoH = erythro-4-amino-2-pentanol, t-aOH = threo-4-amino-2-pentanol.

Analysis

The amount of copper in the complexes was determined electrolytically [20] or by complexometric titration [21]. The chloride and bromide were determined gravimetrically [22]. The results of the elemental analyses are shown in Table I.

Physical Methods

IR spectra were measured with a Perkin Elmer 180 Grating Infrared spectrophotometer either from KBr pellets or with Nujol or hexachlorobutadiene mull techniques at 4000–400 cm^{-1}. The FIR spectra were measured from polyethylene pellets. UV and VIS spectra were measured with a Cary 17 D spectrophotometer in CH_2Cl_2 and the solid state UV and VIS spectra from KBr pellets.

Results and Discussion

The complexes are sparingly soluble in all common organic solvents. Elemental analyses indicate that the complexes have the formula of $[Cu(aO)X]_n$, where aO is deprotonated aminoalcohol and X is Cl or Br.

UV–VIS Spectra

The UV–VIS absorption spectral data of the prepared compounds are presented in Table II.

The band with the smallest energy in the region 14700–16000 cm^{-1} (with molar absorptivity in the range 70–125 l mol^{-1} cm^{-1}) is due to the d–d transitions. Tetrahedral complexes of Cu(II) ion do not absorb in the 10000–20000 cm^{-1} region [23]. Thus we can rule out the possibility of tetrahedral geometry. Regular octahedral complexes of copper(II) are very few due to very strong Jahn–Teller effect. The elongated distortion in octahedral copper(II) complexes makes the structure progressively more square-planar with increasing distortion. If the structure of copper(II) complex is a regular octahedron then the d–d spectrum exhibits only one band. Elongated octahedral distortion however splits this band to 2–4 bands, which may appear in the form of one very broad asymmetric band. The center of this broad band is then moving to higher energy according to the degree of distortion [23–25]. The band maxima observed for our complexes fall in the region 14700–16000 cm^{-1} and we thus conclude from these values that the complexes have nearly square-planar structure.

The second absorption band for these complexes is found in the region 24500–27000 cm^{-1}. This absorption band suggests that the complexes have an alkoxo-bridged binuclear structure and the absorption is attributed to charge transfer transitions from nonbonding orbitals of bridging oxygen atoms to the vacant copper d-orbitals [26–32]. In all the spectra which are measured in CH_2Cl_2 this near-ultraviolet absorption band is rather strong, while the solid state absorption band is very weak or is seen only as a shoulder in the spectra. A similar behaviour has been found in some other oxygen-bridged copper(II) complexes [26–29, 32]. The explanation why the complexes do not show a distinct absorption band in this region in the solid state spectra is that the dimeric complexes are as tetramers or polymers in the solid state. In the tetramer case the bridging oxygens do have only one nonbonding orbital and in the polymer case there are no non-bonding orbitals. Thus the charge transfer band in the region 25000–26000 cm^{-1} in the former case is weak and in the latter case non-existent [29]. Hence we can conclude that the complexes are dimers in solution but tetramers or polymers in the solid state.

TABLE III. Important Infrared Frequency (cm^{-1}) Assignments for Copper(II) Complexes of 3-Amino-1-propanols.

	ν(OH)	ν_{as}(NH)	ν_s(NH)	$\delta(NH_2)$
Free ligands (liquid state)	~3350	3290–80	~3180	1600–1590
Complexes (solid state)				
$[Cu(ap)Cl]_2$		3280	3240, 3145	1580
$[Cu(ap)Br]_2$		3280	3240–20, 3160–20	1610–1570
$[Cu(2\text{-Me-ap})Cl]_2$		3300	3240, 3150	1575
$[Cu(2\text{-Me-ap})Br]_2$		3285	3230, 3140	1575
$[Cu(threo\text{-}1,3\text{-diMe-ap})Cl]_2$		3280	3220, 3140	1585
$[Cu(threo\text{-}1,3\text{-diMe-ap})Br]_2$		3280	3215, 3135	1580
$[Cu(erythro\text{-}1,3\text{-diMe-ap})Cl]_2$		3230	3220, 3140	1595
$[Cu(erythro\text{-}1,3\text{-diMe-ap})Br]_2$		3235	3205, 3135	1590

The third strong band in the spectra measured in solution or in the solid state is found in the region 35700–38500 cm^{-1}. In the literature there is not much information concerning the spectra of these complexes or of this kind of compound in this region. The chlorocomplexes of copper(II) have been investigated in the solutions of N,N-dimethylformamide [33] and water [34]. The UV absorption maximum of $CuCl^+$ is in the 38000–40000 cm^{-1} region. From the above we conclude that the band is due to charge transfer from chloride or bromide ion to the copper ion.

There is one more band in the solution spectra of the complexes which is found in the region 29900–32000 cm^{-1}. The same band exists in the solid spectra as a small shoulder. This could be a normal charge transfer band (probably oxygen or nitrogen → Cu(II) charge transfer excitation) but another interesting possibility is a double excitation of a simultaneous pair (SPE) [31, 15, 36] in coupled Cu(II) systems. This kind of absorption has, however, not yet been proven for Cu^{2+}–Cu^{2+} interaction.

From the solution spectra we can see that the maxima of halogen–copper charge transfer bands are moving to lower energy when the chloride ion is changed to the bromide ion. These band shifts are in accordance with the reducing character of the chloride and bromide ions. In the spectrochemical series the order of bromide and chloride ions is Br < Cl but its influence on the d–d bands is in the present case scarcely notable. From the solid state spectra we cannot compare the halogen–copper charge transfer band maxima of the corresponding chloro- and bromocomplexes because they can be dimers, tetramers or even polymers and hence their structures can differ from each other.

Infrared Spectra

The important IR frequencies of the ligands and the complexes are shown in Table III. The most important difference between the spectra of aminoalcohols and their copper(II) complexes can be found in the region of 3500–3000 cm^{-1}. When going from the free aminoalcohols to the complexes the stretching vibration ν_{OH} disappears, pointing out that the OH group of the aminoalcohol has been deprotonated on coordination to the copper atom.

All of the complexes have three bands in this region. Theoretically only two bands would be expected from asymmetric and symmetric stretching of the $-NH_2$ group. The splitting could be due to a Fermi resonance interaction between the symmetric stretching mode and the overtone of the deformation mode of the NH_2 occurring at about 1600 cm^{-1} (Table III) [37, 38].

In the chelates the NH_2 bending vibration gives a medium to strong band which is shifted to lower frequencies from the band of the free aminoalcohols. This suggests that the amino group is also coordinated to the copper atom. The C–H stretching bands occur in the region 3000–2800 cm^{-1} and are strong sharp peaks. The C–C, C–N and C–O stretching vibrations occur between 1200–800 cm^{-1}. It is impossible to give exact assignments for them.

The IR spectra of the complexes of erythro- and threo-4-amino-2-pentanols differ markedly from each other in accordance with the different structures of these aminoalcohols. Also the FIR spectra (see Fig. 1) confirm the structural differences. Figure 1 shows also that when synthesizing a complex from the mixture of erythro- and threo-4-amino-2-pentanols we actually got the complex corresponding to the pure threo form. This means that the threo form of 4-amino-2-pentanol is reacting faster than the erythro form or the threo complex is more stable than the erythro complex.

When we compare the spectra of the corresponding chloro- and bromocomplexes we can see that there are no remarkable differences in the frequencies

TABLE IV. Selected FIR Spectral Frequencies (cm^{-1}) and Their Assignments of the Prepared Copper(II) Complexes.

Complexes	ν(Cu–O) + ligand	ν(Cu–N)	ν(Cu–Cl)	ν(Cu–Br)	ν(Cu–Br)/ν(Cu–Cl)
[Cu(ap)Cl]$_2$	487, 450	370–350	258		0.71
[Cu(ap)Br]$_2$	490, 445	370–350		180	
[Cu(2-Me-ap)Cl]$_2$	517	410	241		0.73
[Cu(2-Me-ap)Br]$_2$	516	408		177	
[Cu(threo-1,3-diMe-ap)Cl]$_2$	494	390, 345	238		0.75
[Cu(threo-1,3-diMe-ap)Br]$_2$	490	388, 342		179	
[Cu(erythro-1,3-diMe-ap)Cl]$_2$	498	406	260		0.69
[Cu(erythro-1,3-diMe-ap)Br]$_2$	495	402		180	

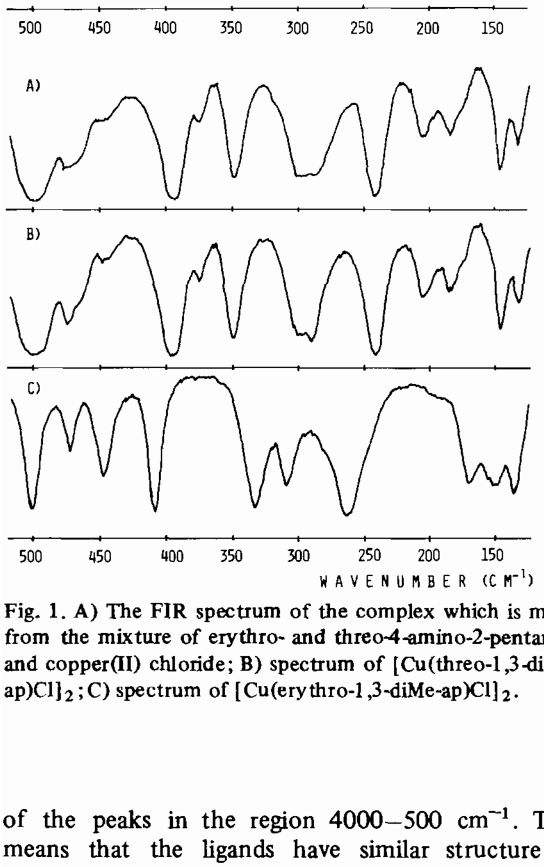

Fig. 1. A) The FIR spectrum of the complex which is made from the mixture of erythro- and threo-4-amino-2-pentanols and copper(II) chloride; B) spectrum of [Cu(threo-1,3-diMe-ap)Cl]$_2$; C) spectrum of [Cu(erythro-1,3-diMe-ap)Cl]$_2$.

of the peaks in the region 4000–500 cm^{-1}. This means that the ligands have similar structure in both chloro- and bromocomplexes.

The most important frequencies of the FIR spectra of the complexes are listed in Table IV. The ligands have no strong absorption in this region, so the frequencies of this region are mainly due to metal–ligand vibrations. The metal–ligand vibrations are unlikely to be pure, because the skeletal vibrations of the chelates are coupling with these vibrations [23, 39, 40]. The assignments of the FIR spectra for these complexes are based on comparison with the spectra of related complexes which have absorption bands in this region. In all the spectra of these complexes there are two rather strong absorption bands in the region 500–450 cm^{-1}, the stronger being near to 500 cm^{-1}. In two cases both of the bands are equally strong (see Table IV). We assign these bands to the ν(Cu–O) vibrations coupled with ligand vibrations. According to Thornton *et al.* [41, 42] the ν(Cu–O) vibration normally exists around 400 cm^{-1} but in the square planar coordination (as we suggest our complexes have) a high-frequency shift results from the lower coordination number and the associated Jahn–Teller stabilization of the Cu–O bonds. Also around 300 cm^{-1} there are several absorption bands in these complexes and some of them are probably pure ν(Cu–O) vibrations [23, 43]. These are not shown in Table IV because we are not able to assign them. The ν(Cu–N) vibrations of several compounds are around 400 cm^{-1}. For example the ν(Cu–N) vibration of the copper(II) complex of ethylenediamine is about 405–380 cm^{-1}. These have been assigned with N-deuteration [44] or by using the ^{65}Cu isotopes [45]. Therefore we assign the vibrations in the region 400–350 cm^{-1} to the ν(Cu–N) vibrations.

The most readily identifiable are the copper–halogen stretching vibrations because of the shift which occurs in their frequencies when the spectra of chlorides and bromides are compared. Moreover these shifts have been found with ratios Cu–Cl/Cu–Br ~0.77 in various compounds [46]. The ν(Cu–Cl) occurs in the region 260–240 cm^{-1} and the ν(Cu–Br) vibration in the region 180–177 cm^{-1}. The ν(Cu–Cl) absorption band is probably due to the terminal chloride atom. If the chloride atom were bridging between two copper atoms, the absorption band would be at a lower frequency [47]. In the same way we conclude that the ν(Cu–Br) absorption band is due to a terminal bromide atom. From the FIR spectra of the complexes we can see that the structures of the corresponding chloro- and bromocomplexes are equal.

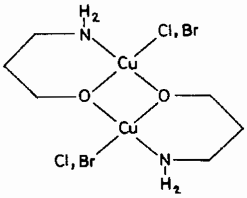

Fig. 2. The basic structural unit of the complexes.

Conclusions

The studied complexes have a 1:1 stoichiometry and the spectral data indicate that the aminoalcohols coordinate to the copper atom as monoanionic, bidentate ligands. Furthermore, the oxygen atoms act as bridging atoms between two copper atoms, and the coordination number of the copper atom is four and the structure of complexes is square planar. The halogen atoms of the complexes are terminal. Thus the basic structural unit of the complexes is the dimer $[Cu(aO)X]_2$ shown in Fig. 2.

When the synthesis of the chelate is carried out from a mixture of the diastereomeric 4-amino-2-pentanols only a chelate from the threo isomer is obtained. This offers a new possibility for separating the isomeric 4-amino-2-pentanols.

Acknowledgements

We thank the Emil Aaltonen Foundation (T.L.) for financial support.

References

1 C. J. Hawkins and J. A. Palmer, *Austral. J. Chem., 31,* 1689 (1978).
2 J. A. Bertrand and P. G. Eller, *Progr. Inorg. Chem., 21,* 29 (1976).
3 B. Kirson, *Bull. Soc. Chim. France,* 223 (1958).
4 M. Brezeanu and I. Jitaru, *Rev. Roumaine Chim., 18,* 2039 (1973).
5 R. Mergehenn and W. Haase, *Acta Cryst., B33,* 1877 (1977).
6 A. Pajunen and K. Smolander, *Finn. Chem. Lett.,* 99 (1974).
7 A. Pajunen and M. Lehtonen, *Suomen Kemistilehti, B44,* 200 (1971).
8 W. Haase, *Chem. Ber., 106,* 3132 (1973).
9 L. Merz and W. Haase, *Acta Cryst., B34,* 2128 (1978).
10 K. Smolander, *Acta Chem. Scand., A35,* 815 (1981).
11 R. Mergehenn and W. Haase, *Acta Cryst., B33,* 2734 (1977).
12 L. Merz and W. Haase, *J. Chem. Soc. Dalton,* 1594 (1978).
13 E. D. Estes and D. J. Hodgson, *Inorg. Chem., 14,* 334 (1975).
14 M. Mikuriya, Y. Nishida, S. Kida, T. Uechi and I. Ueda, *Acta Cryst., B33,* 538 (1977).
15 K. Freudenberg, *Chem. Ber., 63,* 2380 (1930).
16 G. T. Morgan and H. Burgess, *J. Chem. Soc., 119,* 697 (1921).
17 J. Sicher, M. Pankova, J. Jonas and M. Svoboda, *Coll. Czech. Chem. Commun., 24,* 2727 (1959).
18 D. W. White, D. E. Gibbs and J. G. Verkade, *J. Am. Chem. Soc., 101,* 1937 (1979).
19 F. Hein and W. Beerstecher, *Z. anorg. allg. Chem., 282,* 93 (1955).
20 W. D. Treadwell, 'Tabellar und Vorschriften zur Quantitativen Analyse', Franz Deuticke, Leipzig und Wien, 1938, p. 107.
21 G. Schwarzenbach, 'Die Komplexometrische Titration', Ferdinand Enke, Stuttgart, 1963, p. 73.
22 J. S. Fritz and G. H. Schenk, Jr., 'Quantitative Analytical Chemistry', Allyn and Bacon, Boston, 1969, p. 505.
23 V. H. Kulkarni and B. K. Prabhakar, *J. Mol. Struct., 78,* 77 (1982).
24 B. J. Hathaway, *J. Chem. Soc. Dalton,* 1196 (1972).
25 D. Forster and D. M. L. Goodgame, *J. Am. Chem. Soc.,* 2790 (1964).
26 E. Uhlig and K. Staiger, *Z. anorg. allg. Chem., 346,* 21 (1966).
27 E. Uhlig and K. Staiger, *Z. anorg. allg. Chem., 360,* 39 (1968).
28 Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem., 38,* 451 (1976).
29 Y. Nishida, F. Numata and S. Kida, *Inorg. Chim. Acta, 11,* 189 (1974).
30 M. Mikuriya, H. Okawa and S. Kida, *Bull. Chem. Soc. Japan, 53,* 3717 (1980).
31 S. Kida, Y. Nishida and M. Sakamoto, *Bull. Chem. Soc. Japan, 46,* 2428 (1973).
32 Y. Ishimura, Y. Nonaka, Y. Nishida and S. Kida, *Bull. Chem. Soc. Japan, 46,* 3728 (1973).
33 M. Elleb, J. Meullemeestre, M-J. Schwing-Weill and F. Vierling, *Inorg. Chem., 19,* 2699 (1980).
34 M. A. Khan and M-J. Schwing-Weill, *Inorg. Chem., 15,* 2202 (1976).
35 J. A. Larrabee, T. G. Spiro, N. S; Ferris, W. H. Woodruff, W. A. Maltese and M. S. Kerr, *J. Am. Chem. Soc., 99,* 1979 (1977).
36 H. J. Schugar, E. I. Solomon, W. L. Cleveland and L. Goodman, *J. Am. Chem. Soc., 97,* 6442 (1975).
37 T. G. Appleton and J. R. Hall, *Inorg. Chem., 9,* 1800 (1970).
38 G. W. Watt, B. B. Hutchinson and D. S. Klett, *J. Am. Chem. Soc., 89,* 2007 (1967).
39 G. C. Percy, *Spectrochim. Acta, A32,* 1287 (1976).
40 C. Engelter, D. A. Thornton and M. R. Ziman, *J. Mol. Struct., 49,* 7 (1978).
41 G. S. Shepard and D. A. Thornton, *J. Mol. Struct., 34,* 83 (1976).
42 P. R. Johnson and D. A. Thornton, *J. Inorg. Nucl. Chem., 37,* 461 (1975).
43 G. Nieuwpoort and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas, 99,* 394 (1980).
44 Z. Gabelica, *Spectrochim. Acta, A32,* 337 (1976).
45 G. W. R. Canham and A. B. Lever, *Can. J. Chem., 50,* 3866 (1972).
46 R. H. Nuttall, *Talanta, 15,* 157 (1968).
47 J. R. Ferraro, 'Low Frequency Vibrations of Inorganic and Coordination Compounds', Plenum Press, New York, 1971.