Inorganica Chimica Acta, *78* (1983) 269–274

Copper(II) Perchlorate Complexes with N-Methyl Substituted Xanthines*

CHESTER M. MIKULSKI, THU BA TRAN, LINDA MATTUCCI
Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038, U.S.A.
and NICHOLAS M. KARAYANNIS
Amoco Chemicals Corporation, Naperville, Ill. 60566, U.S.A.

Received December 16, 1982

Monomeric complexes of the [$CuL_2(OClO_3)_2$] type (L = theophylline, theobromine, caffeine) were synthesized by refluxing 2:1 mixtures of N-methyl substituted xanthine and $Cu(ClO_4)_2$ in ethanol–triethyl orthoformate. Characterization studies suggest that the complexes are distorted tetrahedral with terminal unidentate L and $-OClO_3$ ligands. Most likely binding sites for caffeine and theophylline are the N(9) and N(7) imidazole nitrogens, respectively, in view of previously reported crystal structures of Cu^{2+} complexes with these ligands. For the theobromine complex, the N(1) pyrimidine and N(9) imidazole nitrogens are almost equally likely to function as the binding site.

Introduction

Numerous studies of metal complexes of purine (puH; I) and its biologically important derivatives (adenine (adH) and guanine (guH), which are major constituents of DNA and RNA; and xanthine (xnH; II) and hypoxanthine (hxH), which are minor constituents of RNA) have appeared in recent years [2–6]. However, interest has also been shown for the metal complexes of N-methyl substituted xanthines, such as theophylline (tpH; 1,3-dimethylxanthine; III), theobromine (tbH; 3,7-dimethylxanthine; IV) and caffeine (caf; 1,3,7-trimethylxanthine; V); these compounds are not nucleic acid constituents but can serve as models of biologically important analogs [2, 7], and have found application as stimulants of the central nervous system, to promote diuresis and for their cardiovascular effects [8]. Among these ligands, theophylline has been studied most intensively, *i.e.*: Crystal structure determinations of various Cu^{2+} or Co^{3+} complexes, including $Cu(tpH)Cl_2 \cdot 2H_2O$ [9], established that tpH or its monoanion (tp^-) act most frequently as terminal unidentate ligands, coordinating through the N(7) nitrogen to the 3d metal ion [9–12]. However, in (N-salicylidene-N′,N′-dimethylethylenediamine)(theophyllinato)Cu(II) - 3.5 water, tp^- acts as a chelating agent, coordinating through the O(6), N(7) sites [13]. On the other hand, in its complexes with 4d or 5d metal ions, tpH was found to function as terminal unidentate, but binding through the N(9) nitrogen, in Rh^{2+} [14] and Pt^{2+} [15] complexes, while tp^- acts as bridging bi- or tri-dentate, N(7),N(9)- or O(6),N(7),N(9)-bonded, in a Pt^{4+} complex [16]. Other theophylline complexes reported include $M(tp)_2$ (M = Mn, Cu), Ag(tp) [17], mixed tp^--ammonia or amine complexes with Cu^{2+}, Zn^{2+} and Cd^{2+} [18], a tpH complex with Mg^{2+} salicylate [8], $Cu(tp)_2 \cdot 2H_2O$ [19] and $Cu(tp)_2 \cdot 5H_2O$ [20]. UV, IR and NMR spectral studies of Cu^{2+} theophylline complexes were also reported [21], while the formation constants of Cu^{2+} complexes with this ligand were found to be the lowest relative to other substituted purines (*i.e.*, 6-diethylaminopurine > 2,6-diaminopurine > adH > puH > hxH > 7-methylhypoxanthine > 9-methylhypoxanthine > xnH ⩾ tpH [22]. A number of studies indicated that metal complexes with theobromine or caffeine are more difficult to isolate as solids, relative to the corresponding theophylline complexes [18, 20]. Nevertheless, caffeine complexes with Cu^{2+} ([$Cu(caf)Cl_2(OH_2)$] [23] and [$Cu(caf)(ONO_2)(OH_2)_3$](NO_3) [24] and Rh^{2+} [14] have been prepared and their structure determinations revealed that caf acts as terminal unidentate, N(9) nitrogen-bonded [14, 23, 24]. C(8) carbon-bonded unidentate caf is present in [$Ru(caf)(NH_3)_3Cl_2$]$Cl \cdot H_2O$ [25], whilst in the molecular complexes [$Mg(OH_2)_6$]$Br_2 \cdot 2caf$ and [$Mn(OH_2)_6$]$I \cdot I_3 \cdot 2caf$, the caffeine molecules are uncoordinated [26]. Other studies of caf complexes include the preparation and characterization of an adduct of caf with Cu^{2+} acetate [27], and solution studies of Ca^{2+} and Cu^{2+} caf complexes [21, 28]. As far as theobromine complexes are concerned, the information available is limited to only a few studies, including the crystal structure of $(tbH)_2I_2O_8$ [29], and spectral investigations of the complexation of this compound with sodium benzoate [30] and various Brönsted (HCl, HI, $HSbCl_6$, HPF_6, $HAsF_6$) [31] and carboxylic [32] acids (studies of caf complexes with Brönsted [33]

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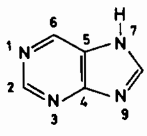
*Ref. 1.

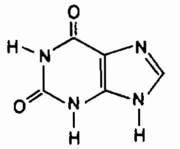
0020-1693/83/$3.00

and carboxylic [32] acids were also reported). Finally, a number of theophylline complexes with heavy transition metal carbonyls (M = Mo, W, Rh, Ir) or bis-(trialkylphosphine)Pd^{II} or Pt^{II}, as well as a complex of theobromine with $Rh(CO)(PPh_3)_2$, have also been reported [34].

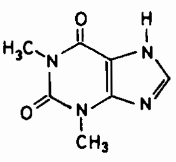
Previous work in these laboratories has dealt with the syntheses and characterization of puH [5], adH [35] and guH [36] complexes with 3d metal perchlorates, while most recent studies concerned the complexes isolated by interaction between $Cu(ClO_4)_2$ and xnH, hxH or guH from ethanol–triethyl orthoformate (teof) [1, 37]. These latter studies have now been extended to include the complexes formed by interaction between $Cu(ClO_4)_2$ and tpH, tbH or caf, and this work is reported herein.



(I)



(II)



(III)

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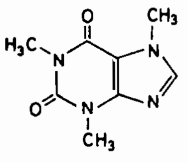

(V)

Experimental

The synthetic conditions were the same as those employed in our previous work [37], *viz.*: 2.5 mmol ligand (tpH, tbH or caf) and 1.25 mmol hydrated Cu^{2+} perchlorate were premixed and added to a mixture of 35 ml absolute ethanol and 15 ml teof. The resultant mixture was swirled for 5–10 minutes and subsequently refluxed for 7–10 days. Under these conditions, tbH and caf produced solid complexes, which were separated by filtration, washed with anhydrous diethyl ether and stored *in vacuo* over anhydrous $CaCl_2$. In the case of tpH, which would be anticipated [18, 20] to produce a solid complex more readily than tbH or caf, no solid product had formed after 10 days of refluxing. A solid complex eventually formed by reducing the volume of the tpH-$Cu(ClO_4)_2$ solution to *ca.* 10 ml by heating, dissolving the viscous residue in acetone, allowing the acetone to evaporate, and storing the semi-solid residue in an evacuated desiccator over anhydrous $CaCl_2$; the complex solidified to a hard, glassy material after 1–2 weeks. Analytical data for the new complexes (Table I) indicate that they are adducts of the general type $CuL_2(ClO_4)_2$ (L = tpH, tbH, caf). The complexes show some solubility in organic media, and especially in binary solvent mixtures, such as nitromethane–acetone.

Infrared spectra (Table II) were recorded on Nujol and hexachloro-1,3-butadiene mulls between NaCl windows (4000–500 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra, magnetic susceptibility (298 K) and conductance measurements (Table III) were obtained by methods previously described [38].

Discussion

Infrared Data

Complete [17, 18, 39] and partial [31–34, 40] IR spectral data for the ligands of interest [4000–600 cm^{-1}], including assignments for some of the absorption bands [31–34, 39, 40] have been published. Mull spectra of the free ligands in the above region, obtained during this work (Table II), are in agreement with previously published spectra. Band assignments were based on these previous works [31–34, 39, 40] and the complete IR band assignment of Shirotake and Sakaguchi for another oxopurine, namely guH [41]. The ν_{NH} bands of tpH or tbH remain intact in the spectra of the Cu^{2+} complexes, as was expected for adducts of these neutral ligands [5, 6]; caffeine does not contain NH groups, and the only absorption present at 2825 cm^{-1} is due to ν_{CH} [40]. The $\nu_{C=O}$ doublets of the three ligands show very little sensitivity to Cu^{2+} complex formation; consequently, coordination of the ligands through either of the exocyclic potential O-ligand sites (O(2)

TABLE I. Analytical Data for $CuL_2(ClO_4)_2$ Complexes.

L	Color	Yield%	%C		%H		%N		%Cu		%Cl	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
tpH	Green	88.7	27.00	26.92	2.59	2.70	17.99	18.28	10.20	9.82	11.39	11.25
tbH	Light yellow	73.4	27.00	27.17	2.59	2.78	17.99	18.15	10.20	9.97	11.39	11.47
caf	Pale green	39.3	29.53	29.76	3.10	3.23	17.22	17.46	9.76	10.05	10.89	11.13

TABLE II. Infrared Data for tpH, tbH, caf and their $CuL_2(ClO_4)_2$ Complexes (cm^{-1})[a].

Free tpH	tpH complex	Free tbH	tbH complex	Free caf	caf complex	Band assignment
2840s, 2710s, 2670s, 2615s, b	2850s, 2730m, sh, 2700m, sh, 2640mw, b	2820m, 2710m, 2660m, 2620m	2820mw, 2715 w, 2660w 2625w, sh	2825w, sh	2805w, sh	$\nu_{NH} + \nu_{CH}$
1713vs, 1668vs, b	1711vs, 1663vs, b	1685vs, b, 1660vs, b	1690vs, b	1702vs, 1667vs, b	1709vs, 1673vs, b	$\nu_{C=O}$
1613s, sh, 1563ms, b	1619s, sh, 1560ms	1595s, sh, 1547m, b	1600mw, sh, 1559mw, sh, 1543m	1605ms, sh, 1548ms	1613ms, sh, 1568s, 1550s	$\nu_{C=C} + \nu_{C=N}$
1478m, sh, 1450vs, 1443 vs, 1427s, sh, 1372s, 1348 ms, sh, 1311m, 1279m, 1239m, 1218m, 1176s, 1150m, sh, 1099m, sh	1492m, 1446m, 1400mv, 1382 mw, 1350, w, sh, 1321w, 1299w, b, 1250vw, sh, 1241w, 1195vw	1479w, sh, 1449s, 1422m, sh, 1360s, 1335m, sh, 1290m, 1222m, b, 1152mw, b, 1121mw, b	1490w, sh, 1454s, 1430m, sh, 1369s, 1361m, sh, 1346mw, sh, 1303w, 1275w, 1250w, sh, 1188 w, 1119w, sh,	1477m, sh, 1460s, 1445m, sh, 1380ms, 1368m, sh, 1335w, sh 1283w, 1236m, 1210w, sh, 1185w, 1140w, sh, 1100vw	1507m, 1490w, sh, 1451s, 1440m, sh, 1400w, 1367m, 1320w, 1281w, 1254vw, 1215 mw, sh, 1173w	Ring vibrations $+ \nu_{C-N} + \delta_{CH_3}$[b]
	1112s, 1047s		1097s, sh, 1062s		1104vs, sh, 1053vvs	$\nu_3(ClO_4)$
1038m, 960s, 913s	984w, sh, 962w, 909vw, sh	1050w, b, 1010w, b, 960 vw, 932w, sh	1050ms, sh, 1012w, sh, 922 w, 955w, vb	1070w, b, 1011w, 961w, 937w, sh	1029m, sh, 978mw	Ring vibrations[b]
	922w		925w, b		921w	$\nu_1(ClO_4)$
835ms, 780m, 752ms, 730s, 653w	830w, b, 775w, 760m, 739m	880w, sh, 845 mw, b, 775vw, 750w, 735w, 712mw, 655w, b	860w, vb, 802 w, 775w, 753w, 728w, b, 666w, sh	850w, b, 811w, sh, 749w, 732 m, 712w, 698w, sh	862w, 821w, 810w, sh, 750 mw, 740m, 718 w, sh, 680w, sh	Ring vibrations[b] $+ \delta_{NH} + \delta_{CH}$
	639m, sh, 617ms		642ms, 619ms		633m, 620m	$\nu_4(ClO_4)$
603m, 555w, vb, 503w, sh, 490w, sh, 463 w, b, 420vw, 390vw, sh, 305vvw, 238 mw, b	602m, 535w, vb, 512w, sh, 461w, sh, 449w, 409 vw, 387w, 252mw, b	598m, 552w, 525w, 505w, sh, 489w, 435w, sh, 402vw, 381 vw, 350vw, b, 310vvw, 261 w, 235mw, b	598m, 552vw, 490vw, b, 440w, 412w, sh, 375w, 240mw, b	597m, 560w, 515w, b, 470w, 449w, 431w, 408w, 390vw, b, 348vw, 311vw, 250mw, b	600m, 567w, sh, 544w, b, sh, 472w, sh, 445w, vb, 370w, b	ν_{ligand}(600–230 cm^{-1})[b]
	472w		475w, sh		481w	$\nu_2(ClO_4)$
	338w		336w, b		333w, b	$\nu_{Cu-O}(OClO_3)$
	303w, 279w		304w, sh, 275w, b		302w, sh, 276w, b	ν_{Cu-N}

[a] The free ligand bands were assigned on the basis of previous partial assignments for these compounds [31–34, 39, 40] and the complete IR assignments for guH [41]. [b] Some of the absorptions in these regions are masked in the spectra of the complexes by $\nu(ClO_4)$ or $\nu_{Cu-ligand}$ bands.

and O(6) oxygens) is ruled out [17, 18, 36, 41]. On the other hand, several of the $\nu_{C=C'}$, $\nu_{C=N}$ and ring vibrations of the ligands undergo sizeable shifts and occasional splittings upon Cu^{2+} complex formation; this suggests that the ligands coordinate through one of the ring nitrogens [5, 6, 17, 18, 35, 36, 41, 42]. All the fundamental vibrational modes of the perchlorate group are IR-active in the spectra of the new complexes; this demonstrates the presence of coordinated perchlorato ligands [43, 44]. More specifically, the $\nu_3(ClO_4)$ mode is doubly split into relatively sharp maxima located at 1112–1097 and 1062–1047 cm^{-1}, while the characteristic very strong and broad band at 1100–1060 cm^{-1}, corresponding to the ν_3 mode of ionic ClO_4^-, is conspicuously absent. These features are definitely in favor of the exclusive presence of unidentate coordinated $-OClO_3$ ligands (and absence of ionic ClO_4^-) [43, 44]. Further support to

TABLE III. Solid-state (Nujol mull) Electronic Spectra, Magnetic Properties (298 K) and Molar Conductivities of $CuL_2(ClO_4)_2$ Complexes.

L	λ_{max}, nm^a	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB	Λ_M, Ω^{-1} cm^2 mol^{-1}^{b}
tpH	200vs, 222s, sh, 250vs, b, 267vs, sh, 279vs, b, 305s, sh, 352s, sh, 407ms, 807m, b	1702	2.02	33
tbH	196vvs, 243vvs, sh, 268vvs, b, 276vs, sh, 307vs, sh, 347s, sh, 405ms, 812m, b	1627	1.98	37
caf	200vvs, 274vs, b, 285vs, sh, 303s, sh, 352s, sh, 404ms, sh, 804m, b	1555	1.93	40

^{a}UV spectra of the ligands (Nujol mulls), nm: tpH 223vvs, 276vs, 300vs, sh; tbH 200vvs, 232vs, 273vvs, 301s, sh; caf 200vs, 252 vs, 277vvs, b, 303s, sh. Aqueous solution spectra from the literature, at pH 6–7 [49]: λ_{max}, nm (logϵ): tpH 270 (4.02); tbH 271 (4.01); caf 272 (4.02). ^{b}Conductance measurements were performed at 25 °C on $10^{-3}M$ solutions of the complexes in a 1:1 (v/v) mixture of nitromethane–acetone.

this assignment is provided by doubly split ν_4 and IR-active ν_1 and $\nu_2(ClO_4)$ absorptions in the spectra of the new complexes [43, 44]. Finally, IR bands attributable to the presence of coordinated or lattice water or ethanol [5, 6, 35–37] were not observed in the spectra of the Cu^{2+} complexes herein reported.

The lower frequency IR spectra of the free ligands (600–200 cm^{-1}) show similarities to the published spectrum of their parent base, xnH [45], as would be anticipated (the Nujol mull spectrum of xnH in this region was also reported in one of our recent works [37]). Tentative $\nu_{Cu-O}(OClO_3)$ and ν_{Cu-N} band assignments were based on previous IR studies of 3d metal complexes with purine ligands [4–6, 35, 36] and perchlorato groups [5, 35, 36, 46]. The locations of these bands are generally in favor of coordination number four for the new Cu^{2+} complexes.

Electronic Spectra, Magnetic Moments and Molar Conductivities (Table III)

The room temperature magnetic moments of the complexes are in the region of normal values for Cu^{2+} [47]. The molar conductivities of $10^{-3}M$ solutions of the new Cu^{2+} complexes in nitromethane–acetone (1:1), at 25 °C, are intermediate between values corresponding to 'non'- and 1:1-electrolytes [48]. The preceding data combined are in favor of monomeric tetracoordinated configurations, in which both perchlorate groups are coordinated, in the solid state. In solution, partial substitution of $-OClO_3$ by acetone or nitromethane ligands apparently occurs, since the Λ_M values are as high as 30–40 Ω^{-1} cm^2 mol^{-1}.

The Nujol mull UV spectra of the free ligands show two $\pi \rightarrow \pi^*$ transition maxima at 220–280 nm; among these, the bands at 270–280 nm appear at somewhat lower energies than the corresponding absorptions in aqueous solutions of the same ligands at pH 6–7 [49]. The spectra of the free ligands show also a shoulder at 300–303 nm ($n \rightarrow \pi^*$ transition) [50]. The UV spectra of the complexes exhibit shifts and splittings of the $\pi \rightarrow \pi^*$ transition bands, relative to the spectra of the free ligands, and detectable $n \rightarrow \pi^*$ transition maxima at 303–307 nm. Strong copper-to-ligand charge-transfer absorption [51], originating in the UV and trailing off well into the visible region, with two distinct maxima at *ca.* 350 and 400 nm, is also observed in the spectra of the complexes. Finally, the d–d transition bands of the complexes appear in the near-IR region, and are characterized by a relatively broad maximum at 804–812 nm (12.44–12.31 kK). This spectral feature is consistent with a distorted tetrahedral geometry for the three new complexes [4, 52, 53]. In fact, several complexes of the type $CuLX_2$ (L = adenine, adenosine, 9-methyladenine; X = Cl, Br), with bidentate L ligands, have been assigned distorted tetrahedral symmetries (intermediate between tetrahedral and square planar), on the basis of spectral and magnetic data, including, *inter alia*, a d–d transition maximum at 11.9–13.7 kK [4, 52, 53]. It is also noteworthy that $Cu(guH)_2Cl_2$ [17] exhibits its d–d band at an even lower energy (920 nm or 10.9 kK) [21].

Conclusion

On the basis of the overall evidence presented, the new Cu^{2+} complexes seem to be of the same general type, *i.e.*, monomeric, distorted tetrahedral, with two unidentate substituted xanthine and two unidentate $-OClO_3$ terminal ligands ($[CuL_2(OClO_3)_2]$; L = tpH, tbH, caf), and involving a CuN_2O_2 absorbing species. As regards the likely binding site of each of the ligands, in the case of caf, N(9) is the obvious coordination site, since the rest of the ring nitrogens are methylated, while the crystal structure determinations of Cu^{2+} complexes with caf have revealed that N(9) is indeed the binding site of the terminal ligand [23, 24]. On the other hand, tpH and tbH contain protonated ring nitrogens (protonation sites N(7) and N(1), respectively). It is generally recognized that purine ligands show the tendency to coordinate through the ring nitrogen that is protonated in the free ligand, whilst, at the same time, the imidazole nitrogens (N(7), N(9)) are stronger ligating atoms than the pyrimidine nitrogens (N(1), N(3)) [2]. In view of this, and the numerous crystal structure determinations reported for complexes with terminal unidentate tpH [9–12], it is reasonable to conclude that $[Cu(tpH_2(OClO_3)_2]$ involves N(7)-bonded tpH. As far as tbH is concerned, both N(1), which is protonated in the free base, and the unsubstituted imidazole N(9) nitrogen would be almost equally likely to act as the binding site, in view of the preceding information [2]. N(9) as the binding site may be favored by some of the IR evidence, since no dramatic differences in the $\nu_{C=O}$, $\nu_{C=C}$, $\nu_{C=N}$ and ring vibration regions are observed between the spectra of the N(9)-bonded $[Cu(caf)_2(OClO_3)_2]$ complex and the $[Cu(tbH)_2(OClO_3)_2]$ compound; whereas in the IR spectrum of the N(7)-bonded tpH complex, some differences from the spectra of the tbH and caf complexes are evident (*e.g.*, negative (L = tpH) *vs.* positive (L = tbH, caf) $\nu_{C=O}$ frequency shifts upon Cu^{2+} complex formation) [31–33]. However, in view of the several occasions on which crystal structure determinations proved that binding site assignments made on the basis of spectral evidence for purine metal complexes were incorrect [2, 3, 5, 54, 55], it would be rather naïf to reach even a tentative conclusion favoring N(9) over N(1) as the binding site of tbH in the new Cu^{2+} complex with this ligand.

References

1 C. M. Mikulski, T. B. Tran, L. Mattucci and N. M. Karayannis, Abstracts, XXII ICCC, Budapest, Hungary, August 23–27, 1982; No. ThP 32.
2 D. J. Hodgson, *Progress in Inorg. Chem., 23,* 211 (1977).
3 L. G. Marzilli, *Progress in Inorg. Chem., 23,* 255 (1977).
4 M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 97,* 295 (1978).
5 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chem., 19,* 3491 (1980).
6 *Idem., Inorg. Chim. Acta, 46,* 235 (1980).
7 L. G. Marzilli, T. J. Kistenmacher and C. H. Chang, *J. Am. Chem. Soc., 95,* 7507 (1973).
8 R. H. Barry, H. Rubin, J. B. Johnson and J. H. Lazarus, *J. Pharm. Sci., 70,* 204 (1981).
9 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio and M. Tiripicchio Camellini, *Transition Met. Chem., 4,* 221 (1979).
10 T. Sorrell, L. G. Marzilli and T. J. Kistenmacher, *J. Am. Chem. Soc., 98,* 2181 (1976).
11 T. J. Kistenmacher, D. J. Szalda and L. G. Marzilli, *Inorg. Chem., 14,* 1686 (1975); D. J. Szalda, T. J. Kistenmacher and L. G. Marzilli, *ibid., 15,* 2783 (1976).
12 T. J. Kistenmacher, *Acta Crystallogr., B31,* 85 (1975); T. J. Kistenmacher and D. J. Szalda, *ibid., B31,* 90 (1975).
13 T. J. Kistenmacher, D. J. Szalda, C. C. Chiang, M. Rossi and L. G. Marzilli, *Inorg. Chem., 17,* 2582 (1978).
14 K. Aoki and H. Yamazaki, *Chem. Commun.,* 186 (1980).
15 E. H. Griffith and E. L. Amma, *Chem. Commun.,* 322 (1979).
16 N. H. Agnew, T. G. Appleton, J. R. Hall, G. F. Kilmister and I. J. McMahon, *Chem. Commun.,* 324 (1979).
17 D. Crăciunescu and A. Fruma, *Inorg. Chim. Acta, 4,* 287 (1970).
18 M. S. Zitzman, R. R. Krebs and W. J. Birdsall, *J. Inorg. Nucl. Chem., 40,* 571 (1978); W. J. Birdsall and M. S. Zitzman, *ibid., 41,* 116 (1979); S. D. Rothenberger, M. S. Zitzman and W. J. Birdsall, *ibid., 43,* 1673 (1981).
19 M. Melník, *Polyhedron, 1,* 143 (1982).
20 R. Weiss and H. Venner, *Hoppe Seyler's Z. Physiol. Chem., 340,* 138 (1965); *345,* 122 (1966).
21 D. Crăciunescu and I. Mihalcea, *Rev. Real Acad. Sci. Ex. Fis. Nat. Madrid, 64,* 1039 (1970).
22 H. Reinert and R. Weiss, *Hoppe Seyler's Z. Physiol. Chem., 350,* 1310 (1969).
23 G. Bandoli, M. Biagini Cingi, D. A. Clemente and G. Rizzardi, *Inorg. Chim. Acta, 20,* 71 (1976).
24 M. Biagini Cingi, A. Chiesi Villa, A. Gaetani Manfredotti and C. Guastini, *Cryst. Struct. Commun., 1,* 363 (1972).
25 H. J. Krentzien, M. J. Clarke and H. Taube, *Bioinorg. Chem., 4,* 143 (1975).
26 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, G. Bandoli and D. A. Clemente, *Inorg. Chim. Acta, 52,* 237 (1981).
27 H. Kothandaraman and P. Gnanasundaram, *J. Ind. Chem. Soc., 55,* 189 (1978).
28 M. Biagini Cingi, R. Borromei and L. Oleari, *J. Chem. Soc., Dalton Trans.,* 2276 (1977).
29 F. H. Herbstein and M. Kapon, *Philos. Trans. Roy. Soc. London, Ser. A, 291,* 14 (1979).
30 J. Nishijo and I. Yonetani, *J. Pharm. Sci., 71,* 354 (1982).
31 D. Cook and Z. R. Regnier, *Can. J. Chem., 45,* 2899 (1967).
32 *Idem., ibid., 46,* 3055 (1968).
33 *Idem., ibid., 45,* 2895 (1967).
34 W. Beck and N. Kottmair, *Chem. Ber., 109,* 970 (1976).
35 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *J. Inorg. Nucl. Chem., 43,* 2771 (1981).
36 C. M. Mikulski, L. Mattuci, Y. Smith, T. B. Tran and N. M. Karayannis, *Inorg. Chim. Acta, 66,* L71 (1982).
37 C. M. Mikulski, T. B. Tran, L. Mattucci and N. M. Karayannis, *Inorg. Chim. Acta, 78,* 211 (1983).
38 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 415 (1969); N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *ibid., 8,* 91 (1974).
39 E. R. Blout and M. Fields, *J. Am. Chem. Soc., 72,* 479 (1950).
40 S. Goenechea, *Mikrochim. Acta,* 276 (1972).
41 S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull., 26,* 2941 (1978).
42 R. Savoie, J.-J. Jutier, L. Prizant and A. L. Beauchamp, *Spectrochim. Acta, 38A,* 561 (1982).
43 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961); B. J. Hathaway, D. G. Holah and M. Hudson, *ibid.,* 4586 (1963).
44 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 4,* 404 (1965); S. F. Pavkovic and D. W. Meek, *ibid., 4,* 1091 (1965); M. E. Farago, J. M. James and V. C. G. Trew, *J. Chem. Soc., A,* 820 (1967).
45 C. P. Beetz, Jr. and G. Ascarelli, *Spectrochim. Acta, 36A,* 299 (1980).
46 J. R. Ferraro and A. Walker, *J. Chem. Phys., 42,* 1273, 1278 (1965).
47 B. N. Figgis and J. Lewis, *Progress in Inorg. Chem., 6,* 37 (1964).

48 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).
49 W. Pfleiderer and G. Nübel, *Justus Liebigs Ann. Chem., 647,* 155 (1961).
50 L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc., 87,* 11 (1965).
51 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.,* 1235 (1962); 3165, 5042 (1963); 1187, 4761 (1964).
52 T. Beringhelli, M. Freni, F. Morazzoni, P. Romiti and P. Servida, *Spectrochim. Acta, 37A,* 763 (1981).
53 N. B. Behrens, D. M. L. Goodgame and Z. Warnke, *Inorg. Chim. Acta, 31,* 257 (1978).
54 E. Sletten, *Acta Crystallogr., B25,* 1480 (1969).
55 P. I. Vestues and E. Sletten, *Inorg. Chim. Acta, 52,* 269 (1981).