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Registry No. $[Cu_2L_2(ClO_4)_2]\cdot[Cu_2L_2(CH_3OH)_2](ClO_4)_2$, 70072-45-6; 1-phenyl-2-oximo-1-propanone, 119-51-7; *N*,*N*-dimethylethylenediamine, 110-18-9.

Supplementary Material Available: Listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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A New Synthesis of Bis(3,3′-dimethyl-2,2′-dipyridylamine)copper(II) and the Crystal Structure of the Complex

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The copper(II) complex (**1**) of the deprotonated form of 3,3′-dimethyl-2,2′-dipyridylamine has been prepared by reacting the ligand with freshly prepared copper(II) hydroxide. The crystal and molecular structure have been determined. Crystal data: space group $P2_12_12_1$, $Z = 4$, $a = 8.639$ (1) Å, $b = 14.358$ (4) Å, $c = 17.510$ (3) Å, $V = 2172$ Å^3, $R = 3.9\%$ for 1875 reflections. The copper environment is pseudotetrahedral, with a dihedral angle of 57.4° between the two CuN_2 ligand planes. This accurate structure provides a new and somewhat better calibrant for the correlation between the spectra and structures of pseudotetrahedral copper(II) complexes than the known $[Cu(HDPA)_2](ClO_4)_2$ complex (**2**) ($R = 9.4\%$), where HDPA = 2,2′-dipyridylamine. The differences between complexes **1** and **2** include a slightly closer approach to tetrahedral configuration of copper(II) in complex **1** and far greater deviation of the ligands from planarity in **2**, as well as a major displacement of the metal atom from one of the ligand planes. Although the difference between the dihedral angles in the two complexes is small (57.4 and 55.6°), the trend is in the right direction when compared to spectral assignments.

Introduction

There has been considerable interest in the relationship of the magnetic, spectroscopic, and structural properties of 2,2′-dipyridylamine (HDPA)[1-15] and its complexes with bivalent transition metals, particularly copper(II),[1-8] nickel(II),[2,9] palladium(II),[10] cobalt(II),[11] and iron(II).[12] A variety of stereochemical arrangements has been inferred for the cobalt, iron, and nickel complexes. Gouge and Geldard[1] have examined $[Cu(HDPA)_2]^{2+}$, $Cu(DPA)_2$, and a series of copper(II) complexes with stereochemically similar ligands, which produced a pseudotetrahedral metal environment. The known structure[7] of $Cu(HDPA)_2(ClO_4)_2$ could then be used to calibrate the spectra of the various copper complexes in terms of distortion from regular tetrahedral geometry. The accuracy of this known structure is limited ($R = 9.4\%$), presumably due to some disorder in the perchlorate groups. Thus, a much more accurate related structure, such as that of the deprotonated 3,3′-dimethyl-2,2′-dipyridylamine complex of copper(II) $[Cu(MPA)_2]$ which we report here, would be very useful for the correlation with spectral and magnetic properties. A further interest in such a structure is that despite the extensive studies on ligands of this type, no crystal structure determination of any first-series transition-metal complexes with a deprotonated ligand has been reported. The only known structure with a deprotonated ligand is that of the DPA complex of palladium(II),[10] in which the ligand is extremely distorted to enable the metal atom to acquire its normal square-planar configuration.

Experimental Section

Preparation of the Complex. To a solution of 0.76 g (3.82 mmol) of 2,2′-iminobis(3-picoline)[16] in 75 mL of distilled benzene was added 0.200 g (2.05 mmol) of $Cu(OH)_2$, freshly prepared by precipitation from a $CuCl_2$ solution by the addition of aqueous KOH. The mixture was heated at reflux for 24 h, during which time the color turned a deep green. The mixture was cooled and filtered and the filtrate concentrated to a volume of about 15 mL on a rotary evaporator. Absolute ether was added to the remaining solution, and when the solution stood in a refrigerator overnight, the complex separated as purple crystals; 531 mg (61%), mp 237–239 °C. When the filtrate was concentrated, followed by refrigeration, an additional 118 mg (13%) of product was obtained; mp 237–239 °C.

Crystal data for $[Cu(MPA)_2]$: $CuN_6C_{24}H_{24}$, mol wt 460, space group $P2_12_12_1$, $Z = 4$, $a = 8.639$ (1) Å, $b = 14.358$ (4) Å, $c = 17.510$ (3) Å, $V = 2172$ Å^3, $\rho_{calcd} = 1.407$ g cm^{-3}, $\rho_{obsd} = 1.41$ g cm^{-3}, μ(Mo Kα) = 10.7 cm^{-1}. Crystal dimensions, distances in mm of faces from centroid: (100) 0.38, $(\bar{1}00)$ 0.38, (011) 0.27, $(0\bar{1}\bar{1})$ 0.27, $(01\bar{1})$ 0.152, $(0\bar{1}1)$ 0.152. Maximum and minimum transmission coefficients are 0.87 and 0.82.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was

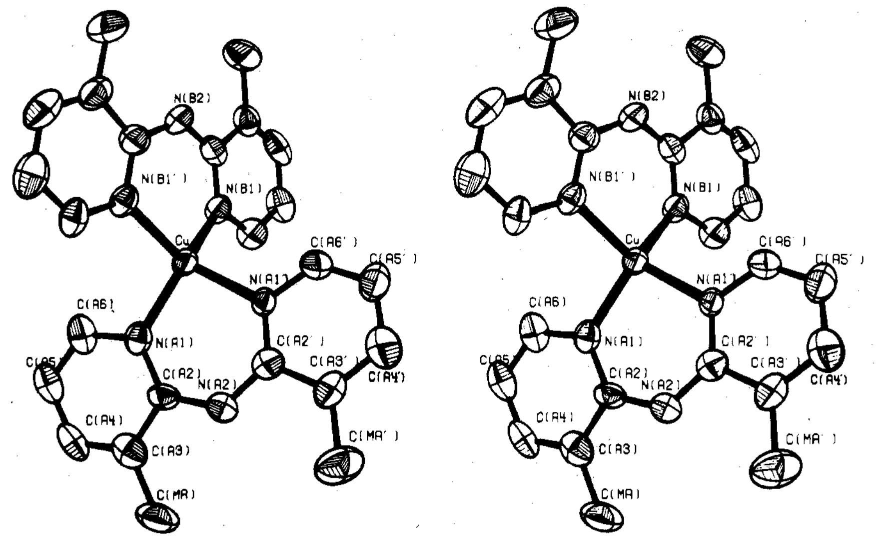

Figure 1. Stereopair view of Cu(MPA)$_2$.

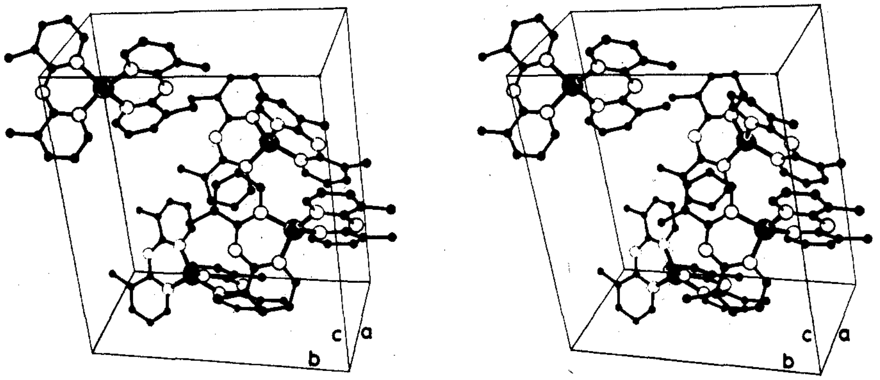

Figure 2. Packing in the unit cell of Cu(MPA)$_2$.

examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer by using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 48°$. Scan widths (SW) were calculated from the formula $\mathrm{SW} = A + B \tan \theta$ 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 0.60 and 0.35°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as $\mathrm{NC} = \mathrm{TOT} - 2(\mathrm{BG1} + \mathrm{BG2})$ where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. The total data set consisted of 1954 independent intensities, of which 1875 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[17] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The position of the metal atom was determined from a three-dimensional Patterson function calculated from all intensity data. The atomic positions of the copper atom phased the data sufficiently well to permit location of the remaining nonhydrogen atoms.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber[18] and those for hydrogen from Stewart et al.[19] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c by using the values of Cromer and Ibers[20] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c|/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Subsequent Fourier difference functions revealed hydrogen atom positions which were included in the refinement, except for the methyl hydrogens which exhibited positional disorder.

Anisotropic temperature factors were introduced for all nonhydrogen atoms, and refinement continued to convergence. The correct absolute configuration was chosen by refinement of all atomic parameters to convergence by using all data. The model converged with $R = 3.9\%$ and $R_w = 5.6\%$. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 4.5\%$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[21] The principal programs used are as previously described.[22]

Results and Discussion

Final positional and thermal parameters for [Cu(MPA)$_2$] are given in Table I. Tables II and III contain the bond lengths and 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 the stereopair view of the molecule, while Figure 2 shows the molecular packing in the unit cell.

The complex consists of well-separated, neutral molecules, with no unusually close intermolecular approaches. The closest

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $CuN_6C_{24}H_{24}$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.78600 (7)	0.81410 (4)	0.91514 (3)	3.25 (2)	2.72 (2)	2.28 (2)	−0.60 (2)	0.29 (2)	−0.28 (2)
N(A1)	0.7755 (5)	0.6990 (3)	0.9735 (2)	2.7 (2)	3.4 (2)	2.7 (1)	−0.4 (2)	0.3 (1)	−0.3 (1)
N(A2)	0.6357 (5)	0.6101 (3)	0.8798 (2)	3.1 (2)	2.6 (1)	3.3 (2)	−0.5 (2)	0.2 (2)	0.1 (1)
N(A1′)	0.6866 (5)	0.7597 (3)	0.8247 (2)	3.0 (2)	2.6 (1)	2.0 (1)	0.2 (1)	0.1 (1)	−0.3 (1)
N(B1)	0.9370 (5)	0.8910 (3)	0.8623 (2)	3.3 (2)	3.4 (2)	2.7 (1)	−0.7 (2)	0.1 (2)	−0.6 (1)
N(B2)	0.8581 (6)	1.0346 (3)	0.9168 (2)	5.0 (2)	3.0 (2)	3.4 (2)	−0.5 (2)	−0.5 (2)	−0.4 (2)
N(B1′)	0.7441 (5)	0.9101 (3)	0.9914 (2)	3.0 (2)	3.3 (2)	2.9 (2)	−0.3 (1)	0.6 (1)	−0.7 (1)
C(A2)	0.7165 (6)	0.6168 (3)	0.9452 (3)	2.6 (2)	2.8 (2)	3.0 (2)	−0.5 (2)	0.7 (2)	0.3 (2)
C(A3)	0.7396 (6)	0.5317 (4)	0.9863 (3)	3.6 (2)	4.0 (2)	3.9 (2)	0.4 (2)	1.5 (2)	0.5 (2)
C(A4)	0.8184 (7)	0.5354 (4)	1.0546 (3)	4.0 (3)	5.3 (2)	3.4 (2)	0.2 (2)	0.7 (2)	1.8 (2)
C(A5)	0.8766 (6)	0.6187 (4)	1.0838 (3)	3.3 (2)	5.5 (3)	3.3 (2)	0.1 (2)	0.0 (2)	1.4 (2)
C(A6)	0.8548 (6)	0.6978 (4)	1.0420 (3)	2.8 (2)	5.7 (3)	3.1 (2)	−0.8 (2)	−0.3 (2)	0.8 (2)
C(A2′)	0.6166 (5)	0.6750 (3)	0.8258 (3)	2.5 (2)	3.1 (2)	2.8 (2)	0.2 (2)	0.4 (2)	−0.6 (2)
C(A3′)	0.5163 (7)	0.6492 (4)	0.7633 (3)	3.3 (2)	3.4 (2)	3.3 (2)	0.1 (2)	−0.3 (2)	−0.9 (2)
C(A4′)	0.4978 (7)	0.7093 (4)	0.7041 (3)	4.3 (2)	4.7 (3)	3.7 (2)	0.4 (2)	−0.4 (2)	−0.0 (2)
C(A5′)	0.5734 (7)	0.7961 (4)	0.7043 (3)	4.9 (3)	4.3 (2)	3.4 (2)	0.7 (2)	−0.7 (2)	−0.5 (2)
C(A6′)	0.6638 (7)	0.8170 (3)	0.7633 (3)	4.0 (2)	2.7 (2)	3.3 (2)	0.2 (2)	0.1 (2)	0.3 (2)
C(B2)	0.9406 (6)	0.9849 (3)	0.8675 (3)	3.3 (2)	3.5 (2)	2.7 (2)	−0.6 (2)	−0.6 (2)	0.9 (2)
C(B3)	1.0423 (7)	1.0351 (4)	0.8157 (3)	3.9 (2)	4.3 (2)	3.3 (2)	−0.7 (2)	−0.4 (2)	0.9 (2)
C(B4)	1.1298 (7)	0.9899 (4)	0.7662 (3)	3.7 (2)	6.0 (3)	3.4 (2)	−1.2 (2)	−0.3 (2)	2.1 (2)
C(B5)	1.1288 (7)	0.8914 (4)	0.7629 (3)	3.2 (2)	5.5 (3)	3.6 (2)	−0.1 (2)	0.4 (2)	0.5 (2)
C(B6)	1.0311 (7)	0.8467 (4)	0.8104 (3)	3.2 (2)	4.7 (2)	3.6 (2)	−0.1 (2)	0.8 (2)	0.1 (2)
C(B2′)	0.7706 (7)	1.0038 (3)	0.9767 (3)	3.4 (2)	3.4 (2)	3.0 (2)	−0.2 (2)	−0.4 (2)	−0.0 (2)
C(B3′)	0.7088 (7)	1.0730 (3)	1.0253 (3)	4.5 (2)	3.6 (2)	4.1 (2)	0.7 (2)	−1.4 (2)	−0.9 (2)
C(B4′)	0.6265 (7)	1.0472 (4)	1.0889 (3)	4.0 (2)	5.6 (3)	4.6 (2)	1.3 (2)	−0.5 (2)	−2.5 (2)
C(B5′)	0.5963 (7)	0.9505 (5)	1.1036 (3)	4.0 (3)	6.7 (3)	4.1 (2)	0.3 (3)	0.3 (2)	−1.4 (3)
C(B6′)	0.6553 (7)	0.8883 (4)	1.0538 (3)	3.1 (2)	5.0 (2)	2.7 (2)	−0.4 (2)	0.5 (2)	−0.7 (2)
C(MA)	0.6766 (9)	0.4425 (4)	0.9551 (4)	6.5 (4)	2.7 (2)	6.0 (3)	−0.3 (3)	0.8 (3)	0.8 (2)
C(MA′)	0.4379 (8)	0.5539 (4)	0.7626 (4)	4.6 (3)	4.7 (3)	6.9 (3)	−1.7 (3)	−1.4 (3)	−0.6 (3)
C(MB)	1.0385 (10)	1.1434 (4)	0.8226 (4)	8.5 (4)	3.9 (2)	5.8 (3)	−2.2 (3)	1.1 (3)	1.3 (2)
C(MB′)	0.7440 (11)	1.1745 (4)	1.0095 (4)	11.0 (6)	4.0 (3)	6.5 (3)	2.5 (3)	−1.7 (4)	−1.4 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(A4)	0.807 (8)	0.464 (4)	1.096 (3)	6.4 (15)	H(B4)	1.181 (6)	1.015 (3)	0.732 (2)	3.4 (11)
H(A5)	0.929 (5)	0.619 (3)	1.127 (2)	1.8 (8)	H(B5)	1.212 (7)	0.862 (4)	0.744 (3)	5.9 (14)
H(A6)	0.895 (5)	0.760 (3)	1.062 (2)	1.5 (8)	H(B6)	1.035 (5)	0.769 (3)	0.820 (3)	2.9 (10)
H(A4′)	0.413 (6)	0.674 (3)	0.660 (3)	3.8 (11)	H(B4′)	0.589 (6)	1.078 (3)	1.110 (3)	4.0 (12)
H(A5′)	0.541 (6)	0.841 (3)	0.664 (3)	3.0 (10)	H(B5′)	0.515 (5)	0.934 (3)	1.156 (2)	2.2 (9)
H(A6′)	0.726 (4)	0.868 (3)	0.771 (2)	1.7 (8)	H(B6′)	0.636 (6)	0.806 (3)	1.064 (2)	2.9 (9)

[a] The form of the anisotropic thermal parameters is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)$.

Table II. Bond Lengths (Å) for $CuN_6C_{24}H_{24}$

Cu-N(A1)	1.945 (2)	C(A4)-C(A5)	1.395 (5)
Cu-N(A1′)	1.963 (2)	C(A5)-C(A6)	1.363 (4)
Cu-N(B1)	1.943 (2)	C(A2′)-C(A3′)	1.445 (4)
Cu-N(B1′)	1.954 (2)	C(A3′)-C(A4′)	1.356 (5)
N(A1)-C(A2)	1.378 (3)	C(A3′)-C(MA′)	1.526 (4)
N(A1)-C(A6)	1.382 (4)	C(A4′)-C(A5′)	1.408 (5)
N(A2)-C(A2)	1.344 (4)	C(A5′)-C(A6′)	1.329 (4)
N(A2)-C(A2′)	1.337 (4)	C(B2)-C(B3)	1.455 (4)
N(A1′)-C(A2′)	1.360 (3)	C(B3)-C(B4)	1.321 (5)
N(A1′)-C(A6′)	1.368 (3)	C(B3)-C(MB)	1.559 (5)
N(B1)-C(B2)	1.351 (4)	C(B4)-C(B5)	1.415 (5)
N(B1)-C(B6)	1.377 (4)	C(B5)-C(B6)	1.347 (5)
N(B2)-C(B2)	1.327 (4)	C(B2′)-C(B3′)	1.413 (4)
N(B2)-C(B2′)	1.366 (4)	C(B3′)-C(B4′)	1.372 (5)
N(B1′)-C(B2′)	1.388 (4)	C(B3′)-C(MB′)	1.514 (5)
N(B1′)-C(B6′)	1.371 (4)	C(B4′)-C(B5′)	1.437 (6)
C(A2)-C(A3)	1.431 (4)	C(B5′)-C(B6′)	1.348 (5)
C(A3)-C(A4)	1.377 (5)	C(A6′)-C(MA′)	3.544 (5)[a]
C(A3)-C(MA)	1.495 (5)		

[a] Closest intermolecular contact; symmetry transformation $1 - x$, ${}^1/_2 + y$, $1 - z$.

intermolecular distance is 3.544 (5) Å between a ring carbon atom, C(A6′), and a methyl group, C(MA′), of adjacent molecules. The copper environment is four-coordinated and pseudotetrahedral. This is in sharp contrast with the analogous nickel complex of the related DPA ligand, which is believed to be octahedral and polymeric from spectroscopic data.[2] The dihedral angle τ between the planes defined by N(A1), Cu, N(A1′) and N(B1), Cu, N(B1′) is 57.4°, and the angle between the two ligand planes, θ, is 67.1°. Angles of 90° are a necessary but not sufficient condition for regular tetrahedral geometry; planar geometry requires a 0° angle. The dihedral angle τ may be compared with the analogous angle of 55.6° in $[Cu(HDPA)_2](ClO_4)_2$,[7] although the detailed nature of the distortion is very different in the two complexes (vide infra).

The pseudotetrahedral geometry of $Cu(MPA)_2$ is a compromise between the effects of crystal field stabilization energy and steric interaction, which favor planar and tetrahedral geometries, respectively. This compromise not only prevents the copper(II) environment from approaching planarity but also causes some distortion of the ligands from planarity. The two pyridyl rings make angles of 8.4 and 6.8° with the central N(1), C(2), N(2), C(2′), N(1′) fragment, respectively, for ligand A; the analogous angles are 6.2 and 4.1° for ligand B. The two pyridyl rings are at 14.9° to each other in ligand A and at 9.7° in ligand B. This distortion is presumably kept from being larger by the fact that on deprotonation the entire ligand becomes pseudoaromatic. By comparison, the pyridine rings are inclined at 22.5° to each other in each ligand of $[Cu(HDPA)_2](ClO_4)_2$.[7] The neutral undeprotonated HDPA ligand is more flexible than MPA^- and is therefore able to absorb much more of the strain when steric and crystal field energies compete.

The crystal field splitting energy, Δ, is much smaller in tetrahedral ligand environments than in the corresponding square-planar ones. Thus, increase in distortion of perfect tetrahedral geometry toward planar will cause an increase in Δ, as well as a twofold splitting of both the upper ^2E and lower

Table III. Bond Angles (deg) for $CuN_6C_{24}H_{24}$

N(A1)-Cu-N(A1′)	93.75 (9)	Cu-N(B1)-C(B6)	116.6 (2)	N(A1)-C(A6)-C(A5)	123.0 (3)	C(B2)-C(B3)-C(MB)	115.6 (3)
N(A1)-Cu-N(B1)	139.8 (1)	C(B2)-N(B1)-C(B6)	119.5 (3)	N(A2)-C(A2′)-N(A1′)	125.3 (3)	C(B4)-C(B3)-C(MB)	123.7 (3)
N(A1)-Cu-N(B1′)	103.4 (1)	C(B2)-N(B2)-C(B2′)	128.4 (3)	N(A2)-C(A2′)-C(A3′)	115.7 (3)	C(B3)-C(B4)-C(B5)	121.0 (3)
N(A1′)-Cu-N(B1)	97.80 (9)	Cu-N(B1′)-C(B2′)	121.7 (2)	N(A1′)-C(A2′)-C(A3′)	119.0 (3)	C(B4)-C(B5)-C(B6)	117.1 (3)
N(A1′)-Cu-N(B1′)	138.7 (1)	Cu-N(B1′)-C(B6′)	119.1 (2)	C(A2′)-C(A3′)-C(A4′)	119.2 (3)	N(B1)-C(B6)-C(B5)	123.9 (3)
N(B1)-Cu-N(B1′)	92.8 (1)	C(B2′)-N(B1′)-C(B6′)	117.6 (3)	C(A2′)-C(A3′)-C(MA′)	120.0 (3)	N(B2)-C(B2′)-N(B1′)	123.3 (3)
Cu-N(A1)-C(A2)	123.8 (2)	N(A1)-C(A2)-N(A2)	123.9 (2)	C(A4′)-C(A3′)-C(MA′)	120.8 (3)	N(B2)-C(B2′)-C(B3′)	116.3 (3)
Cu-N(A1)-C(A6)	116.3 (2)	N(A1)-C(A2)-C(A3)	120.0 (3)	C(A3′)-C(A4′)-C(A5′)	120.4 (3)	N(B1′)-C(B2′)-C(B3′)	120.4 (3)
C(A2)-N(A1)-C(A6)	119.0 (3)	N(A2)-C(A2)-C(A3)	116.1 (3)	C(A4′)-C(A5′)-C(A6′)	118.3 (3)	C(B2′)-C(B3′)-C(B4′)	119.6 (3)
C(A2)-N(A2)-C(A2′)	128.1 (2)	C(A2)-C(A3)-C(A4)	118.2 (3)	N(A1′)-C(A6′)-C(A5′)	124.1 (3)	C(B2′)-C(B3′)-C(MB′)	119.4 (3)
Cu-N(A1′)-C(A2′)	122.6 (2)	C(A2)-C(A3)-C(MA)	119.8 (3)	N(B1)-C(B2)-N(B2)	124.6 (3)	C(B4′)-C(B3′)-C(MB′)	120.8 (3)
Cu-N(A1′)-C(A6′)	117.3 (2)	C(A4)-C(A3)-C(MA)	122.0 (3)	N(B1)-C(B2)-C(B3)	117.8 (3)	C(B3′)-C(B4′)-C(B5′)	120.1 (3)
C(A2′)-N(A1′)-C(A6′)	119.0 (2)	C(A3)-C(A4)-C(A5)	121.9 (3)	N(B2)-C(B2)-C(B3)	117.6 (3)	C(B4′)-C(B5′)-C(B6′)	117.1 (3)
Cu-N(B1)-C(B2)	123.4 (2)	C(A4)-C(A5)-C(A6)	117.9 (3)	C(B2)-C(B3)-C(B4)	120.7 (3)	N(B1′)-C(B6′)-C(B5′)	125.1 (3)

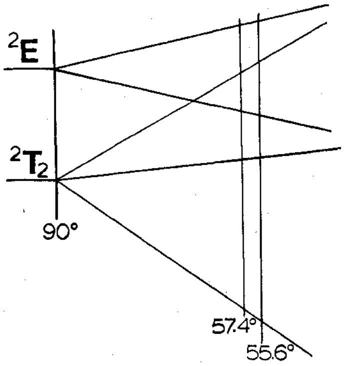

Figure 3. Schematic view of level splitting as a function of the two known dihedral angles ϕ.

$^2T_2$ states. This is well represented by operation on the d-orbital wave functions with $l_z{}^2\delta$, corresponding to flattening of the cube, four of whose vertices form the tetrahedron. In real complexes, the distortion is not uniaxial, particularly when the ligands are bidentates, and a further distortion operator $\epsilon(l_+{}^2 + l_-{}^2)$ is needed to simulate the off-axial distortion. Now all degeneracy is removed from the "tetrahedral" $^2T_2$ ground state, resulting in four spin-allowed d–d transitions which can be used to evaluate Δ, δ, and ϵ, provided accurate spectral data are available. In suitable cases, two of the parameters, δ and ϵ, can be represented by a single parameter, the dihedral angle ϕ (vide infra).

Gouge and Geldard[1] have assigned the four ligand field transitions in a series of related pseudotetrahedral bis-bidentate complexes, arranged them in order of increasing distortion from tetrahedral symmetry, and suggested a correlation with ϕ, the dihedral angle. This can be justified by the fact that ϕ gives a direct measure of the flattening of the tetrahedron, while the main off-axial distortion is the intraligand N–Cu–N angles which should also vary monotonically with ϕ. The correlation could not be made quantitative with specific dihedral angle values, as only the HDPA ϕ value was known, but it could be used effectively for spectral assignments. Quantifying the correlation and accurate testing of the hypothesis require more than one compound of accurately known structure, preferably as widely spaced as possible on the ϕ scale. Unfortunately, the two complexes in the series with known structure, $[Cu(HDPA)_2](ClO_4)_2$ and $[Cu(MPA)_2]$, are too close in ϕ value (55.6 and 57.4°, respectively), and the structural accuracy of the former complex is limited by anion disorder. The $Cu(MPA)_2$ structure does offer a better initial calibration point. On the assumption of the correctness of the spectral assignments, ϕ values can now be assigned as shown in Figure 3, though linearity of the scale cannot be assumed.

Despite the limitations imposed by accuracy and closeness of the ϕ values, the spectral and crystallographic data are seen to be in good qualitative agreement. Crystal structures of related compounds with a wider range of ϕ values would be useful to further test the model and to qualify the relation between structural and spectral features.

The normal synthesis of DPA complexes and their analogues, involves the initial formation of ionic complexes with the neutral ligands, such as $Cu(HDPA)_2(ClO_4)_2$. This complex is then deprotonated in situ to form the neutral complex. The present study shows that copper(II) hydroxide is basic enough to form the neutral complex $[Cu(MPA)_2]$ directly with HMPA. Similar reactions carried out in this laboratory with a series of related ligands suggest that this reaction is fairly general and provides a facile synthesis for such complexes.

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Registry No. $Cu(MPA)_2$, 70072-37-6.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes and a table of least-squares planes data (10 pages). Ordering information is given on any current masthead page.

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