Inorganica Chimica Acta, 67 (1982) 61–66

Lanthanide(III) and Actinide(IV) Chloride Complexes with Purine and Adenine

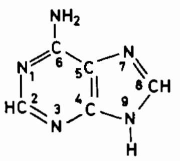
CHESTER M. MIKULSKI, SUSAN COCCO, NANCY DE FRANCO
Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038, U.S.A.
NICHOLAS M. KARAYANNIS
Amoco Chemicals Corporation, Naperville, Ill. 60566, U.S.A.

Received March 6, 1982

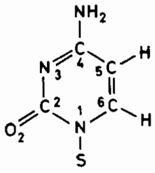
Well-defined complexes of the types $Dy(LH)LCl_2 \cdot H_2O$ and Ml_2Cl_2 (M = Th, U; LH = purine or adenine) were prepared by refluxing mixtures of purine or adenine and $DyCl_3$, $ThCl_4$ or UCl_4 in ethanol–triethyl orthoformate for 2–5 days. The new complexes, which are insoluble in organic media, were characterized by means of ir spectral and magnetic studies. Most likely structural types involve a linear polymeric backbone (–M–L–M–L– sequences) with single purine or adenine bridges. The Dy^{3+} complexes are linear polymers, containing also terminal purine or adenine, chloro and aqua ligands, whereas in the Th^{4+} and U^{4+} compounds, higher polymeric structures arising by cross-linkage of linear –M–L–M–L– units seem most probable; the only terminal ligands present in the Th^{4+} and U^{4+} complexes are chloro groups. All the new complexes are hexacoordinated. The likely binding sites of terminal unidentate and bridging bidentate purine and adenine are discussed [1].

Introduction

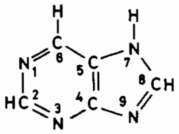
Metal complexes formed by interaction of free purinic bases with salts of a wide variety of metal ions have been quite extensively studied in recent years [2–4]. However, there is a relative paucity of information on complexes of these free bases with lanthanide and actinide ions. Thus, there is only one study in which the stability of an actinide ion (UO_2^{2+}) complex with adenine (adH, I) was correlated to those of the corresponding complexes of other metal ions, as follows: $Fe^{3+} > Cr^{3+} > Al^{3+} > UO_2^{2+} > Be^{2+} > Cu^{2+} > Ni^{2+}$ [5]. Raman and ^{13}C nmr studies of Ln^{3+} nitrate (Ln = La, Pr, Lu) interactions with various nucleosides in Me_2SO-d_6, showed detectable interaction of the hard Ln^{3+} ions with cytidine, non-detectable interaction with uridine, and weak or no interaction with adenosine and guanosine [6]; coordination of cytidine (II; S = ribose) to Ln^{3+} is through the O(2) oxygen rather than the N(3) nitrogen [6]. Lanthanide(III) [2, 4, 7, 8] and UO_2^{2+} [2, 9, 10] complexes with adenine nucleotides have been studied to a larger extent; these complexes involve exclusive coordination of the nucleotide through phosphate oxygens [2, 4, 7–10]. Following our recent studies of 3d metal complexes with purine (puH; III) [11] and adenine [12], we became interested in attempting the isolation and characterization of well-defined lanthanide(III) and actinide(IV) complexes with these free bases, which possess only nitrogen potential ligand sites. Accordingly, synthetic work aimed at the isolation of the complexes resulting by interaction of puH or adH with $DyCl_3$, $ThCl_4$ or UCl_4 was undertaken, and our results are reported in the present paper, along with the characterization of the new complexes.



(I)



(II)



(III)

Experimental

Synthetic procedures similar to those previously employed for the isolation of 3d metal complexes with adH [12] were used, *viz.*: 0.8 mmol of metal chloride hydrate were dissolved in a mixture of 15 ml triethyl orthoformate(teof) and 35 ml absolute ethanol, and the resultant solution was heated to 50–60 °C for 2 hr, under stirring. Then, 1.6 mmol puH or adH were added, and the mixture was refluxed for 2–5 days (until a substantial amount of the precipitated

0020-1693/82/0000-0000/$02.75

TABLE I. Analyses and Ambient Temperature (298 K) Magnetic Properties of the New Metal Complexes.

Complex	Color	Analysis, Found (Calc.)%					$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB
		C	H	N	Metal	Cl		
$Dy(puH)(pu)Cl_2 \cdot H_2O$	Tan	24.72	2.06	23.18	33.17	14.82	45,375	10.46
		(24.48)	(1.85)	(22.84)	(33.11)	(14.45)		
$Th(pu)_2Cl_2$	Tan	22.51	1.36	20.45	43.34	12.92	Diamagnetic	
		(22.20)	(1.12)	(20.71)	(42.88)	(13.10)		
$U(pu)_2Cl_2$	Maroon	22.13	1.01	20.59	44.03	13.24	3121	2.74
		(21.95)	(1.11)	(20.48)	(43.50)	(12.96)		
$Dy(adH)(ad)Cl_2 \cdot H_2O$	Off white	22.62	2.26	27.15	30.72	13.85	47,894	10.73
		(23.07)	(2.13)	(26.90)	(31.21)	(13.62)		
$Th(ad)_2Cl_2$	Beige	20.71	1.67	24.33	40.84	12.35	Diamagnetic	
		(21.03)	(1.41)	(24.52)	(40.62)	(12.41)		
$U(ad)_2Cl_2$	Cocoa brown	21.14	1.22	24.59	41.88	12.58	3136	2.75
		(20.81)	(1.40)	(24.27)	(41.24)	(12.28)		

TABLE II. Pertinent Infrared Data for the New Purine Complexes (cm^{-1})

puH	$M = Dy^{3+}$	$M = Th^{4+}$	$M = U^{4+}$	Band assignment[a]
	3400m, b			ν_{OH} (water)
2725s, b	2700m, b			ν_{NH}
1613vs	1608vs	1627m, 1604s	1628m, 1602s	A′ pym 8a
1568s	1555vs	1553vvs	1556vvs	A′ pym 8b
1499w	1480m, sh	1496w	1497w	A′ im R_1
1421s	1418m, sh	1438m, b	1446w	A′ im R_3
1398vs	1391s	1404m, 1390m	1387m, b	A′ pym 19a
	416m			ν_{M-O}(aqua)
	311w	266m	270m	ν_{M-Cl}
	252mw, b	243m, b	240m, b	ν_{M-N}

[a] Purine band assignment after Lautié and Novak [22]. Abbreviations: im = imidazole; pym = pyrimidine.

TABLE III. Pertinent Infrared Data for the New Adenine Complexes (cm^{-1}).

adH	$M = Dy^{3+}$	$M = Th^{4+}$	$M = U^{4+}$	Band assignment[a]
	3355ms			ν_{OH} (water)
2690w, 2600w	2680m, 2610sh			ν_{NH}
1675vs	1660vvs	1670vs	1667vvs	NH_2, sym-in-plane def.
1600vvs	1647vs, 1600vs	1645s, 1601vs	1600vs, 1643vs	A′ pym 8a
1565m, sh	1550vs	1560m, sh	1555vs	A′ pym 8b
1419ms	1402m	1402w, 1391sh	1406m	A′ im R_3
1252s	1251s	1244mw	1247m	NH_2 as out-of-plane def.
	410w			ν_{M-O} (aqua)
	307w	268m, b	269m, b	ν_{M-Cl}
	246w, b	241m, b	244m, b	ν_{M-N}

[a] Adenine band assignments based on refs. 22–24. Abbreviations as in Table II.

complex had accumulated). Subsequently, the volume of the supernatant was reduced to about one-half its original volume by heating, and the new complexes were separated by filtration, washed with ethanol-teof mixture and stored *in vacuo* over P_4O_{10}. Analytical data (Table I) indicate that the complexes are of the general type $Dy(LH)LCl_2 \cdot H_2O$ and ML_2Cl_2 (LH = puH, adH; M = Th, U). The ambient temperature (298 K) magnetic moments of the Dy^{3+} and U^{4+} complexes (Table I) were obtained by methods described elsewhere [13]. Tables II and III show pertinent infrared data for the new complexes with purine and adenine, respectively; Ir spectra were obtained on Nujol and hexachloro-1,3-butadiene mulls between IRTRAN 2 windows (4000–700 cm^{-1}) and on Nujol mulls between high-density polyethylene windows (800–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. The complexes herein reported are generally insoluble in organic media.

Discussion

Stoichiometries of the New Metal Complexes

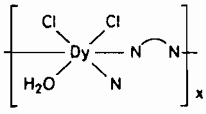
Lanthanide(III) and actinide(IV) chlorides apparently react about as readily as 3d metal chlorides or perchlorates [1, 11, 12] with puH or adH to form well-defined complexes with either exclusively anionic pu^- or ad^- (M = Th^{4+}, U^{4+}) or both neutral and anionic purine or adenine (M = Dy^{3+}). The partial substitution of chloro groups with pu^- or ad^- is due to the extended refluxing period in the synthetic step. In fact, several ad^- complexes with 3d metal perchlorates were isolated when a similar synthetic procedure was employed [12], while in the case of purine complexes with 3d metal(II) chlorides or perchlorates, $M(puH)Cl_2 \cdot xH_2O$ (x = 0–2) and $M(puH)_2(ClO_4)_2 \cdot 3H_2O$ complexes, with exclusively neutral pH, were precipitated either immediately upon mixing ethanol–teof solutions of purine and metal salt or by simply cooling the mixture of the ethanol–teof solutions of ligand and salt and adding an excess of diethyl ether [11]. The stoichiometries of the new complexes are, as already mentioned, $Dy(LH)LCl_2 \cdot H_2O$ and ML_2Cl_2 (M = Th, U; LH = puH, adH). The insolubility of these complexes in organic media, combined by the coordination number six suggested by the metal–ligand ir bands (*vide infra*), favors polymeric structures, involving bidentate bridging, N,N-bonded, purine or adenine [11, 12]. It should be mentioned here that, although rather limited interest has been displayed so far for studies of lanthanide or actinide ion complexes with nitrogen ligands, several such complexes with unidentate (*e.g.*, pyridine, piperidine [14], diakyl amines [15]) and bidentate (*e.g.*, 2,2′-bipyridine, 1,10-phenanthroline [16, 17]) N-ligands have been reported.

Characterization Studies

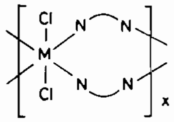
The magnetic moments (Table I) for the new Dy^{3+} complexes are within the range of normal values for this metal ion [18], while those of the U^{4+} compounds are near the spin-only value, *i.e.*, the normal region for octahedral U(IV) [19]. In view of the apparent presence of bridging purinic ligands in all the new complexes, it should be pointed out here that no evidence favoring magnetic exchange interactions would be expected for complexes of this type with paramagnetic Ln^{3+} ions, since their 4f electrons are effectively shielded [20]; but in the case of U^{4+}, whose 5f electrons are not as effectively shielded [20], the effects of magnetic exchange interactions could conceivably be observed even at room temperature. For instance, whereas polymeric Dy^{3+} complexes with multiple $-O-P(R)_2-O-$ bridging ligands exhibit normal magnetic moments, the corresponding U^{4+} complexes show subnormal moments at room temperature [18]. It was, nevertheless, previously established that polymeric puH complexes with Co^{2+}, Ni^{2+} and Cu^{2+} perchlorates are characterized by normal ambient temperature magnetic moments, and show evidence favoring magnetic exchange interactions only at temperatures below *ca.* 110 K [11]; these complexes were considered as involving single (–M–puH–M–puH– sequences) rather than multiple puH bridges, on the basis of the preceding evidence [11]. Hence, the normal room temperature paramagnetism of the new U^{4+} complexes was not unexpected.

As regards the ir evidence (Tables II, III), the new Dy^{3+} complexes show the characteristic ν_{OH} band of water [21], as well as the ν_{NH} mode of neutral puH or adH (protonation site discussed later) [22]. Neither of these bands is present in the spectra of the new Th^{4+} and U^{4+} complexes, as would be anticipated for water-free products, containing exclusively anionic, monodeprotonated pu^- or ad^-. Various pyrimidine and imidazole vibrations undergo shifts and occasional splittings in the spectra of the purine [22] and adenine [22–24] metal complexes. This may be taken as supporting the presence of bidentate bridging ligands in the compounds under study [11, 12, 22–24]. Regarding the NH_2 deformation modes of adenine, only very small shifts are observed upon metal complex formation (Table III), indicating that the NH_2 nitrogen is not involved in coordination [12, 23, 24]. The tentative Dy-ligand band assignments of Tables II and III ν_{Dy-O} at 416–410 cm^{-1} [25], ν_{Dy-Cl} at 311–306 and ν_{Dy-N} at 252– 246 cm^{-1} [26, 27]) are generally in favor of coordination number six for the Dy^{3+} ions, and the exclusive presence of terminal chloro ligands [25–27]. The location of ν_{M-Cl} (M = Th, U) at 270–266 cm^{-1} also favors coordination number six and exclusively terminal Cl ligands for the new actinide(IV) complexes [28, 29]. The ν_{M-N} (M = Th, U) band assignments at 244–240 cm^{-1} seem reasonable for hexacoordinated Th^{4+} and U^{4+} complexes, involving coordination of ring nitrogens of heterocyclic ligands. Although no ν_{M-N} data for actinide(IV) complexes with ligands of this type have been published, a fair estimate of the wavenumber range for this mode can be made from the ν_{M-N} location in hexacoordinated aromatic N-ligand complexes of another M^{4+} ion, which exhibits the metal–nitrogen stretch in the same region as Th^{4+} and U^{4+} in complexes with nitrogen ligands of different types. Thus, for instance, ν_{M-N} appears at 540 cm^{-1} in $Th(NEt_2)_4$ [15a] and at 535 cm^{-1} in $Sn(NMe_2)_4$ [30], while the hexacoordinated Sn-(bipy)X_4 chelates (bipy = 2,2′-bipyridine; X = Cl, Br, I) show ν_{Sn-N} bands in the 260–250 cm^{-1} region [31], which is quite close to the region of our tentative ν_{M-N} (M = Th, U) band assignments in the present work.

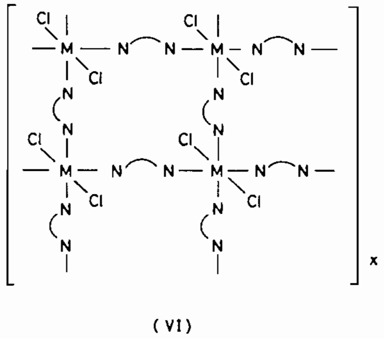
The new Dy^{3+} complexes must involve both terminal unidentate and bridging bidentate ligands (designated as N and N⌒N, respectively), in order to be hexacoordinated, a single-bridged, linear, chainlike polymeric structural type(IV), similar to those previously postulated for many 3d metal complexes with purine and adenine, seems most likely for these compounds. In the case of the Th^{4+} and U^{4+} complexes, both of the purinic ligands would be bidentate, the double-bridged linear polymeric structure (V) is the simplest, but a more complicated cross-linked structural type, such as (VI), which involves crosslinkage between single-bridged –M–L–M–L– sequences, may be more compatible with the normal room temperature magnetic moments of the U^{4+} complexes [11, 12].



(IV)



(V)



(VI)

Numerous crystal structure determinations of metal complexes with adenine (neutral, anionic or the adeninium cation, adH_2^+) have established that, when functioning as terminal unidentate, this ligand usually coordinates through N(9) [3, 32–34] (the only reported exception being $Zn(adH_2)Cl_3$, in which the cationic ligand coordinates through N(7) to Zn^{2+} [35]). When acting as bridging bidentate, adenine has been found to coordinate through N(3), N(9) in Cu^{2+} complexes [32, 36, 37] and through N(7), N(9) in CH_3Hg^+ complexes [38]; whereas in the first established example of a complex with tridentate bridging adenine (μ-(adeninato)tris(methylmercury(II)perchlorate)), the binding sites of the ligand are N(3), N(7) and N(9) [39]. The recent work of Beauchamp *et al.* on CH_3Hg^+ complexes with adenine and 9-methyladenine has demonstrated that any of the five nitrogens of adenine (*i.e.*, N(1), N(3), N(6), N(7), N(9)) can function as a binding site, provided that steric effects do not hinder its coordination to a metal ion [39]. On the basis of the preceding discussion and our previous work on adenine 3d metal complexes [12], the most likely binding sites in the new adenine complexes are N(9) for the unidentate (M = Dy^{3+}) and either the N(3), N(9) or the N(7), N(9) combination for the bidentate bridging ligands. Coordination through the N(6)(NH_2) nitrogen was ruled out by the ir evidence (*vide supra*), whilst the N(1), N(9) combination is less likely than the above combinations [3, 32, 36–39].

In the case of purine metal complexes, a monomeric Cu^{2+} complex of the purinium cation (puH_2^+) was found to involve coordination through the N(3) pyrimidine nitrogen [40], while the fairly recent crystal structure determination of $[Cu(puH)(OH_2)_4](SO_4)\cdot 2H_2O$ established the polymeric single-bridged character of this compound, in which neutral purine functions as bidentate bridging, coordinating through the two imidazole (N(7), N(9)) nitrogens, with the labile proton attached to the N(1) pyrimidine nitrogen [41]. The latter determination [41] confirms our conclusion that polymeric 3d metal complexes with purine or adenine involve single ligand bridges between adjacent metal ions [11, 12], but shows that bridging is through N(7), N(9) rather than through N(3), N(9), at least in the purine complexes of this type [11, 41]. Regarding terminal unidentate purine ligands, the most likely binding site is considered to be the imidazole nitrogen which is protonated in neutral puH [3]. Although a crystal structure determination of puH places the labile proton at N(7) in the crystal [42], it is equally well established from ^{13}C nmr studies that the N(7)-H and N(9)-H tautomers of this compound are of comparable energies [43]. Consequently, the terminal purine ligand in the Dy^{3+} complex would be equally likely to coordinate through N(7) or N(9) [44]. On the other hand, the most probable binding sites of the bidentate bridging purine present in all three of the new complexes with this ligand are the two imidazole N(7) and N(9) nitrogens, in view of the above-mentioned demonstration of the coordination of bridging purine through these sites in a single-bridged polymeric Cu^{2+} complex [41]. However, the possibility of coordination of bidentate purine through one pyrimidine and one imidazole nitrogen (*i.e.*, N(1), N(7) or N(3), N(9) combinations) can not be ruled out, since it is by now well established that a given bidentate purine ligand may be coordinating through a pair of nitrogen sites in its bi- or poly-nuclear Cu^{2+} complexes (N(3), N(9) for L = adenine [32, 36, 37] and N(7), N(9) for L = purine [41])), but may use a different pair of nitrogen sites in its corresponding complexes with other metal ions (*e.g.*, methylmercury(II) complex with adenine, which involves coordination of the bidentate ligand through N(7) and N(9) [38]).

A final point of interest concerns the ν_{NH} band assignment for the neutral ligand in the Dy^{3+} complexes. In previous work we had assumed that in 3d metal complexes with neutral uni- or bi-dentate puH or adH, the labile proton resides on a non-coordinated imidazole nitrogen, so that the above vibration is ν_{NH}(im) [11, 12]. Nevertheless, the recent work of Vestues and Sletten established that neutral bidentate purine, in the N(1)-protonated tautomeric form, coordinates through N(7), N(9) in a $CuSO_4$ complex [41]; thus, some of our previous ν_{NH} assignments in purine complexes (11) were actually for ν_{NH}(pym) modes, which may occur at *ca.* 2700 cm^{-1} (*e.g.*, one of the ν_{NH} modes of cytosine [45]). In the new Dy^{3+} complexes, if neutral puH or adH functions as terminal unidentate or bridging bidentate, N(3), N(9)- or N(1), N(7)-bonded, the labile proton will be still attached on one imidazole nitrogen, but if the ligand acts as bidentate N(7), N(9)-bonded, the proton will be attached on the N(1) pyrimidine nitrogen.

References

1 C. M. Mikulski, S. Cocco, N. DeFranco and N. M. Karayannis, *Abstracts, the 28th IUPAC Congress, Vancouver,* British Columbia, Canada, Aug 16–21, 1981, No IN 156.

2 R. M. Izatt, J. J. Christensen and J. H. Rytting, *Chem. Rev., 71,* 439 (1971)

3 D. J Hodgson, *Progress in Inorg. Chem., 23,* 211 (1977).

4 L. G. Marzilli, *Progress in Inorg Chem., 23,* 255 (1977).

5 R. Nayan and A. K. Dey, *Z Naturforsch., 27b,* 688 (1972).

6 L. G. Marzilli, B. deCastro, J. P. Caradonna, R. C. Stewart and C P. van Vuuren, *J. Am. Chem. Soc., 102,* 916 (1980).

7 D. K Lavallee and A. H. Zeltman, *J. Am. Chem. Soc., 96,* 5552 (1974).

8 G. V. Fazakerley, J. C Russell and M. A. Wolfe, *Chem. Commun.,* 527 (1975), G. V. Fazakerley and D. G. Reid, *Europ. J. Biochem., 93,* 535 (1979).

9 K. E. Rich, R. T. Agarwal and I. Feldman, *J. Am. Chem. Soc., 92,* 6818 (1970).

10 A. Terron and V. Moreno, *Inorg. Chim. Acta, 56,* L57 (1981).

11 A N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta, 46,* 235 (1980), *Inorg. Chem., 19,* 3491 (1980).

12 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta, 37,* L551 (1979); *I. Inorg. Nucl. Chem., 43,* 2771 (1981); A. N. Speca, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Inorg. Chim. Acta, 66,* L53 (1982).

13 N. M. Karayannis, L. L. Pytlewski and M. M. Labes, *Inorg. Chim. Acta, 3,* 415 (1969).

14 E. M. Kirmse and U. Schilbach, *Z. Chem., 7,* 238 (1967).

15 a. D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc., A,* 980 (1969); b. R. A. Andersen, *Inorg. Chem., 18,* 1507 (1979).

16 F. A. Hart and F. P. Laming, *J. Inorg. Nucl. Chem., 26,* 579 (1964); *27,* 1605, 1825 (1965).

17 B. W. Fitzsimmons, P. Gans, B. C. Smith and M. A. Wassef, *Chem. Ind. (London),* 1698 (1965), G. D. Piero, G. Perego, A. Zazzetta and G. Brandi, *Cryst. Struct. Commun., 4,* 521 (1975).

18 C. M. Mikulski, N. M. Karayannis and L. L. Pytlewski, *J. Inorg. Nucl. Chem., 36,* 971 (1974); C. M. Mikulski, N. Harris, P. Sanford, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *ibid., 43,* 2753 (1981).

19 B. Jeżowska-Trzebiatowska and K. Bukietynska in 'Theory and Structure of Coordination Compounds', pp. 311–314, MacMillan, N. Y. (1964); G. A. Candella, C. A. Hutchison and W. B. Lewis, *J. Chem. Phys., 30,* 246 (1959).

20 C. Wiedenheft, *Inorg. Chem., 8,* 1174 (1969).

21 I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta, 20,* 429 (1964)

22 A. Lautié and A. Novak, *J. Chim. Phys. Physicochim. Biol., 65,* 1359 (1968), *68,* 1492 (1971).

23 J. Brigando and D. Colaitis, *Bull. Soc. Chim. France,* 3445, 3449 (1969).

24 T. Fujita and T. Sakaguchi, *Chem. Pharm. Bull., 25,* 1055, 1694, 2419 (1977).

25 C. Postmus and J. R. Ferraro, *J. Chem. Phys., 48,* 3605 (1968).

26 J. R. Ferraro, L. J. Basile and D. L. Kovacic, *Inorg. Chem., 5,* 391 (1966).

27 D. M. Adams and D. M. Morris, *J. Chem. Soc., A,* 694 (1968), N. P. Crawford and G. A. Melson, *ibid., A,* 427 (1969).

28 D. M. Adams, J. Chatt, J. M. Davidson and J. Gerratt, *J. Chem. Soc.,* 2189 (1963).

29 J. Goffart, J. Fuger, B. Gilbert and G. Duyckaerts, *Inorg. Nucl. Chem. Lett., 11,* 569 (1975).

30 H. Buerger and W. Sawodny, *Inorg. Nucl. Chem. Lett., 2,* 209 (1966).

31 M. F. Farona and J. C. Grasselli, *Inorg. Chem., 6,* 1675 (1967).

32 P. deMeester and A. C. Skapski, *J. Chem. Soc., A,* 2167 (1971); *Dalton Trans.,* 2400 (1972); 424, 1596 (1973); P. deMeester, D. M. L. Goodgame, K. A. Price and A. C. Skapski, *Nature, 229,* 191 (1971).

33 T. J. Kistenmacher, *Acta Crystallogr., B30,* 1610 (1974); T. J. Kistenmacher, L. G. Marzilli and C.-H. Chang, *J. Am. Chem. Soc., 95,* 5817 (1973).

34 H. Sakaguchi, H. Anzai, K. Furuhata, H. Ogura, Y. Iitaka, T. Fujita and T. Sakaguchi, *Chem. Pharm. Bull., 26,* 2465 (1978).

35 L Srinivasan and M. R. Taylor, *Chem. Commun.,* 1668 (1970); M. R. Taylor, *Acta Crystallogr., B29,* 884 (1973).

36 E Sletten, *Acta Crytallogr., B25,* 1480 (1969).

37 A. Terzis, A. L. Beauchamp and R. Rivest, *Inorg. Chem., 12,* 1166 (1973).

38 L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, *J. Am. Chem. Soc., 101,* 2765 (1979), A. L. Beauchamp, *J. Cryst. Mol. Struct., 10,* 149 (1980).

39 J. Hubert and A. L. Beauchamp, *Can. J. Chem., 58,* 1439 (1980), *Acta Crystallogr., B36,* 2613 (1980).

40 W. S. Sheldrick, *Acta Crystallogr., B37,* 945 (1981).

41 P. I. Vestues and E. Sletten, *Inorg. Chim. Acta, 52,* 269 (1981).

42 D. G. Watson, R. M. Sweet and R. E. Marsh, *Acta Crystallogr., 19,* 573 (1965).

43 R. J. Pugmire and D. M. Grant, *J. Am. Chem. Soc., 93,* 1880 (1971); M.-T. Chenon, R. J. Pugmire, D. M. Grant, R. P. Panzica and L. B. Townsend, *ibid., 97,* 4636 (1975).

44 C. M. Mikulski, R. DePrince, T. B. Tran and N. M. Karayannis, *Inorg. Chim. Acta, 56,* 27 (1981).

45 S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull., 26,* 2941 (1978).