Inorganica Chimica Acta, 19 (1976) 133–137

Bis(benzoyl-β-alaninate)copper(II) Complexes and Their Amine Adducts

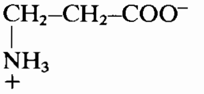
G. MARCOTRIGIANO
Cattedra di Chimica, Facoltà di Medicina Veterinaria, University of Bari, 70126 Bari, Italy
L. MENABUE and G. C. PELLACANI
Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy

A compound of the type $Cu(Bz\text{-}\beta\text{-}ala)_2$ *(Bz-β-ala = benzoyl-β-alanine anion) was prepared. Amine adducts of the type* $Cu(Bz\text{-}\beta\text{-}ala)_2B_n$ *(n = 1 and B = pipz, 3-pic, 2,2′-bipy, 4,4′-bipy and o-phen; n = 2 and B =* CH_3*-pipz, pipd, morph, py, 4-pic and en) were obtained by reaction of the amines with* $Cu(Bz\text{-}\beta\text{-}ala)_2$*. Each complex was characterized by elemental analysis, solid and solution spectroscopy and magnetic moment. For the solid* $(Cu(Bz\text{-}\beta\text{-}ala)_2)_n$*, solid and solution* $(Cu(Bz\text{-}\beta\text{-}ala)_2\cdot 3\text{-}pic)_2$ *and solution* $(Cu(Bz\text{-}\beta\text{-}ala)_2B)_2$ *(B = py and 4-pic) complexes the physical measurements support a copper acetate monohydrate type coordination. For the* $Cu(Bz\text{-}\beta\text{-}ala)_2\cdot o\text{-}phen$ *complex in the solid state and in solution the presence of two bands (10500 and 14000* cm^{-1}*) in the electronic spectra and their position suggest a six-coordinate, cis-octahedral* CuO_4N_2 *chromophore, confirmed by the i.r. spectra which give evidence of bidentate coordination of the amino acid through the carboxylic group. The electronic spectra of all the other complexes (one band at 15500–17000* cm^{-1}*) are consistent with the presence of square-planar (or strongly tetragonal distorted) coordination with* CuN_2O_2 *chromophores. I.r. spectra suggest a monodentate coordination of the amino acids and confirm the amine coordination toward the nitrogen atom. In the* $Cu(Bz\text{-}\beta\text{-}ala)_2(en)_2$ *complex a bidentate coordination of the en molecules with the formation of square planar species with* CuN_4 *chromophores, with a weak monodentate interaction of the amino acid in the polar position is proposed. A concentration-dependent colour change with a red shift of the d–d band are also discussed for the solution* $Cu(Bz\text{-}\beta\text{-}ala)_2B_2$ *(B = py, 4-pic,* CH_3*-pipz, morph and pipd).*

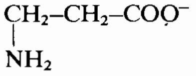
Introduction

There are numerous examples of the *in vivo* interaction of transition metal ions with amino acids and peptides, and these interactions are of considerable biological importance[1]. The major interest has been focused on the simplest amino acids, glycine and alanine, and the biologically important compounds containing histidine and related species.

α- and β-alanine exist as zwitterions, LH, in the solid state, but almost invariably coordinate as the anionic species L^-, *via* Cu–O and Cu–N bonds[2–6]:

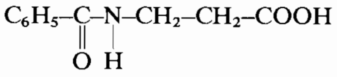


$$\underset{\overset{+}{NH_3}}{CH_2}\text{–}CH_2\text{–}COO^-$$



$$\underset{NH_2}{CH_2}\text{–}CH_2\text{–}COO^-$$

In this work we have studied the interaction of the copper(II) ion with benzoyl-β-alanine, in which a peptide group, –NH–CO–, is present:



$$C_6H_5\text{–}\underset{\|\atop O}{C}\text{–}\underset{|\atop H}{N}\text{–}CH_2\text{–}CH_2\text{–}COOH$$

The aim of this study was to evaluate the effects of the substituent on the amino group and of the amines on the copper(II) ion on the coordination properties of the amino acid.

This work represents also an extension of our previous research on the coordination properties of simple amino acids, containing a peptide group, such as N-acetyl- and N-benzoyl-glycine[7].

Experimental

Preparation of the Complexes

The anydrous bis(benzoyl-β-alaninate)copper(II), Cu $(Bz\text{-}\beta\text{-}ala)_2$ was prepared by mixing a potassium benzoyl-β-alaninate (2 × $10^{-2}M$) (prepared by adding stoichiometric amounts of KOH in methanol and benzoyl-β-alanine in ethanol–methanol (1 : 1) and diethyl ether and by cooling at 5° C) solution in methanol to a copper(II) perchlorate hexahydrate (1 × $10^{-2}M$) solution in ethanol at room temperature. After cooling at 5° C for one hour and filtering the $KClO_4$ precipitated, by slow evaporation of the solution at room temperature the compound precipitated.

The $Cu(Bz\text{-}\beta\text{-}ala)_2B_n$ (n = 1 and B = pipz, 2,2′-bipy and *o*-phen; n = 2 and B = CH_3-pipz, pipd, morph, py, 3-pic, 4-pic and en) complexes were prepared in general by suspending the anhydrous bis(benzoyl-β-alaninate)copper(II) salt (0.40 g) in 5–10 ml of absolute ethanol and adding an excess of the corresponding base or suspending the copper(II) salt directly in the amine (in the case of 3-pic and 4-pic), at 40–60° C, until a clear solution was obtained. For the pipz and en complexes methanol was used. For the 3-pic adduct acetone and diethyl ether was added. The compounds precipitated by cooling at 5° C, while the 4-pic adduct precipitated by adding diethyl ether.

Cu(Bz-β-ala)$_2$·4,4'-bipy was obtained by adding a 4,4'-bipy solution in methanol to the ethanolic–methanolic solution obtained by mixing copper(II) perchlorate hexahydrate and potassium benzoyl-β-alaninate in 1 : 2 molar ratio after filtration of the potassium perchlorate precipitated. The adduct precipitated instantaneously.

Physical Measurements

The electronic spectra of the compounds were recorded with a Beckman DK 1A spectrophotometer. Solid samples were prepared by grinding the complexes on a filter paper as support. The infrared spectra of KBr pellets, nujol mulls and chloroform solutions were recorded with a Perkin–Elmer 521 spectrophotometer.

The room temperature magnetic moments were measured with the Gouy method by using $HgCo(NCS)_4$ or $Ni(en)_3S_2O_3$ as calibrants and correcting for diamagnetism with the appropriate Pascal constants.

Analyses

Nitrogen, carbon and hydrogen were analysed by Mr. G. Pistoni using a Perkin–Elmer 240 Elemental Analyser of the Istituto di Chimica Generale e Inorganica of the University of Modena.

Results and Discussion

The prepared compounds, their analyses and the abbreviated names of the amino acids and of the amines are reported in Table I. All the compounds are stable in air. Data concerning their electronic and infrared spectra are given in Tables II and III, respectively. The assignment of the antisymmetric and symmetric carboxy stretching frequencies and of the CO ketonic and NH stretching frequencies of the benzoyl-β-alanine, which are considered very important in the assignment of the coordination sites on the amino acid, are made by comparing the amino acid, its potassium salt and their deuterated analogues.

The peptide group is uncoordinated in all the complexes reported in this work, as the shift to higher energies of the NH and CO ketonic stretching bands with respect to the free ligands suggests.

Cu(Bz-β-ala)$_2$ and Cu(Bz-β-ala)$_2$·3-pic Complexes

Of the reported complexes, the green Cu(Bz-β-ala)$_2$ and Cu(Bz-β-ala)$_2$·3-pic show similar magnetic and spectroscopic properties, for which they are considered together. The stereochemistry of these complexes is established as that of the parent dimeric copper acetate monohydrate from the following observations. The complexes exhibit the carboxylate stretching frequencies, $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$ (Table III) at very similar energies to those reported for copper acetate anhydrous, monohydrate and similar complexes, having dimeric carboxylate structure[8–14].

The room temperature solid electronic spectra of our complexes and those of the copper acetate monohydrate and of similar binuclear complexes strongly resemble one another[14–16]. Of particular importance is the presence of the band at 27 000 cm^{-1} in our complexes, a band which is peculiar to the dimeric carboxylates and their adducts[14, 16].

In addition the subnormal room temperature magnetic moments of our complexes (1.41 and 1.42 B.M.) strictly agree with those of the dimeric copper acetate monohydrate and similar complexes[11, 14, 17, 18]. This antiferromagnetism seems to result from a magnetic interaction probably operating through the bridging oxygen atoms.

For all these reasons we may conclude that our complexes have structures similar to those of the dimeric copper acetate monohydrate and in particular, in the (Cu(Bz-β-ala)$_2$·3-pic)$_2$ complex, the fifth coordination position is occupied by the 3-pic molecule, while in the (Cu(Bz-β-ala)$_2$)$_n$ it may be occupied by adjacent molecules, with formation of a polynuclear compound which is supported by its insolubility in the common organic solvents.

Cu(Bz-β-ala)$_2$B$_n$ (n = 1 and B = 2,2'-bipy, 4,4'-bipy, o-phen and pipz; n = 2 and B = CH_3-pipz, pipd, morph, py, 4-pic and en)

All these complexes are blue, except the en adduct which is violet, and show "normal" room-temperature magnetic moments (Table I) and similar spectroscopic properties in the solid state (Table II).

The Cu(Bz-β-ala)$_2$·*o*-phen complex shows two absorption bands in the solid state and in methanol or chloroform solution at 10 530–10 640 and 13 510–14 710 cm^{-1} (Table II) which are similar to those exhibited by the copper(II) nitroketonate adduct of bipy and their parent complexes derived from 2-nitroacetophenone reported by Attanasio *et al.*[19, 20] and recognized to be six-coordinate, *cis*-octahedral with a CuO_4N_2 chromophore. The low molar extinctions in solution support the six-coordination. A similar conclusion we have previously proposed for the Cu(Hippu)$_2$ ·*o*-phen complex, where Hippu is the hippurate anion, which shows absorption bands at 10 530 and 14 700 cm^{-1} [7].

The i.r. spectra of this complex in the solid state and in chloroform solution agree with a bidentate coordination of the carboxylate group, as they show differences between the $\nu(COO)_{as}$ and $\nu(COO)_s$ ($\Delta\nu$ = 145–134) and a $\nu(COO)_{as}$ position which are the lowest

TABLE I. Analytical Results.[a]

Compound	Colour	C %		H %		N %		μ_{eff} B.M.
		Calcd	Found	Calcd	Found	Calcd	Found	
Cu(Bz-β-ala)$_2$	Green	53.60	53.90	4.50	4.64	6.26	6.26	1.41
Cu(Bz-β-ala)$_2$ pipz	Blue	53.95	53.38	5.66	6.32	10.49	9.83	1.74
Cu(Bz-β-ala)$_2$(CH$_3$-pipz)$_2$	Blue	55.56	55.15	6.85	7.20	12.97	12.25	1.81
Cu(Bz-β-ala)$_2$(pipd)$_2$	Blue	58.26	59.21	6.85	6.59	9.07	8.80	1.87
Cu(Bz-β-ala)$_2$(morph)$_2$	Blue	54.03	54.17	6.16	6.92	9.01	8.96	1.74
Cu(Bz-β-ala)$_2$(py)$_2$	Blue	59.42	59.40	4.99	5.12	9.25	9.39	1.85
Cu(Bz-β-ala)$_2$ · 3-pic	Green	57.70	57.74	5.03	5.20	7.77	7.83	1.42
Cu(Bz-β-ala)$_2$(4-pic)$_2$	Blue	60.58	59.90	5.41	5.58	8.84	8.86	1.83
Cu(Bz-β-ala)$_2$ · 2,2′-bipy	Blue	59.62	60.24	4.68	4.91	9.28	9.68	1.78
Cu(Bz-β-ala)$_2$ · 4,4′-bipy	Blue	59.62	60.32	4.68	5.11	9.28	10.21	1.71
Cu(en)$_2$(Bz-β-ala)$_2$	Violet	50.71	50.63	6.39	6.82	14.80	14.35	2.04
Cu(Bz-β-ala)$_2$ · *o*-phen	Blue	61.16	61.74	4.49	4.70	8.93	9.24	1.70

[a] Abbreviations: Bz-β-ala = benzoyl-β-alaninate anion; pipz = piperazine; CH$_3$-pipz = N-methyl-piperazine; pipd = piperidine; morph = morpholine; py = pyridine; 3-pic and 4-pic = 3- and 4-methylpyridine; 2,2′-bipy and 4,4′-bipy = 2,2′- and 4,4′-bipyridine; en = ethylendiamine; *o*-phen = 1,10-phenanthroline.

TABLE II. Electronic Spectra (cm^{-1}) of the Complexes (in parenthesis ε = 1 mol^{-1} cm^{-1}).

Cu(Bz-β-ala)$_2$	Solid	Green		14930	27030
Cu(Bz-β-ala)$_2$ · 3-pic	Solid	Green		13990	27400
	CHCl$_3$	Green		13990(180)	27400(75)
	CHCl$_3$+3-pic	Blue		15150(60)	
	MeOH	Green		14490(115)	
	MeOH+3-pic	Blue		15500(70)	
Cu(Bz-β-ala)$_2$ · pipz	Solid	Blue		16950	
Cu(Bz-β-ala)$_2$(CH$_3$-pipz)$_2$	Solid	Blue		15630	
	CHCl$_3$	Green		14390(77)	
	CHCl$_3$+CH$_3$-pipz	Blue		15630(100)	
	MeOH	Green		14390(55)	
	MeOH+CH$_3$-pipz	Blue		15750(95)	
Cu(Bz-β-ala)$_2$(pipd)$_2$	Solid	Blue		16130	
	CHCl$_3$	Blue		15390(97)	
	CHCl$_3$+pipd	Blue		16000(120)	
Cu(Bz-β-ala)$_2$(morph)$_2$	Solid	Blue		16000	
	CHCl$_3$	Green		14090(100)	
	CHCl$_3$+morph	Blue		16130(120)	
	MeOH	Green		14490(70)	
	MeOH+morph	Blue		15630(85)	
Cu(Bz-β-ala)$_2$(py)$_2$	Solid	Blue		16130	
	CHCl$_3$	Green		13990(188)	
	CHCl$_3$+py	Blue		15150(70)	
	MeOH	Green		14090(110)	
	MeOH+py	Blue		15630(80)	
Cu(Bz-β-ala)$_2$(4-pic)$_2$	Solid	Blue		16130	
	MeOH	Green		14350(86)	
	MeOH+4-pic	Blue		15630(70)	
Cu(Bz-β-ala)$_2$ · 2,2′-bipy	Solid	Blue		15870	
	CHCl$_3$	Blue		15270(81)	
	MeOH	Blue		15500(60)	
Cu(Bz-β-ala)$_2$ · 4,4′-bipy	Solid	Blue		16000	
Cu(en)$_2$(Bz-β-ala)$_2$	Solid	Violet		18020	
	MeOH	Violet		17860(70)	
Cu(Bz-β-ala)$_2$ · *o*-phen	Solid	Blue	10530	13510	
	CHCl$_3$	Blue	10530sh(25)	14710(60)	
	MeOH	Blue	10640(55)	14600(70)	

TABLE III. Infrared Spectra (cm^{-1}) of the Solid and Solution Complexes.

		ν(NH)	ν(NH)[a]	$\nu(COO)_{as}$	$\nu(COO)_s$	$\Delta\nu$(COO)
Bz-β-alaH	KBr	3300s		1693vs	1255s	438
Bz-β-alaK	KBr	3365m 3322w 3300m		1555vs	1410s	145
$Cu(Bz\text{-}\beta\text{-}ala)_2$	KBr	3360w 3310s		1583vs	1430vs	153
$Cu(Bz\text{-}\beta\text{-}ala)_2 \cdot pipz$	KBr	3260mb	3175m 3145sh	1570vs	1395s	175
$Cu(Bz\text{-}\beta\text{-}ala)_2(CH_3\text{-}pipz)_2$	KBr	3287sb	3260sh	1548vs	1393vs	155
	$CHCl_3$	3400sh 3320m	3250w	1590vs	1398s	192
	$CHCl_3+CH_3$-pipz	3400sh 3320m	3250sh	1585vs	1395s	190
$Cu(Bz\text{-}\beta\text{-}ala)_2(pipd)_2$	KBr	3332w 3308ms	3255w 3122m	1550vs	1395vs	155
	$CHCl_3$	3400w 3315w	3255w	1570vs	1400vs	170
	$CHCl_3$+pipd	3315s		1582vs	1400ms	182
$Cu(Bz\text{-}\beta\text{-}ala)_2(morph)_2$	KBr	3315s	3232m	1570vs	1398vs	172
	$CHCl_3$	3425m 3330s	3200w	1630vs	1400sb	230
	$CHCl_3$+morph	3420sh 3315s	3220sh	1580vs	1388ms	192
$Cu(Bz\text{-}\beta\text{-}ala)_2(py)_2$	KBr	3320m		1572vs	1403s	169
	$CHCl_3$	3330ms		1615vs	1400sh	215
	$CHCl_3$+py	3330ms		1575vs	1395m	180
$Cu(Bz\text{-}\beta\text{-}ala)_2 \cdot 3\text{-}pic$	KBr	3340sh 3320ms		1627vs	1418sh	209
	$CHCl_3$	3418ms		1610vs	1418ms	192
	$CHCl_3$+3-pic	3400sh 3330ms		1570vs	1403s	167
$Cu(Bz\text{-}\beta\text{-}ala)_2(4\text{-}pic)_2$	KBr	3312ms		1570vs	1408vs	162
$Cu(Bz\text{-}\beta\text{-}ala)_2(2,2'\text{-}bipy)$	KBr	3355ms 3295m		1588vs	1395s	193
	$CHCl_3$	3380mb 3322w		1595vs	1400s	195
$Cu(Bz\text{-}\beta\text{-}ala)_2(4,4'\text{-}bipy)$	KBr	3320ms		1570vs	1402s	168
$Cu(en)_2(Bz\text{-}\beta\text{-}ala)_2$	KBr	3282ms (3250m)	(3250m) 3210sh	1540vs	1375vs	165
$Cu(Bz\text{-}\beta\text{-}ala)_2(o\text{-}phen)$	KBr	3370sh 3320sh 3270mb		1565vs	1420vs	145
	$CHCl_3$	3325s		1550vs	1416vs	134

[a] ν(NH) stretching of the amines.

found in this study. Furthermore the presence of two new bands at 1142 and 850 cm^{-1} in the *o*-phen complex with respect to free amine is typical of coordinate *o*-phen[21, 22].

The room temperature solid electronic spectra of $Cu(Bz\text{-}\beta\text{-}ala)_2B_n$ (n = 1 and B = pipz, 2,2'-bipy and 4,4'-bipy; n = 2 and B = CH_3-pipz, pipd, morph, py and 4-pic) complexes present only one absorption band at 15500–17000 cm^{-1} and therefore they must possess an identical chromophore group. The position of the *d–d* band in these complexes is consistent with a square-planar or strongly tetragonal distorted coordination involving probably a N_2O_2 donor set, as is found by comparing these spectral data with those of an extensive selection of copper(II) model complexes containing N_xO_y donor atom sets, for which direct structural information is available from X-ray analysis and e.s.r. spectra[19, 20, 23–25].

The $Cu(Bz\text{-}\beta\text{-}ala)_2B_2$ and $Cu(Bz\text{-}\beta\text{-}ala)_2 \cdot 3$-pic complexes in methanol or chloroform solution in presence of amine excess and the $Cu(Bz\text{-}\beta\text{-}ala)_2 \cdot 2,2'$-bipy complex in methanol or chloroform solution show electronic spectra quite similar to those of the solid compounds, but show a little red shift, indicating a diminished tetragonal distortion. The i.r. spectra of these complexes, especially in chloroform solution with amine excess, are consistent with a monodentate coordination of the carboxylate group, as the ν(COO) values are greater than those found for the potassium salt and lower than those reported for the dimeric compounds. The coordination of the amines toward the nitrogen atom is confirmed by the shift of the ν(NH)B to lower frequencies, with respect to the free amines[26–28], in the aliphatic heterocyclic amine adducts and of the bands in the 800–500 cm^{-1} region, with respect to the free amines,[29–31] in the py, 4-pic and bipy adducts.

The insolubility in the common organic solvents of the $Cu(Bz\text{-}\beta\text{-}ala)_2B$ (B = pipz and 4,4'-bipy) complexes, the similarity of the i.r. spectrum of pipz adduct with that of the $CdCl_2 \cdot pipz$ complex and the structural conformation of these amines support the hypothesis that these complexes are polymeric in the solid state, with amine molecules "bridging" metal ions[7].

Of further interest is the different behaviour of the $Cu(Bz\text{-}\beta\text{-}ala)_2B_2$ (B = CH_3-pipz, pipd, morph, py and 4-pic) complexes in solution, if B is an aromatic or an aliphatic heterocyclic amine. In fact all these complexes in chloroform or methanol solution give a concentration-dependent colour change from blue (higher concentration) to green (lower concentration), with a consequent red shift of the *d–d* band from 15000–17000 to 14000–14500 cm^{-1}. This shift may be attributed to the formation of dimeric copper acetate monohydrate type species in solution due to a dissociation of the type $2CuL_2B_2 \rightleftharpoons (CuL_2B)_2+2B$, in the aromatic heterocyclic amine adducts, as supported by the molar extinction greater in the green species than in the blue species. In the aliphatic heterocyclic amine adducts a progressive concentration dependent dissociation of the amines gives rise to a final green solution in which the complete dissociation of the amines, replaced by solvent molecules, is obtained. The solution complexes should have an elongated tetragonal stereochemistry which also accounts for the lower molar extinction of the green solution complexes relative to the blue solution complexes. All the $Cu(Bz\text{-}\beta\text{-}ala)_2B_2$ (B = py, 4-pic, CH_3-pipz, pipd and morph) adducts in the solid state, invariably lose both the amines by warming at 100–110° C.

The $Cu(en)_2(Bz\text{-}\beta\text{-}ala)_2$ complex presents a *d–d* band in solution and in the solid state at ~18000 cm^{-1} which is in the range found for other $Cu(en)_2^{2+}$ complexes and other complexes with a square planar structure with CuN_4 chromophorcs[25]. In thc i.r. spectrum of this complex the position of the $\nu(NH)_B$ and of the $\nu(COO)$ bands is consistent with a bidentate coordination of the en and with a weak monodentate coordination toward the carboxyl oxygen of the amino acid in the polar position, respectively. Its electronic spectra suggest that the amino acid interactions with the Cu $(en)_2^{2+}$ cation are stronger than those of the ClO_4^- anions in the $Cu(en)_2(ClO_4)_2$ complex[33].

Acknowledgments

The authors are grateful to Prof. Giorgio Peyronel of the Istituto di Chimica Generale e Inorganica of the University of Modena for making the instruments available to us.

References

1 S.T. Chow and C.A. McAuliffe, *Progr. Inorg. Chem., 19,* 51 (1975) and ref. cited therein.
2 A. Dijkstra, *Acta Cryst., 20,* 588 (1966).
3 R.D. Gillard, R. Mason, N.C. Payne and G.B. Robertson, *Chem. Comm.,* 155 (1966).
4 C.A. McAuliffe, J.V. Quagliano and L.M. Vallarino, *Inorg. Chem., 5,* 1996 (1966).
5 K. Tomita, *Bull. Chem. Soc. Japan, 34,* 297 (1961).
6 C.A. McAuliffe and W.D. Perry, *J. Chem. Soc. A,* 634 (1969).
7 G. Marcotrigiano and G.C. Pellacani, *Can. J. Chem., 52,* 3607 (1974); *ibid., Z. Anorg. Allgem. Chem., 413,* 171 (1975); *ibid., Inorg. Nucl. Chem. Lett., 11,* 643 (1975) and ref. cited therein.
8 C. Oldham, *Progr. Inorg. Chem., 10,* 223 (1968) and ref. cited therein.
9 K. Nakamoto, Y. Morimoto and A.E. Martell, *J. Am. Chem. Soc., 83,* 4528 (1961).
10 Y. Kuroda, A. Sasano and M. Kubo, *Bull. Chem. Soc. Japan, 39,* 1002 (1966).
11 M. Kato, H.B. Jonassen and J.C. Fanning, *Chem. Rev., 64,* 99 (1964) and ref. cited therein.
12 N.F. Curtis. *J. Chem. Soc. A,* 1579 (1968).
13 S.F.A. Kettle and A.J.P. Pioli, *J. Chem. Soc. A,* 1243 (1968).
14 D. Hibdon and J.H. Nelson, *Inorg. Chim. Acta, 7,* 629 (1973) and ref. cited therein.
15 A.B.P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, New York, N.Y., 1968.
16 W. Harrison, S. Rettig and J. Trotter, *J. Chem. Soc. Dalton,* 1852 (1972) and ref. cited therein.
17 A. Earnshow and K.S. Patel, *J. Inorg. Nucl. Chem., 27,* 1805 (1965).
18 J.R. Wasson, Chin-I Shyr and C. Trapp, *Inorg. Chem., 7,* 469 (1968).
19 D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc. Dalton,* 2516 (1971).
20 D. Attanasio, I. Collamati, C. Ercolani and G. Rotilio, *J. Chem. Soc. Dalton,* 2242 (1973) and ref. cited therein.
21 J.R. Ferraro and W.R. Walker, *Inorg. Chem., 4,* 1382 (1965).
22 B.F.G. Johnson and R.A. Walton, *Inorg. Chem., 5,* 49 (1966).
23 D. Attanasio, I. Collamati and C. Ercolani, *J. Chem. Soc. Dalton,* 2442 (1974) and ref. cited therein.
24 J.I. Bullock, R.J. Hobson and D.C. Povey, *J. Chem. Soc. Dalton,* 2037 (1974) and ref. cited therein.
25 R.C. Rosemberg, C.A. Root, P.K. Bernstein and H.B. Gray, *J. Am. Chem. Soc., 97,* 2092 (1975) and ref. cited therein.
26 G. Marcotrigiano, R. Battistuzzi and G.C. Pellacani, *Can. J. Chem., 50,* 2557 (1972).
27 I.S. Ahuja, *Inorg. Chim. Acta, 3,* 110 (1969).
28 I.S. Ahuja and A. Garg, *Inorg. Nucl. Chem. Lett., 7,* 937 (1971).
29 N.N. Greenwood and K. Wade, *J. Chem. Soc.,* 1130 (1960).
30 E. Konig and E. Lindner, *Spectrochim. Acta, 28A,* 1393 (1972) and ref. cited therein.
31 F. Micheel and B. Schleppinghof, *Chem. Ber., 88,* 763 (1955).
32 W. Berg and K. Rasmussen, *Spectrochim. Acta, 29A,* 319 (1973).
33 I.M. Procter, B.J. Hathaway and P. Nicholls, *J. Chem. Soc. A,* 1678 (1968).