some position along the geometric pathway relating the two ideal nine-coordinate polyhedra. It is interesting to note that in spite of the large distortion present in this complex the average shape parameters as shown in Table V compare quite closely to Robertson's ideal values for the charged monocapped square antiprism.

We believe that one of the major purposes of assigning coordination polyhedra to real complexes is to aid in visualization of the complex. For this reason a model based on the seven-coordinate pentagonal bipyramid was examined. The bipyridine ligands were considered to occupy single coordination sites by placing atoms B(1) and B(2) equidistant between N(A) and N(B) and between N(C) and N(D), respectively, and normalizing them. The two positions can be considered to occupy the two axial positions of a pentagonal bipyramid with the five thiocyanato ligands forming the pentagonal girdle.

Figure 4 shows a projection of the coordination group onto the best plane through atoms B(1), N(1), U, and B(2). Best planes were calculated for the bipyridine ligands, and the dihedral angle between them was calculated to be 90.1°. Deviations of carbon atoms from the calculated best planes do not exceed 0.10 Å. The B(1)–U–B(2) angle was calculated to be 174.7°. The equatorial plane N(2), N(3), N(4), and N(5) is perpendicular (90.7°) to the quasi mirror plane. In this figure the bipyridine ligand represented by B(1) is in the plane of the paper while the bipyridine ligand represented by B(2) is approximately perpendicular to the plane of the paper. The close contact of 2.37 Å between N(1) and H(A1) causes atom N(1) to be pushed up away from the equatorial plane. Close contacts between N(3) and H(D1) and between N(5) and H(C1) of 2.39 and 2.62 Å cause these two atoms to be displaced downward away form the equatorial plane. Shape parameters for the seven-coordinate model are found in Table VI.

Uranium–nitrogen bond lengths are between 2.61 and 2.65 Å for the two bipyridine ligands. Uranium–nitrogen bond distances for the five thiocyanato ligands vary between 2.35 and 2.47 Å, in reasonable agreement with the uranium–nitrogen bond distance of 2.38 Å in $[(Et_4N)_4]^{4+}[U(NCS)_8]^{4-}$.[22] Nitrogen–carbon bond distances of 1.10–1.17 Å agree with distances reported for other structures containing the thiocyanato group as do the carbon–sulfur bond distances of 1.59–1.72 Å. N–C–S bond angles are all effectively 180° as expected for the predominantly sp-hybridized interligand bonding. U–N–C bond angles of 155, 161, 163, 165, and 174° differ significantly from the theoretical value of 180°. Deviations from linearity of M–N–C bond angles in thiocyanato ligands have been reported previously[23] and are attributed to crystal-packing effects. Close contacts between the sulfur atoms of the thiocyanato ligands and hydrogen atoms of the tetraethylammonium cation are presumably the cause of the distortion; in this case, however, incomplete resolution of the tetraethylammonium ion made calculation of these contacts impossible.

Acknowledgment. We wish to thank Dr. John Witschel for IR and NMR spectra and Dr. James Einck for many helpful discussions. A generous allocation of computer time by Arizona State University is gratefully acknowledged.

Registry No. $[Et_4N]^+[U(NCS)_5(bpy)_2]^-$, 74511-91-4; $(Et_4N)_4U(NCS)_8$, 33724-34-4.

Supplementary Material Available: Structure factor tables (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, University of Virginia, Charlottesville, Virginia 22901, and Clemson University, Clemson, South Carolina 29631

Relation between the Structure and Spectra of Pseudotetrahedral CuN_4 Complexes and the Crystal Structure of $[CuL_2](ClO_4)_2$, L = 2-Pyridyl-2-pyrimidylamine

E. M. GOUGE,[1a] J. F. GELDARD,*[1a] and E. SINN*[1b]

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The crystal structure of the title complex has been determined. The copper environment is pseudotetrahedral, with a dihedral angle, ϕ, of 53.8° between the two CuN_2 ligand planes. The two ligands are identical as required by crystallographic symmetry. The two perchlorate groups are ionic, 3.369 (1) Å away from the copper atom on opposite sides. This result suggests the hypothesis of a correlation between the spectra and structures of pseudotetrahedral CuN_4 species. The electronic spectrum of $[Cu(MPA)_2]$, which has $\phi = 57.4°$, is very similar to that of $[Cu(PTA)_2]$, suggesting similar values of ϕ for the two complexes and contradicting an earlier postulate of a less tetrahedral structure for $[Cu(PTA)_2]$ (HMPA = 3,3′-dimethyl-2,2′-dipyridylamine, HPTA = 2-pyridyl-2-thiazolylamine). Crystal data for $[Cu(HPPA)_2](ClO_4)_2$: space group $C2/c$, $Z = 4$, $a = 9.356$ (8) Å, $b = 12.752$ (2) Å, $c = 19.353$ (4) Å, $\beta = 101.56$ (3)°, $V = 2262$ Å^3, $R = 4.6\%$ for 1893 reflections.

Introduction

The CuN_4 chromophore usually has a square-planar structure in four-coordinate copper(II) complexes. The series of complexes with general formulas $Cu(HL)_2(ClO_4)_2$ and $Cu(L)_2$,[2] however, contain CuN_4 chlorophores that have pseudotetrahedral structures.[3] These geometries have been assigned by crystallographic studies[4,5] and by analysis of the electronic spectra of members of these series.[3]

The differences in the band positions of the d–d transitions in the electronic spectra suggest differences in the dihedral

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(1) (a) Clemson University. (b) University of Virginia.

(2) In this paper HL is the generic name for a bidentate ligand and L⁻ is the deprotonated form. Specific names: 2,2′-dipyridylamine, HDPA; 2-pyridyl-2-pyrimidylamine, HPPA; 2-pyridyl-2-thiazolylamine, HPTA; 3,3′-dimethyl-2,2′-dipyridylamine, HMPA.

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Cu(HPPA)_2](ClO_4)_2$ [a]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.0000 (0)	0.19278 (4)	0.2500 (0)	2.08 (2)	3.33 (2)	1.92 (2)	0.0000 (0)	0.52 (1)	0.0000 (0)
Cl(1)	0.18319 (8)	0.05008 (6)	0.61407 (4)	3.16 (3)	3.06 (3)	3.20 (3)	0.49 (2)	0.98 (2)	−0.12 (2)
O(1)	0.1038 (3)	0.0169 (2)	0.6663 (1)	4.9 (1)	4.9 (1)	5.3 (1)	1.1 (1)	2.59 (8)	1.75 (9)
O(2)	0.3163 (3)	0.0979 (2)	0.6472 (2)	4.4 (1)	5.9 (1)	8.4 (2)	−1.2 (1)	1.43 (12)	−2.07 (12)
O(3)	0.2177 (4)	−0.0379 (2)	0.5754 (2)	6.9 (1)	6.0 (1)	10.2 (2)	−1.5 (1)	4.58 (11)	−4.80 (11)
O(4)	0.0999 (4)	0.1272 (3)	0.5704 (2)	7.0 (1)	11.0 (2)	5.2 (1)	4.3 (1)	2.39 (12)	4.21 (12)
N(1)	−0.0989 (3)	0.2497 (2)	0.3233 (1)	2.46 (9)	2.32 (9)	2.43 (9)	0.15 (8)	0.90 (7)	0.31 (7)
N(2)	0.1737 (3)	0.1480 (2)	0.3191 (1)	2.08 (8)	2.38 (8)	2.62 (9)	0.11 (8)	0.43 (7)	−0.12 (8)
N(3)	0.0739 (3)	0.1858 (2)	0.4206 (1)	2.73 (10)	3.70 (11)	2.12 (9)	0.18 (9)	0.59 (8)	0.11 (8)
N(4)	−0.1222 (3)	0.2791 (2)	0.4429 (2)	4.03 (12)	4.27 (11)	3.25 (11)	0.47 (11)	1.70 (9)	−0.24 (10)
C(1)	−0.2225 (4)	0.3066 (2)	0.3020 (2)	3.6 (1)	3.0 (1)	3.0 (1)	0.51 (11)	0.73 (11)	0.50 (10)
C(2)	−0.2997 (4)	0.3464 (3)	0.3489 (2)	3.8 (1)	4.1 (1)	4.1 (1)	1.58 (12)	1.34 (11)	0.39 (12)
C(3)	−0.2467 (4)	0.3318 (3)	0.4198 (2)	4.2 (1)	3.8 (1)	4.1 (1)	0.96 (12)	1.88 (11)	−0.22 (12)
C(5)	−0.0525 (3)	0.2396 (2)	0.3926 (1)	2.7 (1)	2.4 (1)	2.6 (1)	−0.14 (10)	1.12 (9)	−0.08 (9)
C(6)	0.2888 (4)	0.1100 (3)	0.2943 (2)	3.0 (1)	3.7 (1)	2.5 (1)	0.60 (11)	0.46 (10)	−0.55 (10)
C(7)	0.4144 (4)	0.0745 (3)	0.3377 (2)	3.0 (1)	5.0 (2)	4.1 (1)	1.01 (13)	1.01 (11)	0.08 (13)
C(8)	0.4238 (4)	0.0802 (3)	0.4098 (2)	3.0 (1)	5.2 (2)	3.6 (1)	0.72 (13)	0.24 (12)	0.47 (13)
C(9)	0.3095 (4)	0.1162 (2)	0.4358 (2)	2.7 (1)	4.1 (1)	2.4 (1)	0.31 (11)	0.14 (10)	0.09 (11)
C(10)	0.1847 (3)	0.1497 (2)	0.3899 (1)	2.7 (1)	2.2 (1)	2.3 (1)	−0.26 (9)	0.40 (9)	0.00 (9)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(1)	−0.251 (5)	0.319 (3)	0.256 (2)	1.5 (8)	H(6)	0.276 (6)	0.104 (3)	0.255 (3)	3.8 (11)
H(2)	−0.380 (8)	0.381 (4)	0.321 (3)	6.2 (16)	H(7)	0.481 (7)	0.077 (4)	0.311 (3)	4.6 (13)
H(3)	−0.284 (7)	0.363 (4)	0.474 (3)	4.4 (13)	H(8)	0.520 (8)	0.064 (4)	0.467 (3)	6.4 (16)
H(N3)	0.092 (6)	0.183 (4)	0.483 (3)	3.9 (12)	H(9)	0.314 (6)	0.125 (4)	0.487 (3)	3.7 (12)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$.

angle, ϕ, between the two CuN_2 planes; the planes are defined by the two donor nitrogen atoms of each ligand and the copper atom. It has been proposed that the variation in ϕ correlates with the energies of the d–d transitions.[3] This parallels the correlation that has been established between ϕ and the highest energy d–d transition in a number of tetrachlorocuprate(II) compounds containing different cations.[6–11]

To verify this hypothesis, we have undertaken the determination of the crystal structure of members of the two series. In this paper, we report the crystal structure of $[Cu(HPPA)_2](ClO_4)_2$ and the electronic spectrum of $[Cu(MPA)_2]$. The similarity of the spectra of $[Cu(MPA)_2]$ and $[Cu(PTA)_2]$ suggests that these two complexes should have similar values of ϕ.

Experimental Section

Preparation of the Complex. $[Cu(HPPA)_2](ClO_4)_2$ was prepared by the method reported in ref 3. Crystals suitable for structure determination were obtained by slow evaporation of a solution of the complex in acetone/water.

Crystal Data for $[Cu(HPPA)_2](ClO_4)_2$. $CuCl_2O_8N_8C_{18}H_{16}$: mol wt 607, space group $C2/c$, $Z = 4$, $a = 9.356$ (8) Å, $b = 12.752$ (2) Å, $c = 19.353$ (4) Å, $\beta = 101.56$ (3)°, $V = 2262$ Å^3, $\rho_{calcd} = 1.78$ g cm^{-3}, $\rho_{obsd} = 1.73$ g cm^{-3}, μ (Mo Kα) = 13.0 cm^{-1}; crystal dimensions (distances in mm of faces from centroid) (100) 0.45, $(\bar{1}00)$ 0.45, (120) 0.45, $(\bar{1}\bar{2}0)$ 0.45, $(\bar{1}20)$ 0.35, $(1\bar{1}0)$ 0.34, (001) 0.09, $(00\bar{1})$ 0.09; maximum, minimum transmission coefficients 0.92, 0.64.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described,[12] to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 46°$. Scan widths were calculated as $A + B \tan \theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.6 and 0.35°, respectively.

Table II

Bond Lengths (Å)			
Cu-N(1)	1.980 (1)	N(3)-C(5)	1.381 (2)
Cu-N(2)	1.971 (1)	N(3)-C(10)	1.373 (2)
Cl(1)-O(1)	1.433 (1)	C(1)-C(2)	1.365 (2)
Cl(1)-O(2)	1.419 (1)	C(2)-C(3)	1.375 (2)
Cl(1)-O(3)	1.421 (1)	C(3)-N(4)	1.342 (2)
Cl(1)-O(4)	1.423 (1)	N(4)-C(5)	1.372 (2)
N(1)-C(1)	1.358 (2)	C(6)-C(7)	1.376 (2)
N(1)-C(5)	1.330 (2)	C(7)-C(8)	1.382 (2)
N(2)-C(6)	1.355 (2)	C(8)-C(9)	1.350 (2)
N(2)-C(10)	1.353 (2)	C(9)-C(10)	1.385 (2)
Closest Interionic Contacts (Å)			
Cu-O(1)	3.369 (1)[a,b]	O(3)-C(5)	3.126 (2)[b]
O(1)-C(6)	3.168 (2)[c]	O(3)-N(4)	3.203 (2)[b]
O(2)-C(5)	3.233 (2)[d]	O(4)-N(3)	2.956 (2)[e]
O(2)-N(1)	3.239 (2)[d]		

[a] $x, -y, z - 1/2$. [b] $-x, -y, 1 - z$. [c] $x, -y, z + 1/2$. [d] $1/2 - x, 1/2 - y, 1 - z$. [e] x, y, z.

The intensities of four standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 2004 independent intensities, there were 1893 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[13] These data were used in the final refinement of the structural parameters.

Structure Determination. The positions of the copper and chlorine atoms were determined from a three-dimensional Patterson function. The intensity data were phased sufficiently well by these positional coordinates to permit location of the other nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[12] Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for two cycles of least squares and then held fixed. The model converged with $R = 4.6$ and $R_w = 6.5\%$. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors and calculated least-squares planes

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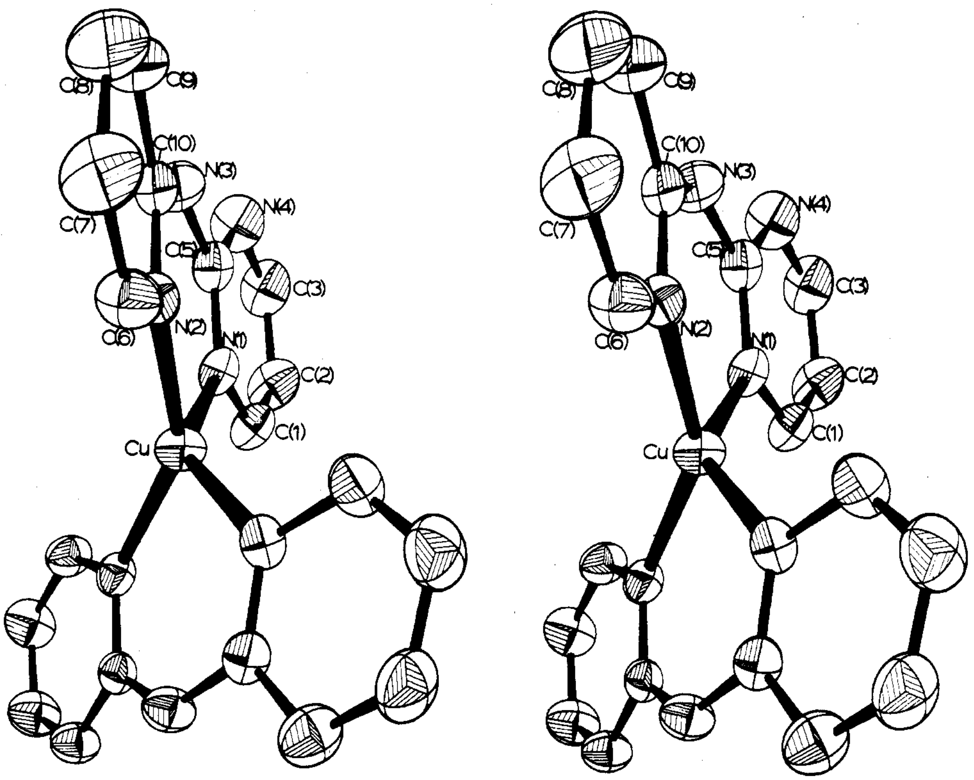

Figure 1. Stereopair view of the $[Cu(HPPA)_2]^{2+}$ cation.

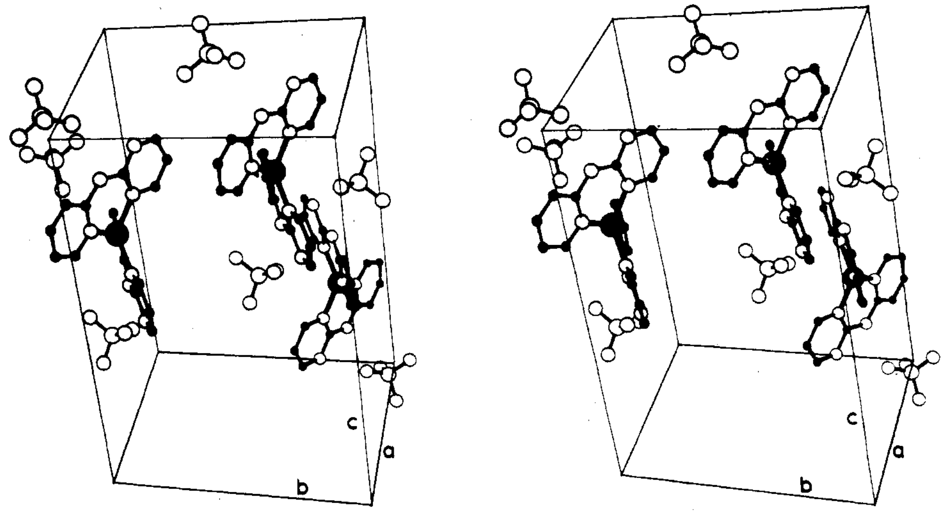

Figure 2. Molecular packing in the $[Cu(HPPA)_2](ClO_4)_2$ lattice.

are available.[14] The principal programs used are as previously described.[12]

Solid-state spectra were obtained on a Cary 14 recording spectrophotometer modified with a Varian 1411 diffuse-reflectance accessory. Solution spectra were determined with the Cary 14 spectrophotometer.

Results and Discussion

Final positional and thermal parameters for $[Cu(HPPA)_2](ClO_4)_2$ are given in Table I. Table II contains the bond lengths and nearest intermolecular contacts and Table III the bond angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows a stereoview of the $[Cu(HPPA)_2]^{2+}$ cation. Figure 2 shows the ionic packing in the unit cell, and it shows that the anions and cations are reasonably well separated. Thus the cationic metal complex can be considered separately. In

Table III. Bond Angles (Deg)

N(1)-Cu-N(1′)	137.01 (6)	C(5)-N(3)-C(10)	131.2 (1)
N(1)-Cu-N(2)	93.42 (5)	N(1)-C(1)-C(2)	121.9 (1)
N(1)-Cu-N(2′)	98.77 (5)	C(1)-C(2)-C(3)	118.7 (1)
N(2)-Cu-N(2′)	146.35 (6)	C(2)-C(3)-C(4)	121.1 (1)
O(1)-Cl(1)-O(2)	109.87 (9)	C(3)-N(4)-C(5)	116.8 (1)
O(1)-Cl(1)-O(3)	110.04 (9)	N(1)-C(5)-N(3)	121.6 (1)
O(1)-Cl(1)-O(4)	108.89 (8)	N(1)-C(5)-N(4)	125.1 (1)
O(2)-Cl(1)-O(3)	107.84 (9)	N(3)-C(5)-N(4)	113.3 (1)
O(2)-Cl(1)-O(4)	107.3 (1)	N(2)-C(6)-C(7)	122.9 (1)
O(3)-Cl(1)-O(4)	112.8 (1)	C(6)-C(7)-C(8)	118.2 (1)
Cu-N(1)-C(1)	118.07 (9)	C(7)-C(8)-C(9)	120.0 (1)
Cu-N(1)-C(5)	125.57 (9)	C(8)-C(9)-C(10)	119.7 (1)
C(1)-N(1)-C(5)	116.3 (1)	N(2)-C(10)-N(3)	122.1 (1)
Cu-N(2)-C(6)	117.95 (9)	N(2)-C(10)-C(9)	121.8 (1)
Cu-N(2)-C(10)	124.60 (9)	N(3)-C(10)-C(9)	116.0 (1)
C(6)-N(2)-C(10)	117.4 (1)		

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(14) Supplementary material.

Table IV. Diffuse-Reflectance and Solution Spectra of Pseudotetrahedral Copper(II) Complexes

complex		ϕ,[g] deg	$\bar{\nu}_{max}$, 10^3 cm^{-1} (ϵ_{max}, L cm^{-1} mol^{-1})		
$Cu(HPPA)_2(ClO_4)_2$[a]	b	53.8	7.5	10.3	15.9[d]
$Cu(HDPA)_2(ClO_4)_2$[a]	b	55.6	7.5[d]	10.1	16.0[d]
$Cu(PTA)_2$	b		8.7		16.9
	c		8.9 (87)	13.0[d]	17.4 (826)
$Cu(MPA)_2$	e	57.4	8.7		16.3
	f		8.5 (51), 22.0,[d] 29.9 (18 200)	12.5,[d] 24.7 (44 700), 33.3 (37 500)	15.9 (737), 26.0 (40 500), 28.6 (19 900), 40.0 (23 000)

[a] Solution spectra not given because of solvation to six-coordinate species. [b] Near-IR diffuse-reflectance spectra from ref 3. [c] Near-IR solution spectra from ref 3; solvent = acetonitrile. [d] Shoulder. [e] Near-IR diffuse-reflectance spectrum. [f] Near-IR and UV-visible solution spectra; solvent = dichloromethane. [g] Dihedral angle (see text).

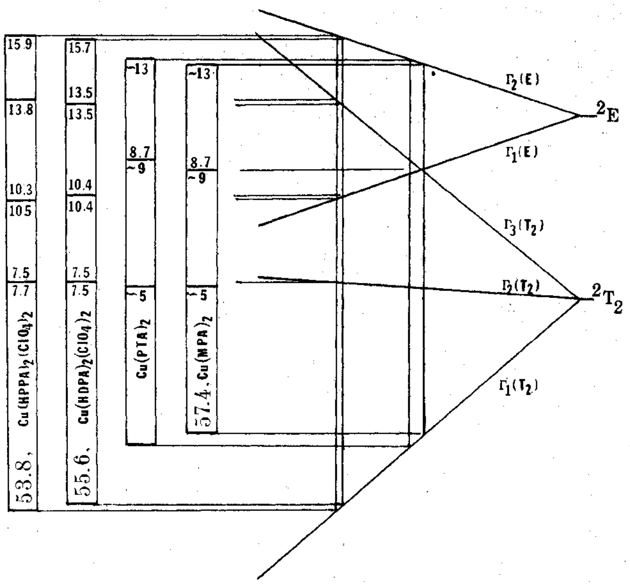

Figure 3. State diagram for pseudotetrahedral copper(II) complexes, showing values of the dihedral angle, ϕ, and the observed and predicted d–d transition energies. $[Cu(PTA)_2]$ has been relocated from its position in Figure 1 of ref 3.

fact, the closest interionic approach is between the uncoordinated ligand nitrogen atom N(3) and the perchlorate oxygen O(4), which at 2.956 (2) Å is a weak hydrogen-bonding interaction. The closest approach of perchlorate to copper is 3.369 (1) Å, a weak interaction with each of O(1) and O(1′) on opposite sides.

Crystallographic symmetry requires twofold symmetry within the $[Cu(HPPA)_2]^{2+}$ ion. The two ligands are therefore identical. The dihedral angle between the two CuN_2 coordination planes is 53.8 (2)°. The ligand itself is buckled, with angles of 4.9 and 4.1° between the central CuN_3C_2 ring and each of the outside rings, which in turn are tilted at 8.9° to each other.

The crystal structures of three members of the series have now been determined. The values of ϕ and observed energies of the d–d transitions are compared in Table IV and illustrated in Figure 3. The correlation between ϕ and the transition energies suggested by Gouge and Geldard[3] appears to be borne out; the value of ϕ in $[Cu(HDPA)_2](ClO_4)_2$ shows its CuN_4 chromophore to be more tetrahedral than that in $[Cu(HPPA)_2](ClO_4)_2$.

This correlation parallels that observed in $CuCl_4^{2-}$ ions, where the highest energy d–d transitions are a linear function of the dihedral angle.[11] Variations in ϕ are effected by different cations. A linear correlation for the CuN_4 chromophore cannot be assumed because the dihedral angle will be affected not only by interligand interactions but also by intraligand effects.

The value of ϕ in $[Cu(MPA)_2]$ is 57.4°; the CuN_4 chromophore is thus more tetrahedral than in either $[Cu(HDPA)_2](ClO_4)_2$ (55.6°) or $[Cu(HPPA)_2](ClO_4)_2$ (53.8°). We have measured the diffuse-reflectance and the solution spectra of $[Cu(MPA)_2]$ in the ultraviolet, visible, and near-infrared regions (see Table IV). As can be seen in Table IV, the energies of the d–d transitions in $[Cu(MPA)_2]$ are very similar to those in $[Cu(PTA)_2]$. This fact suggests that the two complexes have similar CuN_4 chromophores, i.e., that the values of ϕ are similar and that $[Cu(PTA)_2]$ is more tetrahedral than $[Cu(HDPA)_2](ClO_4)_2$. This contradicts the earlier assignment of a less tetrahedral structure.[3] That assignment, however, was made on the balance of available evidence and with recognition that there were two ways to interpret the spectrum of $[Cu(PTA)_2]$—one in terms of a less and the other in terms of a more tetrahedral structure.

The near-IR spectra of $[Cu(MPA)_2]$ and $[Cu(PTA)_2]$ show a shoulder near 12 500 and 13 000 cm^{-1}, respectively. If the bands at 16 000 and 17 000 cm^{-1} are also due to d–d transitions, then some nonlinearity in the variation of transition energy as a function of ϕ is indicated, especially in the region where the states $\Gamma_3(T_2)$ and $\Gamma_1(E)$ cross (Figure 3).

A final understanding of the behavior of the energies of the d states of the copper(II) ion as a function of ϕ in these complexes must await the determination of more crystal structures for the members of these series.

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Registry No. $[Cu(HPPA)_2](ClO_4)_2$, 64682-68-4; $Cu(MPA)_2$, 19358-74-8.

Supplementary Material Available: Tables of observed and calculated structure factors and calculated least-squares planes (10 pages). Ordering information is given on any current masthead page.