proximation is obtained by assuming random redistribution of alkyl groups, where steric hindrance is not a factor. Preparations of mixed alkyl phosphites (including the "dialkyl phosphonates") reorganize at room temperature. For example, pure dimethyl ethyl phosphite isolated as a gas chromatography fraction was found to reorganize appreciably within several days, as evidenced by the appearance and growth of three additional peaks in the gas chromatogram. This means that data obtained on so-called "pure" mixed esters of this type, as made by conventional methods, may be questionable, especially if the data were obtained on aged samples.

The results given herein show that even ester interchange deviates from randomness when sufficiently precise measurements are employed. Moreover, there seems to be no simple relationship between the devia-

tions from randomness for scrambling equilibria involving exchange of RO– and PO– substitutents of the esters of polyacids and the deviations for RO– and R'O– exchange in the esters of ortho acids.

Thermodynamic treatment of the data of this paper shows that, in all cases, the free energy of formation of the mixed esters from the compounds containing only one kind of alkoxyl group deviates from the random case by less than 0.25 kcal., which probably represents the enthalpy of the ester-interchange reaction.[6]

Nonaqueous Coordination Phenomena—Complexes of Hexamethylphosphoramide. III. Other Cationic Complexes

BY JOHN T. DONOGHUE[1] AND RUSSELL S. DRAGO

The following complexes of hexamethylphosphoramide, $OP[N(CH_3)_2]_3$ (HMPA), have been prepared: $[Fe(HMPA)_6](ClO_4)_3$, $[Cr(HMPA)_6](ClO_4)_3$, $[Fe(HMPA)_4](ClO_4)_2$, $[Cu(HMPA)_4](ClO_4)_2$, $[Mn(HMPA)_4](ClO_4)_2$, $[Mg(HMPA)_4](ClO_4)_2$, $[Ca(HMPA)_4](ClO_4)_2$, $[Ba(HMPA)_4](ClO_4)_2$, $[Al(HMPA)_4](ClO_4)_3$, $Pb(HMPA)_3](ClO_4)_2$, $[Ag(HMPA)_2]ClO_4$, and $[Ag(HMPA)](ClO_4)$. In this article, we report for the first time conclusive evidence to establish a tetrahedral structure for a cationic iron(II) complex. The spectral and magnetic data for $[Fe(HMPA)_4]^{+2}$ support a tetrahedral configuration for the cation and the X-ray powder pattern indicates strict isomorphism with known tetrahedral structures such as those of the M-$(HMPA)_4^{+2}$ complexes of Zn^{+2}, Co^{+2}, and Ni^{+2}. Spectral data on the Fe^{+3} and Cr^{+3} compounds indicate an octahedral configuration for the $[M(HMPA)_6^{+3}]$ complexes and suggest that toward Cr^{+3} HMPA is nearly as strong a donor as dimethyl sulfoxide. The unexpected four-coordinate HMPA complexes of Ca^{+2}, Mg^{+2}, Ba^{+2}, and Mn^{+2} also appear to be tetrahedral on the basis of X-ray powder pattern evidence.

Introduction

In earlier papers, it was shown that hexamethylphosphoramide (HMPA) formed tetrahedral complexes with Co(II) and Ni(II).[2,3] A planar complex was isolated with copper(II) nitrate[3] and a D_{2d}-like structure was proposed for the complex obtained with $Ni(NO_3)_2$. The unusual tetrahedral coordination of HMPA with Ni(II) prompted us to investigate the coordinating properties of this ligand toward other metal ions. In this paper, we report some unexpected four-coordinate cations of Ca(II), Mg(II), Ba(II), and Al(III). Spectral data for a four-coordinate Mn(II) complex of HMPA are in accord with properties reported for other tetrahedral manganese complexes.[4-11]

Iron(II) complexes present an interesting situation. The difference in crystal field stabilization energies for tetrahedral and octahedral fields is only 3 kcal. mole^{-1} in favor of the octahedral complex.[12] Yet, until very recently tetrahedral Fe(II) was unknown. In 1961, Gill[12] reported the preparation and isolation of solid compounds of FeX_4^{-2} (X = halogen). These compounds are cream-colored solids exhibiting magnetic moments of ∼5.3 B.M. The solution spectra are interesting in that there are no apparent (d–d) transitions between ∼500 and 2000 mμ. Below 450 mμ, very intense charge-transfer bands are observed. The X-ray powder diagrams of these halo complexes indicate strict isomorphism with the corresponding derivatives of Mn(II), Co(II), Ni(II), and Zn(II),[13] a fact which would

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TABLE I

ANALYTICAL, INFRARED, AND MAGNETIC SUSCEPTIBILITY DATA FOR HMPA COMPLEXES

Compound	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found	$\nu P=O$, cm.$^{-1}$	$10^6 \chi_M$	Diamag. corr. $\times 10^6$	$10^6 \chi$ '$_M$	μ_{eff}, B.M.
O≡[P[N(CH$_3$)$_2$]$_3$	40.21	40.01	10.12	10.23	23.45	22.84	1208 (smear)	...	...	...	...
Fe(HMPA)$_6$](ClO$_4$)$_3$	30.25	30.17	7.63	7.67	17.64	17.30	1191 (Nujol)	15,161	880	16,041	6.25 ± 0.04
[Fe((HMPA)$_4$](ClO$_4$)$_2$	29.66	29.85	7.49	7.44	17.30	17.21	1185 (Nujol)	10,450	550	11,000	5.19 ± 0.04
[Cu(HMPA)$_4$](ClO$_4$)$_2$	29.43	29.25	7.43	7.60	17.17	17.13	1191 (KBr)	1,206	550	1,756	2.07 ± 0.06
[Cr(HMPA)$_6$](ClO$_4$)$_3$	30.33	30.29	7.65	7.66	17.69	16.71	1191 (KBr)	5,220	880	6,100	3.85 ± 0.04
[Mn(HMPA)$_4$](ClO$_4$)$_2$	29.76	30.05	7.50	7.43	17.36	17.06	1190 (KBr)	10,697	550	11,247	5.24 ± 0.04
[Ag(HMPA)]ClO$_4$	18.64	18.87	4.70	5.00	10.87	10.60	1190 (Nujol)	...	...	...	...
[Ag(HMPA)$_2$]ClO$_4$	25.47	25.32	6.43	6.38	14.86	14.59	1190 (Nujol)	...	...	...	...
[Mg(HMPA)$_4$](ClO$_4$)$_2$	30.66	30.96	7.74	7.33	17.87	17.57	1188 (Nujol)	...	...	...	...
[Pb(HMPA)$_3$](ClO$_4$)$_2$	22.90	23.46	5.78	5.85	13.36	13.54	1190 (Nujol)	...	...	...	...
[Ca(HMPA)$_4$](ClO$_4$)$_2$	30.15	30.25	7.61	7.61	17.59	17.41	1189 (Nujol)	...	...	...	...
[Ba(HMPA)$_4$](ClO$_4$)$_2$	27.37	27.50	6.90	7.02	15.96	16.07	1189 (Nujol)	...	...	...	...
[Al(HMPA)$_4$](ClO$_4$)$_3$	27.65	27.63	6.98	7.06	16.13	15.47	1190 (Nujol)	...	...	...	...

tend to support a tetrahedral formulation for the Fe(II) derivatives.

Structural evidence is lacking, but it has been suggested that the complexes FeX$_2$·2P(C$_6$H$_5$)$_3$, Fe(P-(C$_6$H$_5$)$_3$)$_4$$^{+2}$, and Fe(As(C$_6H_5$)$_3$)$_4$$^{+2}$ contain tetrahedral Fe(II).[14,15] A similar report exists for [((C$_2$H$_5$)$_2$PH)$_2$FeCl$_2$] and [{(C$_6$H$_{11}$)$_2$PH}$_2$FeCl$_2$].[15]

A tetrahedral complex of Fe(II) is formed with HMPA. This is the first tetrahedral, cationic complex of iron(II) that is reported with data to support the structural assignment.

Experimental

Preparation of Complexes. [Fe(HMPA)$_6$](ClO$_4$)$_3$.—2,2-Dimethoxypropane was employed to dehydrate Fe(ClO$_4$)$_3$·6H$_2$O (0.05 mole) by a procedure previously described.[2,3] An excess of HMPA was added to the resulting solution and the red-brown solution thus obtained was allowed to stir for 4–5 hr. at 0°. Excess ether was then added to complete precipitation. The solid was collected by filtration, washed several times with ether, then dried *in vacuo* over H$_2$SO$_4$. The compound is nearly white and was obtained in 82% yield. Analytical data for this and other HMPA complexes are given in Table I.

[Fe(HMPA)$_4$](ClO$_4$)$_2$.—This complex was prepared at room temperature from Fe(ClO$_4$)$_2$·6H$_2$O by a procedure similar to that outlined above. This treatment yielded a cream-colored solid in 98% yield.

[Cu(HMPA)$_4$](ClO$_4$)$_2$.—This compound was prepared from Cu(ClO$_4$)$_2$·6H$_2$O in the same manner as the preceding complexes. The result is a 91% yield of a light green solid.

[Cr(HMPA)$_6$](ClO$_4$)$_3$.—Precipitation of this complex by the procedure outlined above resulted in the deposition of a dark green oil, which was dissolved in a minimum amount of A.R. acetone and reprecipitated slowly with ether. The final product is a dark green solid, which, on standing *in vacuo* for several weeks, reverts to an oil. The yield was 81% of theoretical.

[Mn(HMPA)$_4$](ClO$_4$)$_2$.—This compound was prepared from Mn(ClO$_4$)$_2$·6H$_2$O in the manner described above. The solid, obtained in 90% yield, is nearly pure white.

[Ag(HMPA)]ClO$_4$ and [Ag(HMPA)$_2$]ClO$_4$.—The first compound was prepared by mixing the reactants in stoichiometric ratios in acetone, followed by precipitation with ether. The latter compound was prepared by employing excess HMPA.

[Mg(HMPA)$_4$](ClO$_4$)$_2$, [Ca(HMPA)$_4$](ClO$_4$)$_2$, and [Ba-(HMPA)$_4$](ClO$_4$)$_2$.—The hydrated alkaline earth perchlorates were dissolved in acetone (0.05 mole in 20 ml.) containing excess 2,2-dimethoxypropane. The resulting solution was stirred for 2 hr. Excess HMPA was added. A large excess of ether was then added to induce precipitation. The precipitates were filtered, washed with ether, and dried *in vacuo* over H$_2$SO$_4$. The yields were 95, 99, and 90%, respectively.

[Al(HMPA)$_4$](ClO$_4$)$_3$.—This complex was prepared from Al-(ClO$_4$)$_3$·9H$_2$O by the method used for the alkaline earth complexes. The solid, obtained in 89% yield, is colored a very pale tan (probably impurity) and often exploded violently during the course of analysis for carbon and hydrogen.

[Pb(HMPA)$_3$](ClO$_4$)$_2$.—This complex, obtained in 90% yield, was prepared by procedures similar to those employed for the alkaline earth complexes.

Conductance Measurements.—Conductivities of dilute nitromethane solutions of the complexes were measured using an Industrial Instruments bridge and cell which had been previously calibrated with aqueous KCl solutions. The results are indicated in Table II.

TABLE II

CONDUCTIVITIES OF NITROMETHANE SOLUTIONS OF HMPA COMPLEXES

Compound	Concn., M	Temp., °C.	Λ_{molar}
[Fe(HMPA)$_6$](ClO$_4$)$_3$	0.0005	25.9	236
[Fe(HMPA)$_4$](ClO$_4$)$_2$	.002	26.5	185
[Cu(HMPA)$_4$](ClO$_4$)$_2$	.004	29.4	184
[Cr(HMPA)$_6$](ClO$_4$)$_3$	.005	29.0	253
[Mn(HMPA)$_4$](ClO$_4$)$_2$	.005	29.0	185
[Ag(HMPA)]ClO$_4$	.002	25.8	87
[Ag(HMPA)$_2$]ClO$_4$	.002	25.7	85
[Mg(HMPA)$_4$](ClO$_4$)$_2$	.001	25.9	153
[Pb(HMPA)$_3$](ClO$_4$)$_2$	.002	26.5	149
[Ca(HMPA)$_4$](ClO$_4$)$_2$	.001	26.2	146
[Al(HMPA)$_4$](ClO$_4$)$_3$	.0005	25.9	241
[Ba(HMPA)$_4$](ClO$_4$)$_2$	.0005	26.2	145

Spectral Measurements.—The infrared absorption frequencies of the phosphoryl group both in the free ligand and its complexes are contained in Table I. These data suggest coordination through oxygen in all cases. The spectra of Nujol mulls of the solid compounds also definitely indicate the absence of water in the complexes.

Electronic solution spectra were obtained using a Cary Model 14M recording spectrophotometer. Diffuse reflectance spectra were obtained using the standard reflectance attachment with a Bausch and Lomb Spectronic 505 recording spectrophotometer. Blocks of MgCO$_3$ were employed as the standard. The results from the electronic spectra are given in Table III.

Magnetic Measurements.—Magnetic susceptibilities of the solid transition metal complexes were evaluated using a Gouy balance with a Newport electromagnet.[2,3] The Gouy tubes were calibrated using Hg[Co(NCS)$_4$] according to the procedure of Figgis and Nyholm.[16,17] The results are given in Table I. The moments as reported are room temperature (30°) values and are

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Compound	Medium	λ_{max}, mμ	ϵ_{max}
[Fe(HMPA)$_6$](ClO$_4$)$_3$	0.0002 M in CH$_3$NO$_2$	<400	>5000
[Fe(HMPA)$_4$](ClO$_4$)$_2$	0.0005 M in CH$_3$NO$_2$	<400	>2500
[Cr(HMPA)$_6$](ClO$_4$)$_3$	Solid, reflectance	~460	
		~620	sh
		~650	
		~700	sh
	0.016 M in CH$_3$NO$_2$	435	40
		628	53
		690	sh
[Mn(HMPA)$_4$](ClO$_4$)$_2$	Solid, reflectance	~410	
		~420	
		~470	sh
	0.2 M in CH$_3$NO$_2$	412	0.95
		422	0.50
		~444	sh
[Cu(HMPA)$_4$](ClO$_4$)$_2$	Solid, reflectance	<400 >700	
	0.01 M in CH$_3$NO$_2$	~375	2500
		~430	sh
		~720	~50
		1100	sh
		1475	5.5
CuCl$_4$$^{-2}$ [a]	In CH$_3$NO$_2$	890	88
		435	sh
		360	4000
CuBr$_4$$^{-2}$ [a]	In CH$_3$NO$_2$	870	122
		643	1774
		433	1995
		369	~3000
[Cu(HMPA)$_4$](ClO$_4$)$_2$	Mull	740	
		580	
		520	sh
		<350	

[a] See ref. 13.

corrected for diamagnetic contributions of the ligands and metal ions. The contributions of all metal ions not in the literature were assumed to have constant values of 12.8 × 10^{-6}.

X-Ray Powder Patterns.—Patterns were obtained as previously described.[2]

Calculation of Dq and β.—The spectrochemical parameters Dq and β were calculated for the Cr(III) complexes by a reported procedure.[18]

Discussion

The infrared spectral data contained in the Experimental section indicate that coordination with all the metal ions studied has occurred through the oxygen atom of the ligand. These spectra also showed the absence of characteristic water vibrations. The conductivity data[13] show that formulation of these compounds as complex cations with uncoordinated anions is justified. The structures of many of the individual complexes can be inferred from spectral, magnetic, and X-ray powder diffraction data.

The analyses and conductance support the formulation of the iron(II) complex as Fe(HMPA)$_4$$^{+2}$ and the

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electronic spectrum indicates a tetrahedral Fe(II) complex. The spectrum in nitromethane solvent shows no absorption in the 500–2000 mμ region in accord with the results for FeCl$_4$$^{-2}$ reported by Gill.[12] The magnetic moment of the compound shows a small orbital contribution, as is expected[12] for tetrahedral Fe(II). The X-ray pattern of this complex indicates strict isomorphism with the HMPA complexes of Co(II), Ni(II), and Zn(II), all of which have tetrahedral structures.[2]

The stoichiometry and absorption spectrum of [Mn(HMPA)$_4$](ClO$_4$)$_2$ are suggestive of tetrahedral geometry. The main difference in the spectra of octahedral and tetrahedral manganese(II) is the greater intensity of absorption of the T$_d$ species.[13] Octahedral Mn(II) complexes have extinction coefficients in the range 0.001 to 0.01 compared to values of 0.1 or greater for the tetrahedral species. The powder pattern of this complex is identical with those of the HMPA derivatives of Zn(II), Co(II), Ni(II), and Fe(II) except for two additional very weak lines appearing in the powder pattern of the Mn(II) complex. It was concluded that the compounds were isomorphous and thus [Mn(HMPA)$_4$]$^{+2}$ is tetrahedral.

The alkaline earth complexes are quite interesting since four-coordinate complexes of these ions with monodentate ligands are uncommon. The existence of CaCl$_4$$^{-2}$ has not yet been demonstrated.[13] The strongest evidence to support tetrahedral formulations for these complexes is the high degree of similarity in the powder patterns of these ions and the Mn(II) complex. The patterns are indistinguishable, suggesting that the alkaline earth complexes are tetrahedral. On the basis of this evidence, we believe that the HMPA is coordinated and not simply trapped in the crystal lattices of the alkaline earth perchlorates. The P–O stretching vibration in the infrared spectra of these compounds is shifted to a lower wave number than that in the free ligand, in accord with the expectations for coordinated HMPA. This shift does not establish true coordination because the spectra were obtained on solids but is in agreement with the powder pattern evidence.

The spectral, analytical, conductivity, and magnetic data presented indicate that [Cr(HMPA)$_6$](ClO$_4$)$_3$ contains Cr(III) octahedrally coordinated to the oxygen of the six HMPA ligands. The electronic spectrum of the compound is nearly identical with that of the octahedral complex [Cr(DMSO)$_6$]$^{+3}$ (DMSO = dimethyl sulfoxide).[19] The magnetic moment of the compound is very close to the spin-only value, a result expected for octahedral Cr(III). Thus, it is concluded that this cation is octahedral.

Spectrochemical data were calculated from the electronic spectrum of the octahedral Cr(III) complex. A value of 1540 ± 20 cm.$^{-1}$ is obtained for the parameter Dq while a value of 19.0 ± 1.5 is obtained for β, defined as the percentage lowering of the P–F term as compared to the free ion.

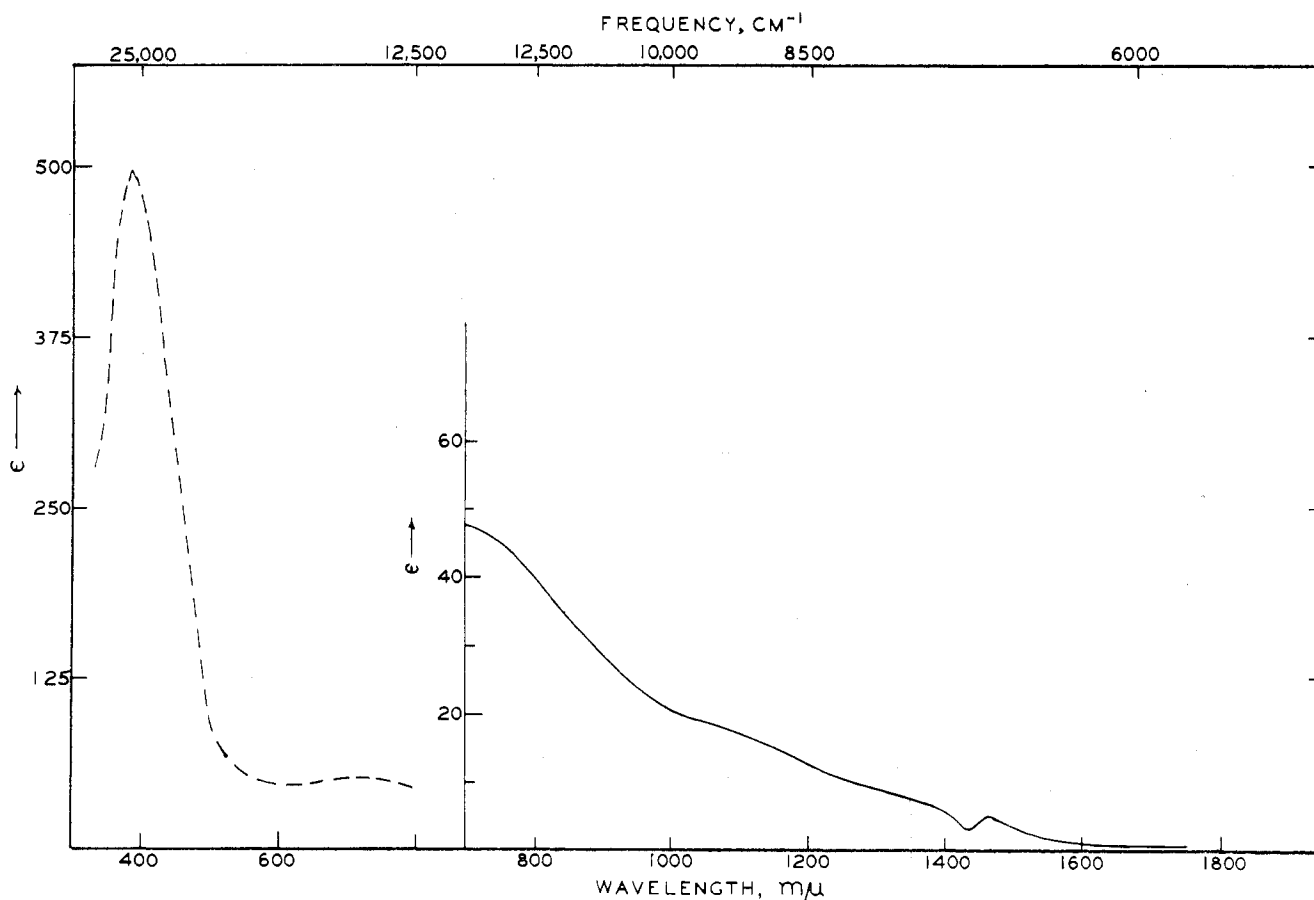(19) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960).

FREQUENCY, CM⁻¹

Fig. 1.—Visible and near-infrared spectrum of [Cu(HMPA)₄](ClO₄)₂—0.004 M in CH_3NO_2.

On the basis of stoichiometry and the absence of free P=O in the infrared spectrum, the Fe(III) complex appears to be six-coordinate. The spectrum (Table III) is in accord with this conclusion. Conductivity values suggest a 3:1 electrolyte in nitromethane. It is thus concluded that this complex is octahedral. The magnitude of the magnetic moment would suggest an orbital contribution, though appreciable orbital contributions are not expected for this case. The cause for this behavior is not clear.

The complex $Al(HMPA)_4^{+3}$ is assumed to have a tetrahedral structure similar to that of $AlCl_4^-$. The structure of the lead compound is unknown. The infrared spectrum indicates that all the HMPA is coordinated in this complex, and the conductivity would tend to exclude perchlorate coordination in nitromethane, at least. Present data do not allow further statements to be made about the structure of this ion. No attempt was made to study the structures of the Ag(I)–HMPA complexes.

It has long been thought that Cu(II) in tetrahedral circumstances must show serious distortion from regular symmetry. The crystal structure of $CuCl_4^{-2}$ [20] (i.e., a flattened tetrahedron) would seem to support this contention. Recently, Liehr[21] has pointed out that if spin-orbit coupling is accounted for, a nondegenerate ground state is obtained and regular tetrahedral copper-(II) complexes could exist. Liehr predicts that tetra-

hedral copper(II) should show a transition at 5000–7000 cm.⁻¹, without visible electronic transitions. The color of the compound should be due to charge-transfer transitions. The spectrum of Cu(II) in a ZnO lattice (tetrahedral holes) has been reported and is in agreement with these predictions.[22] Cotton[23] has reported $[Cu((C_6H_5)_3PO)_2Cl_2]$ and $[Cu((C_6H_5)_3PO)_2Br_2]$ and has concluded that the structures are distorted tetrahedra.

The spectrum of $[Cu(HMPA)_4]^{+2}$ shows a transition in the range predicted by Liehr (6800 cm.⁻¹). However, strong visible absorption is in evidence (i.e., ~720 mμ). The spectrum is not that expected for a tetrahedral cation. The magnetic moment (2.07 B.M.) approaches the value of 2.2 predicted for tetrahedral copper.[24] However, there are only slight differences in magnetic moment values for Cu(II) in various stereochemical environments and deduction of structure from magnetic moments is very difficult for Cu(II) complexes. The evidence for $[Cu(HMPA)_4]^{+2}$ is not at all clear-cut and does not allow an unambiguous structural assignment.

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