Tetrahedral 1:1 Adducts of Guanine with Cobalt(II), Copper(II) and Zinc(II) Chlorides

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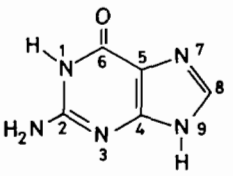
Abstract

Adducts of the $M(guH)Cl_2$ type were prepared by refluxing 2:1 molar mixtures of guanine (guH) and MCl_2 (M = Co, Cu, Zn) in ethanol–triethyl orthoformate for 2–3 days. Characterization studies suggest that all three new complexes involve distorted tetrahedral configurations. A linear chainlike polymeric structural type with a single-bridged $\{M\text{-}guH\}_n$ backbone and two terminal chloro ligands per metal ion (MN_2Cl_2 chromophore) is proposed for these compounds, in view of their poor solubility in organic media, their stoichiometry in conjunction with their tetrahedral symmetry, and the reported crystal structures of 9-methyladenine analogs (M = Co, Zn), which are polymeric with single bridges of the adenine derivative between adjacent metal ions. Bidentate bridging guH coordinates exclusively through ring nitrogens, and is most probably N(7), N(9)-bonded. The possibility of use of exocyclic potential ligand sites of guH (C=O oxygen or NH_2 nitrogen) in coordination is ruled out by the infrared evidence [1].

Introduction

Previous work in these laboratories has dealt with guanine (guH; **I**) complexes with 3d metal perchlorates [2, 3] and with a number of M^{3+} (M = Al [4], Cr, Fe [5], V [6], Dy [7]) and M^{4+} (M = Th, U) [7] chlorides and $VOCl_2$ [5]. The synthetic procedure employed in these studies involved refluxing mixtures of ligand and metal salt in ethanol–triethyl orthoformate (teof), until a sufficient amount of the solid metal complex was accumulated [2–7]. Under these rather drastic preparative conditions, some metal perchlorates or chlorides yielded adducts of neutral guH [2, 3, 5], while other of these salts produced complexes involving substitution of monodeprotonated anionic gu^- for ClO_4^- or Cl^- groups [2–4, 6, 7]. Similar trends were observed during a recent study of the preparation of guanine complexes with divalent 3d metal chlorides (M = Mn, Fe, Co, Ni, Cu, Zn) [1]. Co^{2+}, Cu^{2+} and Zn^{2+} chlorides formed 1:1 adducts of neutral guH after 2–3 days of refluxing 2:1 molar mixtures of guH and MCl_2 in ethanol–teof. The present paper deals with the syntheses and characterization of these adducts. On the other hand, during Mn^{2+}, Fe^{2+} or Ni^{2+} chloride reaction with guH, under the same conditions, formation of sufficient for characterization work quantities of solid metal complexes was considerably slower (1–2 weeks), and the complexes isolated were products of partial substitution of Cl^- by gu^- ligands, and contained also aqua or ethanol ligands; studies of the latter compounds are still in progress and will be reported in the near future.



I

As regards other studies of guanine metal complexes, early work had dealt with Hg^{2+} [8], Cu^{2+} [9–12] and Ag^+ [13] complexes, while the crystal structure determinations of metal complexes of the guaninium cation (guH_2^+) revealed that both $[Zn(guH_2)Cl_3]$ [14] and $[Cu(guH_2)Cl_3]\cdot 2H_2O$ [15, 16] contain terminal unidentate N(9)-bonded guH_2^+. The possibilities of ligand chelation through N(3), N(9) [17] or O(6), N(7) [18, 19] and bridging through O(6), N(7) [20] have been advanced for a number of metal complexes with guanine or derivatives. Other guanine complexes recently reported include $Cu(guH_2)X_3$ (X = F, Cl, Br) [21], $(guH_2)_4Mo_8O_{26}\cdot 4H_2O$ [22], as well as gu^- complexes with

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TABLE I. Analytical Data for $M(guH)Cl_2$ Complexes.

M	Color	C%		H%		N%		M%		Cl%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Co	Blue	21.37	21.64	1.79	1.96	24.93	25.11	20.98	21.21	25.24	24.97
Cu	Green	21.02	20.60	1.76	1.87	24.52	24.81	22.25	22.53	24.83	25.06
Zn	Light beige	20.90	20.82	1.75	2.02	24.37	24.15	22.74	23.03	24.67	24.48

TABLE II. Infrared Spectra of guH and the $M(guH)Cl_2$ Complexes (cm^{-1}).[a]

guH[b]	M = Co	M = Cu	M = Zn	Band assignment
3330s, 3290s,sh, 3160s	3340vs, 3300s, sh, 3160s	3340vs, 3295s, sh, 3155s	3335vs, 3290s, sh, 3150s	ν_{NH_2}
3000s, 2900s, 2850s, 2700s,b	3020s, 2900s, 2845s, 2690s	3040s, 2910s, 2850s, 2695s	3010s, 2905s, 2845s, 2680s	ν_{NH}
1705s	1698vs	1700vs	1692vs	$\nu_{C=O}$
1680s	1673vs	1670vs	1669vs	δ_{NH_2}, scissoring
1635s,sh, 1575m,b	1638s, 1606s, 1568m	1640svs, 1609s, sh, 1572ms	1635s, 1602s, sh, 1567m,sh	$\nu_{C=C} + \nu_{C=N}$
1563m	1559m, 1545m	1560ms, 1549m,sh	1556ms, 1542m,sh	δ_{NH}
1477m, 1464m, 1418m, 1375m	1471m, 1457m, 1411mw, 1370s	1478m, 1460m, 1413mw, 1370s	1470ms, 1457m, b, 1410mw, 1366s	Ring vibrations
1263m	1258m	1260m	1254m	ν_{C-N}
1209m, 1169m	1205w,b 1166m	1210mw, 1169m	1205mw, 1163mw	Ring vibrations
1107m	1110m,b	1110m,b	1108mw	δ_{NH_2}, rocking
1042w	1035w,b	1040w,b	1033w,b	
930w	936w	940mw	936mw	Ring vibration
880m, 851m, 781m, 730w	863m, 833m, 782m,b, 740w	866mw, 840m, 770m,b 745w,sh	861mw, 837m, 775m,b, 740w,sh	$\delta_{NH} + \delta_{CH}$
705m, 689m	690w, 682w	692w, 677w	689w, 671w	Ring vibrations
640m	637w,b	633w,b	632m,b	δ_{NH_2}, wagging
608m, 570m, 544w, 515w, 506w, 440w, 370w, 345w,b	590w, 565w, 541w, 522w, 502vw, 490w, 450vw, 381mw, 340w	590w, 560w, 547w, 528w, 501w, 490w, b, 450w,sh, 381mw, 345w,sh	590mw, 560w, 540w, 522w, 488w,vb, 447w, sh, 379mw, 339w,sh	ν_{Ligand} (600–300 cm^{-1})
	354w, 318w	329w, 313w,sh	323w, 305w,sh	ν_{M-Cl}
	288w, 246w	292w, 253w,b	283w, 236w,b	ν_{M-N}

[a]The spectra of the $M(guH)Cl_2$ complexes are devoid of ν_{OH} bands (3500–3300 cm^{-1}); thus, additional ligands, such as water or ethanol [2–7], are absent from these complexes. [b]Free guH band assignments after Shirotake and Sakaguchi [36].

Mo, Rh and Ir carbonyls and bis(tri-n-butylphosphine)Pd(II) [23]. With respect to substituted guanines, 9-substituted derivatives, including nucleosides and nucleotides, tend to coordinate through N(7) [24–28], whilst 7,9-disubstituted guanines use N(1) as their binding site [29].

Experimental

The synthetic procedure employed involved admixing 0.8 mmol MCl_2 (M = Co, Cu, Zn) and 1.6 mmol guH, addition of 50 ml of a 7:3 (v/v) mixture of ethanol–teof, and refluxing of the resultant mixture for 2–3 days. Following the refluxive step, the mixture was allowed to cool and the solid complexes were separated by filtration, washed with ethanol–teof on the filter and stored *in vacuo* over P_4O_{10}. The new complexes, which were obtained in yields of 50–75% of the theoretical, are of the general $M(guH)Cl_2$ type (Table I). They are very sparingly soluble in organic media. Infrared spectra (Table II) were recorded on KBr pellets and on Nujol and hexachloro-1,3-butadiene mulls between NaCl windows (4000–500 cm^{-1}), as well as on Nujol mulls between high density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin–Elmer 621 spectrophotometer. Solid-state

TABLE III. Solid-state (Nujol mull) Electronic Spectra and Magnetic Properties (298 K) of $M(guH)Cl_2$ Complexes.

M	λ_{max}, nm[a,b]	$10^6\ \chi_M^{cor}$, cgsu	μ_{eff}, μB
Co	200vs, 222vs, 257vvs,b, 286vvs,b, 306vvs,sh, 320vvs, 344vvs, 555s,b 618s,b, 657ms, 699ms,sh, (930mw,b, 1325mw,b), 1390mw,b, 1620w,b 1875w,b, 2150mw	8144	4.42
Cu	201vvs, 225vvs, 253vs, 283vs, 311vs, 323vs, 349s, 715ms,b, 808ms,vb (935m,b, 1340mw,b)	1521	1.91
Zn	198vvs, 225vvs,sh, 254vs,b, 284vs,b, 314vs, 351s,sh, (925mw,b, 1330w,b)	Diamagnetic	

[a]Solid-state (Nujol mull) UV spectrum of guH, nm: 202vvs, 245vs, 276vs,b, 330ms,sh. Aqueous solution spectrum (pH 6.0–6.2) from literature, λ_{max}, nm (log ϵ): 245–246 (4.01–4.04), 274–275 (3.89–3.92) [44, 45]. [b]Most prominent near-IR bands of free guH, attributable to vibrational overtones and combination modes of the ligand [32]: 920w,b, 1310w,b. These bands appear slightly shifted in the spectra of the complexes, and are shown in parentheses in the Table.

(Nujol mull) electronic spectra and magnetic susceptibility measurements at 298 K (Table III) were obtained by using apparatus and techniques described elsewhere [30].

Discussion

The 1:1 adducts of guH with $CoCl_2$, $CuCl_2$ and $ZnCl_2$ are obtained regardless of whether anhydrous or hydrated metal chlorides are used as starting materials for their preparation. The adducts are water- or ethanol-free, as demonstrated by both the analytical data and the absence of ν_{OH} bands in their IR spectra. Similar 1:1 adducts of the chlorides or bromides of the same metal ions with adenine (adH), adenosine (ado) [31] and 9-methyladenine (mad) [32, 33] have been synthesized either by refluxing mixtures of ligand and salt in ethanol [31, 32] or by combining hot ethanol solutions of ligand and salt [33]. On the other hand, use of the synthetic method described in the experimental section for the preparation of adH complexes with divalent 3d metal chlorides (M = Mn, Fe, Co, Ni, Cu, Zn) led invariably to the isolation of complexes involving partial substitution of ad^- for Cl^- groups rather than $M(adH)Cl_2$ adducts [34]. It is, thus, of some interest that guH, upon interaction with MCl_2 at the reflux temperature of the ethanol–teof mixture, readily affords 1:1 adducts when M = Co, Cu, Zn, while with M = Mn, Fe, Ni it reacts forming products of partial substitution of gu^- for Cl^- anions, precipitated at a considerably slower pace. Apparently, the guH adducts with Mn^{2+}, Fe^{2+} and Ni^{2+} chlorides, which are presumably formed at the early stages of the refluxive step, are not stable under the conditions of our synthetic experiments, and undergo anionic ligand exchange reactions rather than being precipitated as such [2, 3, 35].

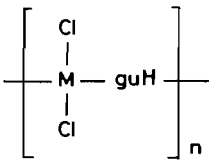
The response of the various vibrational modes of guH [36–38] to MCl_2 adduct formation is generally similar to that previously observed for adducts of this ligand with 3d metal perchlorates [2, 3] and VO^{2+}, Cr^{3+} and Fe^{3+} chlorides [5]. Bands associated with vibrations of the potentially ligating exocyclic substituents of guH (*i.e.*, the amino group nitrogen at C(2) and the carbonyl oxygen at C(6)) [36–38] are rather insensitive to MCl_2 (M = Co, Cu, Zn) adduct formation, so that it can be concluded that these sites do not participate in coordination [2–7, 22, 23, 36]. More significant shifts and occasional splittings are shown by several $\nu_{C=C}$, $\nu_{C=N}$ and ring vibrations of guH upon formation of the adducts herein reported, as would be expected for complexes involving binding of the ligand through one or more ring nitrogens [2–7, 22, 23, 34, 36]. The bands tentatively assigned as ν_{M-Cl} and ν_{M-N} are generally compatible with tetracoordinated configurations for the central metal ions [31–33, 39–43]. The location of the ν_{M-Cl} absorptions is consistent with the presence of two terminal chloro ligands per metal ion [31–33, 39–43].

The UV spectrum of free guH ($\pi \rightarrow \pi^*$ transitions at 245, 276 nm, with the $n \rightarrow \pi^*$ transition band masked) [2, 3, 44, 45] shows shifts of both $\pi \rightarrow \pi^*$ transition bands toward lower energies upon MCl_2 adduct formation (Table III). The $n \rightarrow \pi^*$ transition appears at 306–314 nm in the spectra of the complexes [2, 3, 46]. The spectra of the Co^{2+} and Cu^{2+} complexes are also characterized by strong metal to ligand charge-transfer absorption [47], originating in the UV and trailing off into the visible region. All three adducts exhibit near-IR bands at 925–935 and 1325–1340 nm, which are due to vibrational overtones and combination modes originating from guH [32]; maxima at 920 and 1310 nm are observed in the spectrum of free guH. The d–d transition spectrum of $Co(guH)Cl_2$ is compatible with a distorted tetrahedral configuration, *viz.*, nm: $^4A_{2g} \rightarrow {}^4T_{1g}(P)$ appears as a strong multicomponent peak at 555–699; $\rightarrow {}^4T_{1g}(F)$ 1390, 1620, 1875; $\rightarrow {}^4T_{2g}$ 2150 [31–33]. Co^{2+} and Zn^{2+} chlorides often

form isomorphous tetrahedral complexes with a variety of ligands, which include nucleobases and derivatives [31–33]. Crystal structure determinations have been reported for $M(mad)Cl_2$, where M = Co [48] or Zn [49]. Both these complexes are linear chainlike polymers, with the metal ion tetrahedrally coordinated by two terminal chloro ligands and the N(1) and N(7) nitrogens of bidentate bridging mad [48, 49]. Analogous structural types are most probable for the Co^{2+} and Zn^{2+} adducts under study; however, guH would use N(9), which is not blocked as in mad, as one of its binding sites (*vide infra*). As regards tetracoordinated Cu^{2+} complexes with nucleobases and derivatives, both square-planar complexes exhibiting the d–d band maxima at 550–700 nm [32, 33, 50] and very distorted tetrahedral species showing d–d maxima at 730–920 nm [11, 31–33, 50] were reported. The spectrum of the new Cu^{2+} complex shows maxima at 715 and 808 nm, so that it probably involves a severely distorted tetrahedral symmetry [11, 31–33, 50].

The room temperature magnetic moments of the complexes (Table III) are in the normal regions for high-spin tetrahedral Co^{2+} or for Cu^{2+} compounds [51]. This does not exclude polymeric structural types. In fact, linear chainlike polymeric single-bridged purine complexes with Co^{2+}, Ni^{2+} and Cu^{2+} perchlorates reportedly exhibit normal ambient temperature magnetic moments, but show evidence in favor of magnetic exchange interactions at lower temperatures (below 120 K) [52]. Similar trends have been also reported for various linear polymeric single-bridged Cu^{2+} complexes with diazine (including purines) and related bridging ligands [53–55].

As pointed out above, the three distorted tetrahedral new complexes are probably linear chainlike polymers of type **II** (MN_2Cl_2 absorbing species), in view of their poor solubility in organic media, their stoichiometry, which involves only three ligands per metal ion, while the coordination number is four, and the reported crystal structures of the mad Co^{2+} and Zn^{2+} analogs [48, 49]. Regarding the binding sites of bridging guH in the new adducts, it is generally recognized that purines tend to coordinate through the imidazole nitrogen which is protonated in the free base, and that the imidazole nitrogens are preferred over the pyrimidine nitrogens as binding sites [56]. Free guH is protonated at N(9) and N(1) [57]. Hence, N(9) would certainly be one of the binding sites of bidentate bridging guH [14–16, 56]. As far as the second binding site of bidentate guH is concerned, the N(3), N(9) [58–60] and N(7), N(9) [61–63] combinations have been established for various complexes with bridging purines; the N(1), N(9) combination is less likely. It is most probable that N(7) functions as the second guH binding site in the new complexes, in view of the recently elucidated structure of $[Cu(puH)(OH_2)_4]\cdot SO_4\cdot 2H_2O$, which is linear chainlike polymeric with N(7), N(9)-bonded bridging purine ligands [61], and the fact that the presence of the NH_2 group at C(2) may be introducing sufficient steric hindrance as to impede the coordination of guH through N(3) [2–7, 63].



II

References

1 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Abstracts, the 185th Natl. Meetg., Am. Chem. Soc.*, Seattle, Washington, March 20–25, 1983, No. INOR 167.
2 C. M. Mikulski, L. Mattucci, Y. Smith, T. B. Tran and N. M. Karayannis, *Inorg. Chim. Acta, 80,* 127 (1983).
3 C. M. Mikulski, T. B. Trân, L. Mattucci and N. M. Karayannis, *Inorg. Chim. Acta, 78,* 211 (1983).
4 C. M. Mikulski, S. Cocco, L. Mattucci, N. DeFranco, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 67,* 173 (1982).
5 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 92,* 275 (1984).
6 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 92,* L29 (1984).
7 C. M. Mikulski, L. Mattucci, L. Weiss and N. M. Karayannis, *Inorg. Chim. Acta, 92,* 181 (1984).
8 I. Bayer, E. Posgay and P. Majlát, *Pharm. Zentralhalle, 101,* 476 (1962).
9 R. Weiss and H. Venner, *Hoppe Seyler's Z. Physiol. Chem., 340,* 138 (1965).
10 D. Crăciunescu and A. Fruma, *Inorg. Chim. Acta, 4,* 287 (1970).
11 D. Crăciunescu and I. Mihalcea, *Rev. Acad. Cienc. Exactus Fis. Nat. Madrid, 64,* 1039 (1970).
12 A. T. Tu and C. G. Friederich, *Biochemistry, 7,* 4367 (1968).
13 A. T. Tu and J. A. Reinosa, *Biochemistry, 5,* 3375 (1966).
14 L. Srinivasan and M. R. Taylor, *Chem. Commun.*, 1668 (1970).
15 J. A. Carrabine and M. Sundaralingam, *J. Am. Chem. Soc., 92,* 369 (1970).
16 J. P. Declercq, M. Debbaudt and M. van Meersche, *Bull. Soc. Chim. Belg., 80,* 527 (1971).
17 B. Jeżowska-Trzebiatowska, A. Antonów, H. Kozłowski and T. Cukierda, *Bull. Acad. Pol. Sci., Ser. Sci. Chim., 22,* 1087 (1974).
18 N. Hadjiliadis and T. Theophanides, *Inorg. Chim. Acta, 15,* 167 (1975).
19 G. Pneumatikakis, N. Hadjiliadis and T. Theophanides, *Inorg. Chem., 17,* 915 (1978).
20 H. C. Nelson and J. F. Villa, *J. Inorg. Nucl. Chem., 42,* 133 (1980).
21 J. F. Villa, R. Doyle, H. C. Nelson and J. L. Richards, *Inorg. Chim. Acta, 25,* 49 (1977).
22 P. Piperaki, N. Katsaros and D. Katakis, *Inorg. Chim. Acta, 67,* 37 (1982).

23 W. Beck and N. Kottmair, *Chem. Ber., 109,* 970 (1976).
24 R. W. Gellert and R. Bau, *J. Am. Chem. Soc., 97,* 7379 (1975).
25 R. E. Cramer and P. L. Dahlstrom, *J. Clin. Hematol. Oncol., 7,* 330 (1977).
26 M. Authier-Martin, J. Hubert, R. Rivest and A. L. Beauchamp, *Acta Crystallogr., Sect. B:, 34,* 273 (1978).
27 A. J. Canty, R. S. Tobias, N. Chaichit and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.,* 1693 (1980).
28 G. Makrigiannis, P. Papagiannakopoulos and T. Theophanides, *Inorg. Chim. Acta, 46,* 263 (1980).
29 B. de Castro, C. C. Chiang, K. Wilkowski, L. G. Marzilli and T. J. Kistenmacher, *Inorg. Chem., 20,* 1835 (1981).
30 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, *Inorg. Chim. Acta, 8,* 91 (1974).
31 T. Beringhelli, M. Freni, F. Morazzoni, P. Romiti and R. Servida, *Spectrochim. Acta, Part A:, 37,* 763 (1981).
32 M. A. Guichelaar and J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 97,* 295 (1978).
33 N. B. Behrens, D. M. L. Goodgame and Z. Warnke, *Inorg. Chim. Acta, 31,* 257 (1978).
34 C. M. Mikulski, S. Cocco, N. DeFranco, T. Moore and N. M. Karayannis, *Inorg. Chim. Acta, 106,* 89 (1985).
35 C. M. Mikulski, R. DePrince, T. B. Tran, F. J. Iaconianni, L. L. Pytlewski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta, 56,* 163 (1981).
36 S. Shirotake and T. Sakaguchi, *Chem. Pharm. Bull., 26,* 2941 (1978).
37 E. R. Blout and M. Fields, *J. Am. Chem. Soc., 72,* 479 (1950).
38 J.-M. Delabar and M. Majoube, *Spectrochim. Acta, Part A:, 34,* 129 (1978).
39 R. H. Nuttall, *Talanta, 15,* 157 (1958).
40 R. J. H. Clark and C. S. Williams, *Chem. Ind. (London),* 1317 (1964); *Inorg. Chem., 4,* 350 (1965).
41 N. S. Gill and H. J. Kingdon, *Aust. J. Chem., 19,* 2197 (1966).
42 J. R. Allan, D. H. Brown, R. H. Nuttall and D. W. A. Sharp, *J. Chem. Soc. A:,* 1031 (1966).
43 A. N. Speca, C. M. Mikulski, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chim. Acta, 46,* 235 (1980).
44 S. F. Mason, *J. Chem. Soc.,* 2071 (1954).
45 W. Pfleiderer, *Justus Liebigs Ann. Chem., 647,* 167 (1961).
46 L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc., 87,* 11 (1965).
47 A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.,* 1235 (1962); 3156, 5042 (1963); 1187, 4761 (1964).
48 P. de Meester, D. M. L. Goodgame, A. C. Skapski and Z. Warnke, *Biochim. Biophys. Acta, 324,* 301 (1973).
49 M. J. McCall and M. R. Taylor, *Acta Crystallogr., Sect. B:, 32,* 1687 (1976).
50 C. M. Mikulski, T. B. Tran, L. Mattucci and N. M. Karayannis, *Inorg. Chim. Acta, 78,* 269 (1983).
51 B. N. Figgis and J. Lewis, *Progr. Inorg. Chem., 6,* 37 (1964).
52 A. N. Speca, C. M. Mikuslki, F. J. Iaconianni, L. L. Pytlewski and N. M. Karayannis, *Inorg. Chem., 19,* 3491 (1980).
53 G. W. Inman, Jr. and W. E. Hatfield, *Inorg. Chem., 11,* 3085 (1972).
54 H. W. Richardson, W. E. Hatfield, H. J. Stoklosa and J. R. Wasson, *Inorg. Chem., 12,* 2051 (1973).
55 D. B. Brown, J. R. Wasson, J. W. Hall and W. E. Hatfield, *Inorg. Chem., 16,* 2526 (1977);
D. B. Brown, J. W. Hall, H. M. Helis, E. G. Walton, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem., 16,* 2675 (1977).
56 D. J. Hodgson, *Prog. Inorg. Chem., 23,* 211 (1977).
57 U. Thewalt, C. E. Bugg and R. E. Marsh, *Acta Crystallogr., Sect. B:, 27,* 2358 (1971).
58 E. Sletten, *Acta Crystallogr., Sect. B:, 25,* 1480 (1969); *26,* 1609 (1970).
59 P. de Meester and A. C. Skapski, *J. Chem. Soc. A:,* 2167 (1971).
60 A. Terzis, A. L. Beauchamp and R. Rivest, *Inorg. Chem., 12,* 1166 (1973).
61 P. I. Vestues and E. Sletten, *Inorg. Chim. Acta, 52,* 269 (1981).
62 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).
63 J. Hubert and A. L. Beauchamp, *Can. J. Chem., 58,* 1439 (1980); *Acta Crystallogr., Sect. B:, 36,* 2613 (1980).