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Structural Variations in Macrocyclic Copper(II) Complexes: Crystal and Molecular Structure of (Difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato)-(pyridine)copper(II) Perchlorate, $[Cu(cyclops)py]ClO_4$

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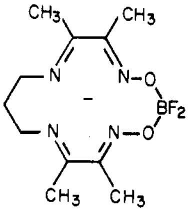
The crystal and molecular structure of $[Cu(cyclops)py]ClO_4$ (**1**, cyclops = difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate, py = pyridine) has been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The purple crystals of **1** were orthorhombic, of space group $P2_12_12_1$ (No. 19), with four formula units in the unit cell (a = 7.898 (5) Å, b = 14.040 (8) Å, c = 19.574 (11) Å). The structure of **1** was refined to R = 0.058 (R_w = 0.060) for 1361 independent reflections for which $F^2 > 3\sigma(F^2)$. The discrete, monomeric complex ions of **1** exhibited a square-pyramidal coordination geometry about the copper(II) ion, with the pyridine ligand occupying the apical position and the four basal coordination sites being occupied by the nitrogen atoms of the quadridentate macrocyclic cyclops ligand. The displacement of the copper(II) ion from the basal plane of four coordinating nitrogen atoms is large (0.40 Å), despite the fact that the Cu(II)–N bonds remain strong (basal Cu–N(av) = 1.97 (1) Å). The observed degree of distortion of the metal ion coordination is achieved by a considerable degree of "flexing" of the macrocyclic ligand, which adopts a "chair"-like conformation, in contrast to that found in earlier copper(II) structures involving this macrocycle. In contrast to the complexes [Cu(cyclops)X] (X^- = I^-, NCO^-) previously studied, where the bond to the anionic apical ligand was unprecedentedly strong, the Cu–N5(py) bond length of 2.170 (9) Å falls at the low end of the normal range for such bonds. This confirms the importance of both variations in the metal ion's apical displacement and the strength of the bond to the apical position in accounting for the spectroscopic properties of compounds in this series.

Introduction

Recent studies of five-coordinate square-pyramidal copper(II) complexes involving the cyclops macrocycle (cyclops = difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate, **2**) have demonstrated the unusual spectroscopic[1]



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and structural[2-4] properties of the species [Cu(cyclops)X] (X^- = anionic ligands) and $[Cu(cyclops)L]^+$ (L = neutral Lewis bases). The spectrochemical series[1] [$H_2O \ll C(CN)_3^- <$ py < imidazole < I^-, $Br^- < N(CN)_2^- < Cl^- < NCS^- \ll CN^-$, NCO^-] constructed from the observed d–d absorption maxima for a series of X^- and L apical ligands was unusual in the relative placement of neutral and anionic ligands. It was argued that observation of such a series demanded a capability for large and highly variable displacement of the copper(II) ion from the plane of the four basal atoms of the macrocyclic ligand (a displacement which shall be termed the "apical" displacement in the remainder of this paper) as the Lewis basicity and ionic character of the apical ligands vary.

The first structural study of a complex in this series, that of [Cu(cyclops)NCO], verified the existence of a very large (0.58 Å) apical displacement of the copper(II) ion.[2] Also, the expected elongation[5] of the bond to the apical position of 0.2–0.6 Å (compared to a similar bond to a basal position) was not present in the cyanato-*N* complex, as the observed Cu(II)–N(cyanato) bond length of 2.038 (6) Å was only slightly longer than would be expected for a basal Cu(II)–N-(cyanato) bond.

These unusual structural features prompted our investigations of the structures of other complexes in this series. At the other end of the observed spectrochemical series, the structure of the complex cation $[Cu(cyclops)H_2O]^+$ exhibited an apical displacement almost 0.3 Å less than that observed in the cyanato-*N* adduct and a bond length to the apical water molecule that fell toward the short end of the known range of such $Cu(II)–OH_2$(apical) bond lengths.[3] To see whether the parameters of apical displacement and apical bond strength varied smoothly and simultaneously throughout this spectrochemical series, we chose to investigate the structures of two compounds toward the center of the series. The first of these structures,[4] that of [Cu(cyclops)I], exhibited an apical displacement only slightly greater than that observed for the $[Cu(cyclops)H_2O]^+$ cation and apparently gained its place in the spectrochemical series by virtue of another abnormally short apical bond (Cu(II)–I = 2.742 (2) Å). The second of these two structures, that of the complex cation $[Cu(cyclops)py]^+$, is the subject of this report.

Experimental Section

Synthesis and Crystallization for (Difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borato)(pyridine)copper(II) Perchlorate, 1, $[Cu(cyclops)py]ClO_4$. Pyridine (32 μL, 0.4 mmol) was added to a boiling solution of $\{[Cu(cyclops)]_2C_4H_8O_2\}ClO_4$[6] (104 mg, 0.21 mmol) in 10 mL of methanol. The resulting purple solution was slowly cooled to room temperature and allowed to stand overnight. Purple crystals of the title compound were separated by filtration and subsequently characterized by means of the visible spectrum.[1]

Crystal data for 1, $[Cu(C_{16}H_{23}N_5O_2BF_2)]ClO_4$: formula weight 529.2, orthorhombic, with a = 7.898 (5) Å, b = 14.040 (8) Å, c = 19.574 (11) Å, and V = 2170.5 Å^3; ρ_{obsd} = 1.60 g cm^{-3} (by neutral buoyancy in 1,2-dibromoethane/chloroform), ρ_{calcd} = 1.62 g cm^{-3}, Z = 4; $F(000)$ = 1084; space group $P2_12_12_1$ (No. 19); Mo Kα radiation, λ_1 = 0.709 30 Å, λ_2 = 0.713 59 Å, μ(Mo Kα) = 12.2 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs of the purple crystals revealed Laue symmetry *mmm*, consistent with the orthorhombic crystal system. These photographs also exhibited the following systematic absences: *h*00,

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[1] Addison, A. W.; Carpenter, M.; Lau, L. K.-M.; Wicholas, M. *Inorg. Chem.* **1978**, *17*, 1545.
[2] Anderson, O. P.; Marshall, J. C. *Inorg. Chem.* **1978**, *17*, 1258.
[3] Anderson, O. P.; Packard, A. B. *Inorg. Chem.* **1979**, *18*, 1941.
[4] Anderson, O. P.; Packard, A. B. *Inorg. Chem.*, in press.
[5] Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.
[6] Gagné, R. R.; Allison, J. L.; Gall, R. S.; Kovall, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170.

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$h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. These conditions are consistent only with the space group $P2_12_12_1$ (No. 19).[7]

The crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the *b* axis approximately coincident with the diffractometer ϕ axis. After the crystal was centered, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations[8] on the automatically determined[9] 2θ, χ, and ϕ settings (20 ± 1 °C) of 29 reflections with $10° < 2\theta < 22°$.

The intensities of 2209 reflections in the octant characterized by indices $-h$, $+k$, and $+l$ and with θ values in the range $4.5° < \theta < 25°$ were measured by θ–2θ scans employing Zr-filtered Mo Kα radiation. The total scan range was 1.0° for all reflections, with a constant scan rate of 10° min^{-1}. The weakest reflections were scanned a maximum of four times, while fewer scans were employed for stronger reflections. Background was counted at both ends of the scan, for a total time equal to the scan time. The takeoff angle was 3.5°, and Zr-foil attenuators were automatically inserted on very strong reflections to keep the counting rate within the linear region of the scintillation detector and counting chain.

The intensity of one of three reference reflections (008, 063, and $\bar{3}$,0,14) was measured every 25 reflections, and no significant changes in the intensities of these reflections were noted during data collection. Lorentz and polarization corrections were applied to the observed data. The uncertainty parameter, *g*, in the formula used for the calculation of the standard deviation in the intensity[10,11] was taken as 0.04. Due to the low absorption coefficient, no absorption correction was performed on the data. The crystal used for data collection measured approximately 0.30 × 0.12 × 0.11 mm, with the longest direction oriented along the diffractometer ϕ axis. Reflections for which $F^2 > 3\sigma(F^2)$ were taken to be observed, and the 1361 unique reflections which met this criterion were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. The position of the copper(II) ion was assigned from the Patterson map, and initial positions for all other nonhydrogen atoms were obtained from Fourier syntheses for which atoms in known positions provided phase information. Scattering factors for copper(II), chlorine, fluorine, oxygen, nitrogen, carbon, boron, and spherical bonded hydrogen[12] were taken from ref 13, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper and chlorine.

Two cycles of refinement in which all atoms were assigned isotropic thermal parameters showed that all of the atoms were correctly placed but that the perchlorate oxygen atoms were subject to a large degree of thermal motion. After careful examination of a difference Fourier map in the region of the perchlorate anion failed to reveal any evidence for additional partially occupied sites, the structural model was converted to one in which Cu(II), N1–N4, the atoms of the pyridine ligand, and the atoms of the perchlorate counterion were assigned anisotropic thermal parameters. Hydrogen atoms were included in the model when they could be observed in a difference Fourier map and were placed in calculated idealized positions 0.95 Å from carbon, with an isotropic thermal parameter 1.0 Å^2 larger than that of the carbon atom to which they were attached. Refinement of this model was terminated when all shifts for parameters involving the copper(II) complex cation were less than 20% of the corresponding standard deviations (although at this point shifts as large as 80% of the esd for some thermal parameters of the perchlorate anion were still observed).

Table I. Atomic Coordinates (Fractional)[a] for [Cu(cyclops)py]ClO$_4$

atom	*x*	*y*	*z*
Cu	0.03188 (17)	0.11741 (9)	0.23322 (7)
Cl	−0.3556 (7)	0.0386 (4)	0.4801 (3)
F1	−0.3404 (10)	0.1486 (5)	0.1760 (4)
F2	−0.3795 (10)	0.3084 (6)	0.1510 (4)
O1	−0.1262 (10)	0.2404 (6)	0.1276 (4)
O2	−0.2303 (9)	0.2674 (5)	0.2468 (4)
O3	−0.5159 (15)	0.0249 (10)	0.5097 (6)
O4	−0.2578 (18)	0.0959 (12)	0.5262 (7)
O5	−0.2800 (30)	−0.0440 (13)	0.4714 (15)
O6	−0.3528 (22)	0.0832 (13)	0.4181 (6)
N1	−0.0043 (11)	0.1750 (6)	0.1421 (4)
N2	0.2349 (12)	0.0708 (7)	0.1851 (5)
N3	0.1226 (12)	0.1094 (7)	0.3280 (5)
N4	−0.1118 (11)	0.2102 (6)	0.2784 (5)
N5	−0.1110 (12)	−0.0145 (6)	0.2367 (7)
C1	0.1124 (16)	0.1617 (9)	0.0976 (6)
C2	0.2451 (14)	0.0942 (8)	0.1224 (6)
C3	0.3530 (15)	0.0080 (9)	0.2209 (6)
C4	0.3965 (17)	0.0436 (9)	0.2898 (6)
C5	0.2599 (20)	0.0412 (11)	0.3444 (7)
C6	0.0449 (18)	0.1628 (9)	0.3705 (6)
C7	−0.0887 (15)	0.2232 (9)	0.3429 (6)
C8	0.1184 (17)	0.2113 (10)	0.0305 (6)
C9	0.3789 (18)	0.0615 (9)	0.0724 (7)
C10	0.0885 (18)	0.1670 (10)	0.4462 (7)
C11	−0.1870 (18)	0.2926 (10)	0.3855 (7)
C12	−0.1541 (18)	−0.0538 (10)	0.2978 (7)
C13	−0.2554 (19)	−0.1335 (11)	0.3004 (9)
C14	−0.3130 (17)	−0.1736 (9)	0.2423 (11)
C15	−0.2694 (19)	−0.1344 (10)	0.1800 (9)
C16	−0.1621 (18)	−0.0551 (10)	0.1808 (8)
B1	−0.2664 (21)	0.2370 (11)	0.1761 (8)
H1(C3)	0.4540	0.0030	0.1948
H2(C3)	0.3030	−0.0532	0.2252
H1(C4)	0.4316	0.1079	0.2850
H2(C4)	0.4888	0.0065	0.3060
H1(C5)	0.3085	0.0575	0.3871
H2(C5)	0.2141	−0.0213	0.3469
H1(C8)	0.2329	0.2184	0.0167
H2(C8)	0.0587	0.1746	−0.0025
H3(C8)	0.0670	0.2722	0.0348
H1(C9)	0.4069	−0.0032	0.0815
H2(C9)	0.3363	0.0670	0.0272
H3(C9)	0.4770	0.1001	0.0773
H1(C10)	−0.0060	0.1459	0.4722
H2(C10)	0.1829	0.1267	0.4549
H3(C10)	0.1159	0.2306	0.4584
H1(C11)	−0.1113	0.3383	0.4043
H2(C11)	−0.2684	0.3238	0.3577
H3(C11)	−0.2424	0.2594	0.4214
H1(C12)	−0.1139	−0.0261	0.3390
H1(C13)	−0.2848	−0.1604	0.3433
H1(C14)	−0.3832	−0.2286	0.2442
H1(C15)	−0.3105	−0.1603	0.1383
H1(C16)	−0.1250	−0.0296	0.1384

[a] Estimated standard deviations are given in parentheses. If no standard deviation is given, the parameter was fixed during refinement.

The final R ($=[\sum||F_o| - |F_c||/\sum|F_o|]$) value was 0.058 (unobserved reflections were not included), while the final R_w ($=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$) value was 0.60. Reversal of signs on all atomic coordinates and refinement of the inverted model to convergence led to $R = 0.064$ and $R_w = 0.069$. Consequently, the initial model was retained for all further computations. The error in an observation of unit weight was 1.58. The NUCLS refinement program minimizes $w(|F_o| - |F_c|)^2$, where w is the weight assigned to each reflection ($=4F_o^2/\sigma^2(F_o^2)$). No extinction correction was carried out, and a final difference Fourier map revealed only one peak higher than 0.5 e Å^{-3}. This peak, with a height of 0.7 e Å^{-3}, was only 1 Å from the copper atom.

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(7) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

(8) The following programs were used in this structure determination: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a group/nongroup least-squares version of the Busing–Levy ORFLS program; Ibers' CELREF for least-squares refinement of cell parameters; ORFFE, Busing and Levy's function and error program; ORTEP, Johnson's thermal ellipsoid plot program; HYDRA, Ibers' program to predict hydrogen atom positions. The program for data reduction and *Lp* correction was locally written for the CDC CYBER 171/172 computers at Colorado State University.

(9) Using the automated routines incorporated in the Enraf-Nonius diffractometer package.

(10) Anderson, O. P.; Packard, A. B.; Wicholas, M. *Inorg. Chem.* **1976**, *15*, 1613.

(11) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table II. Anisotropic and Isotropic Thermal Parameters[a] for [Cu(cyclops)py]ClO$_4$

atom	10^3U_{11}[b]	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu	33.7 (6)	36.8 (7)	36.3 (7)	5.2 (7)	2.3 (7)	1.1 (8)
Cl	104 (4)	114 (4)	86 (3)	−8 (4)	5 (3)	−1 (3)
F1	67 (2)					
F2	75 (2)					
O1	44 (2)					
O2	48 (2)					
O3	62 (7)	162 (12)	138 (10)	−18 (8)	30 (8)	−13 (9)
O4	156 (13)	219 (17)	98 (9)	−85 (13)	−46 (9)	−25 (11)
O5	288 (23)	112 (12)	431 (35)	116 (17)	75 (24)	7 (18)
O6	198 (15)	244 (19)	84 (9)	−97 (15)	−50 (10)	61 (11)
N1	30 (6)	39 (5)	41 (5)	−6 (5)	−2 (5)	−5 (4)
N2	39 (6)	42 (6)	42 (6)	1 (5)	2 (4)	−1 (4)
N3	39 (6)	46 (6)	46 (5)	0 (6)	−7 (5)	9 (6)
N4	40 (5)	42 (6)	39 (6)	10 (5)	−2 (5)	−13 (5)
N5	45 (6)	37 (6)	64 (7)	−3 (5)	−7 (6)	−10 (7)
C1	43 (3)					
C2	38 (3)					
C3	54 (4)					
C4	60 (4)					
C5	66 (4)					
C6	45 (3)					
C7	45 (3)					
C8	61 (4)					
C9	63 (4)					
C10	66 (4)					
C11	65 (4)					
C12	44 (9)	62 (11)	55 (9)	2 (11)	17 (7)	9 (7)
C13	46 (9)	61 (12)	89 (12)	3 (9)	20 (8)	23 (10)
C14	63 (9)	38 (8)	103 (13)	−4 (7)	13 (11)	−1 (14)
C15	63 (10)	39 (10)	95 (12)	−9 (8)	15 (9)	−12 (8)
C16	45 (9)	49 (10)	83 (11)	10 (8)	15 (8)	3 (8)
B1	53 (4)					

[a] Estimated standard deviations are given in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$. [b] When only one value is given, that atom has been refined isotropically, and U_{iso} is reported.

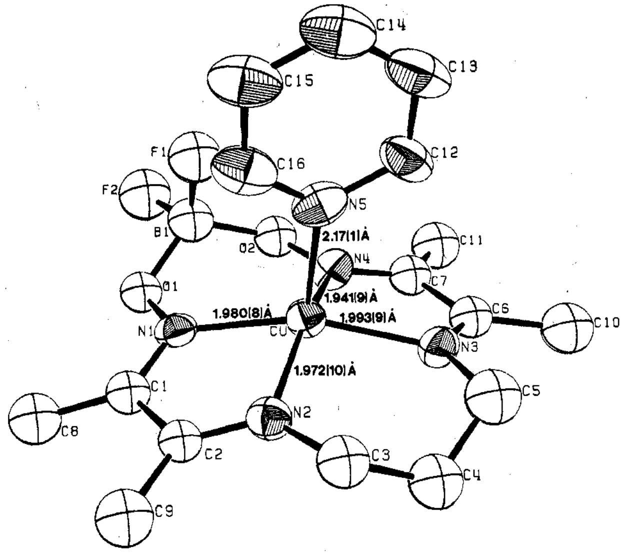

Figure 1. View of the complex cation [Cu(cyclops)py]$^+$. Hydrogen atoms have been omitted, and 50% probability ellipsoids are depicted.

Final atomic positional parameters for **1** are listed in Table I, while the final values of isotropic and anisotropic thermal parameters for **1** are listed in Table II. A listing of observed and calculated structure factor amplitudes (×10) may be found as Table VI in the supplementary material.

Results and Discussion

Crystals of **1** consist of discrete complex cations [Cu(cyclops)py]$^+$ and isolated perchlorate anions. Figure 1 displays the structure found for the complex cation, while Figure 2 contains a view of the way in which the unit cell contents are arranged in the lattice. Table III lists calculated bond lengths and angles for **1**, while Table IV presents results of tests of the planarity of various parts of the complex cation.

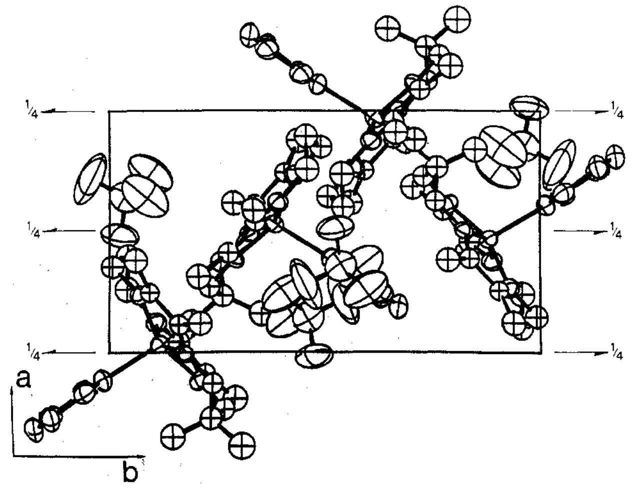

Figure 2. View (down *c*) of the contents of the unit cell for [Cu(cyclops)py]ClO$_4$. Some of the crystallographic symmetry elements which relate the ions shown are also depicted. All hydrogen atoms have been omitted.

As in our earlier studies,[2-4] the coordination geometry about the copper(II) ion can be best described as a distorted square pyramid, with the pyridine ligand occupying the apical position in this case. The coordination geometry cannot be regarded as a distorted trigonal bipyramid, since this would require three angles involving adjacent ligands in a plane to approach 120°. In the observed structure, only the angles N1–Cu–N5 (107.6 (4)°) and N4–Cu–N5 (104.7 (4)°) are greater than 100°, and these three ligand atoms (N1, N4, N5) do not lie in a plane as would be required if they were to be the equatorial ligands of the *tbp* coordination geometry. Instead, these two angles of over 100° presumably arise from the interaction of the

Table III. Bond Lengths and Angles[a] for $[Cu(cyclops)py]ClO_4$

(a) Bond Lengths (Å)

Cu–N1	1.980 (8)	N4–C7	1.29 (2)	C7–C11	1.50 (2)
Cu–N2	1.972 (10)	N5–C12	1.36 (2)	C12–C13	1.38 (2)
Cu–N3	1.993 (9)	N5–C16	1.30 (2)	C13–C14	1.35 (2)
Cu–N4	1.941 (9)	O1–B1	1.46 (2)	C14–C15	1.38 (3)
Cu–N5	2.17 (1)	O2–B1	1.48 (2)	C15–C16	1.40 (2)
N1–O1	1.36 (1)	C1–C2	1.49 (2)	B1–F1	1.37 (2)
N1–C1	1.28 (2)	C1–C8	1.49 (2)	B1–F2	1.43 (2)
N2–C2	1.27 (2)	C2–C9	1.51 (2)	Cl–O3	1.41 (1)
N2–C3	1.46 (2)	C3–C4	1.48 (2)	Cl–O4	1.44 (2)
N3–C5	1.48 (2)	C4–C5	1.52 (2)	Cl–O5	1.32 (2)
N3–C6	1.28 (2)	C6–C7	1.46 (2)	Cl–O6	1.37 (2)
N4–O2	1.38 (1)	C6–C10	1.52 (2)		

(b) Bond Angles (Deg)

N1–Cu–N2	79.8 (4)	N2–C2–C1	115.7 (10)
N1–Cu–N3	156.1 (4)	N2–C2–C9	126.1 (11)
N1–Cu–N4	93.0 (4)	C1–C2–C9	118.2 (10)
N1–Cu–N5	107.6 (4)	N2–C3–C4	112.4 (10)
N2–Cu–N3	97.7 (4)	C3–C4–C5	118.0 (11)
N2–Cu–N4	156.4 (4)	N3–C5–C4	110.7 (11)
N2–Cu–N5	98.9 (4)	N3–C6–C7	116.6 (10)
N3–Cu–N4	79.8 (4)	N3–C6–C10	123.2 (12)
N3–Cu–N5	96.3 (5)	C7–C6–C10	120.2 (11)
N4–Cu–N5	104.7 (4)	N4–C7–C6	112.5 (10)
Cu–N1–O1	124.4 (6)	N4–C7–C11	124.3 (11)
Cu–N1–C1	116.7 (8)	C6–C7–C11	123.1 (11)
Cu–N2–C2	115.3 (8)	N5–C12–C13	120.5 (13)
Cu–N2–C3	119.3 (7)	C12–C13–C14	120.3 (15)
Cu–N3–C5	120.0 (8)	C13–C14–C15	119.6 (13)
Cu–N3–C6	113.6 (8)	C14–C15–C16	117.3 (15)
Cu–N4–O2	125.7 (7)	N5–C16–C15	123.2 (15)
Cu–N4–C7	117.3 (8)	O1–B1–O2	117.0 (12)
Cu–N5–C12	120.3 (9)	O1–B1–F1	110.6 (12)
Cu–N5–C16	120.7 (10)	O1–B1–F2	103.1 (11)
N1–O1–B1	112.3 (9)	O2–B1–F1	110.2 (12)
N4–O2–B2	112.5 (9)	O2–B1–F2	103.9 (11)
O1–N1–C1	117.8 (9)	F1–B1–F2	111.6 (12)
C2–N2–C3	125.3 (10)	O3–Cl–O4	107.6 (8)
C5–N3–C6	126.2 (10)	O3–Cl–O5	110.0 (12)
O2–N4–C7	116.9 (9)	O3–Cl–O6	116.3 (10)
C12–N5–C16	119.0 (11)	O4–Cl–O5	109.3 (13)
N1–C1–C2	112.1 (10)	O4–Cl–O6	107.1 (10)
N1–C1–C8	123.6 (11)	O5–Cl–O6	106.4 (15)
C2–C1–C8	124.2 (11)		

[a] Estimated standard deviations are given in parentheses.

Table IV. Least-Squares Planes for $[Cu(cyclops)py]ClO_4$

(a) Deviations from Planes[a]

plane 1 ($n = 4$): N1 (−0.021), N2 (0.000), N3 (0.000), N4 (0.000), Cu (0.398), O1 (−0.175), O2 (−0.068), C1 (−0.0068), C2 (−0.271), C3 (0.112), C4 (−0.521), C5 (0.129), C6 (−0.264), C7 (−0.297), B1 (0.491)
plane 2 ($n = 4$): N1 (0.179), N2 (0.000), C1 (0.000), C2 (0.001), Cu (0.197), O1 (0.101), C3 (−0.036), C8 (−0.243), C9 (−0.019)
plane 3 ($n = 4$): N2 (0.000), N3 (0.001), C3 (−0.005), C5 (0.012), Cu (0.497), C2 (−0.227), C4 (−0.670), C6 (−0.213)
plane 4 ($n = 4$): N3 (−0.001), N4 (0.001), C6 (0.023), C7 (−0.003), Cu (0.025), O2 (−0.088), C5 (0.043), C10 (0.046), C11 (−0.035)
plane 5 ($n = 4$): O1 (0.000), O2 (0.000), N1 (0.102), N4 (0.000), Cu (0.401), C1 (−0.241), C7 (−0.368), B1 (0.634)
plane 6 ($n = 6$): N5 (−0.016), C12 (−0.001), C13 (0.008), C14 (0.001), C15 (−0.009), C16 (0.022), Cu (−0.189)

(b) Equations of Planes[b]

plane	*A*	*B*	*C*	*D*
1	4.704	11.268	0.647	−2.022
2	4.611	10.860	4.828	−2.745
3	5.164	10.589	1.183	−2.181
4	5.203	10.194	−3.856	−4.883
5	4.856	11.002	1.740	−2.254
6	6.390	−8.242	−0.542	0.702

(c) Dihedral Angles (Deg) between Planes

planes	angle	planes	angle
1–2	12.4	2–5	9.2
1–3	4.6	2–6	89.4
1–4	14.4	3–4	14.9
1–5	3.6	3–5	3.2
1–6	89.4	3–6	85.2
2–3	11.5	4–5	17.0
2–4	26.2	4–6	83.6
		5–6	88.0

[a] Numbers in parentheses refer to the distance (Å) of the given atom from the calculated plane. The first n atoms in each case determine the given plane. [b] In the form $Ax + By + Cz = D$.

pyridyl ligand with fluorine atom F1 of the BF_2 moiety (N5–F1 = 3.15 Å). A similar tilt of the apical ligand was seen in our earlier studies of the cyanato-*N*,[2] aquo,[3] and iodo[4] copper(II)–cyclops complexes, indicating the importance of the interaction between the apical ligand and this fluorine atom in all of these cases.

As was seen in these earlier studies, no significant differences in Cu–N bond lengths for the N(oxime) atoms as opposed to the N(imine) ligand atoms can be seen, although small differences of this type have been reported in related complexes of copper[6,14,15] and other transition metals.[16-18] The only indication of an inequality among the four bond lengths observed here arises for the Cu–N4 bond (1.941 (9) Å), which inexplicably seems somewhat shorter than the other three bonds of this type (Cu–N1 = 1.980 (8) Å, Cu–N2 = 1.972 (10) Å, Cu–N3 = 1.993 (9) Å). The average Cu–N(macrocycle) bond length of 1.97 (1) Å observed in this case is approximately the same as was seen in the iodo complex (Cu–N(av) = 1.956 (7) Å), longer than in the aquo complex (Cu–N(av) = 1.940 (8) Å), and shorter than in the (cyanato-*N*)copper(II)–cyclops complex (Cu–N(av, macrocycle) = 2.001 (4) Å).

These observed changes in the average Cu–N(macrocycle) bond lengths are accompanied by parallel changes in the apical displacement of the copper(II) ion from the basal plane of the four macrocyclic nitrogen atoms, though the effect is not dramatic. The largest such displacement, 0.58 Å, was seen in the (cyanato-*N*)copper(II)–cyclops complex,[2] which was the case in which the Cu–N bond lengths were longest, as noted above. The apical displacement observed here for the pyridyl complex of 0.40 Å is the same as that observed previously for the iodo complex (0.38 Å), in agreement with the close similarity of the Cu–N(macrocycle) bond lengths noted above for these two cases. The structure in which the smallest apical displacement of the metal ion was seen was that of the cationic $[Cu(cyclops)H_2O]^+$ species, where the apical displacement of 0.32 Å was accompanied by the shortest Cu–N(av) bond length in this series of complexes. It may be noted that in all of these cases the degree of apical displacement noted is much larger than would be expected in a "normal" square-pyramidal copper(II) coordination environment.[5]

These changes in the equilibrium bonding position of the copper(II) ion in this series of complexes are also accompanied by changes in the overall conformation of the macrocyclic cyclops ligand. The most significant change of this type, in terms of maintaining strong bonding to the metal ion as it progressively moves farther out of the basal plane, is a "flexing" of the macrocycle to continue to allow effective overlap between $N(sp^2)$ lone pairs and the d orbitals of the metal ion. The magnitude of this "flexing" motion can be seen

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Table V. Structural Parameters for the Species [Cu(cyclops)X] and [Cu(cyclops)L]$^+$

apical ligand	Cu–N(av, macrocycle)	Cu–X$^-$ (Cu–L), Å	metal ion apical displacement, Å	macrocyclic "flexing" angle,[a] deg	macrocycle conformation
H_2O[3]	1.940 (8)	2.253 (9)	0.32	15	chair/boat
I^-[4]	1.956 (7)	2.742 (2)	0.38	11	chair
py	1.97 (1)	2.170 (9)	0.40	13	chair
NCO^-[2]	2.001 (4)	2.038 (6)	0.58	27	boat

[a] The value given is the average of the two slightly different values seen in each case.

in the dihedral angles (Table IV) between the plane of the basal nitrogen atoms (plane 1) and the planes (plane 2, N1–Cl–C2–N2; plane 4, N3–C6–C7–N4) comprising the formally unsaturated portions of the macrocyclic ligand. The macrocyclic "flexing" angle of ~13° seen here for the pyridine adduct is very similar to the corresponding angles in the other complexes (I^-, H_2O) where the degree of apical displacement of the metal was also much less than for the cyanato-*N* complex (see Table V).

In case of the cyanato-*N* complex, the extreme apical displacement of the copper(II) ion is accompanied by the very large "flexing" angle of ~27°. The manner in which the saturated propylene portion and the dioxime-derived section of the macrocycle are folded relative to one another can be specified by the "boat" or "chair" designation, referring in all cases to the relative positioning of C4, N1–N4, and B1. Both the "flexing" angles and the changes in conformation summarized in Table V make clear the high degree of flexibility and relatively low energy barrier to changes in conformation which characterize the cyclops macrocycle. Individual bond lengths and angles within the macrocyclic ligand in the pyridine complex are very similar to those seen in the earlier studies.[2–4]

The observed Cu–N(py) bond length of 2.170 (9) Å is not exceptionally short, as was the case for the apical bonds in the copper(II)–cyclops complexes where anions occupied the apical position. It is certainly much shorter than the Cu–N(py) bond length of 2.31 Å observed[19] when pyridine is bound in the apical position of a bis(*N*-phenylsalicylaldiminato)copper(II) complex. It is, however, comparable to the Cu–N(py) bond lengths of 2.186 (8) and 2.13 (1) Å seen in the two crystalline forms of (pyridine)copper(II) acetate.[20,21] From related structures,[22] a Cu–N(py) bond length of ~2.0 Å would be expected when the pyridine ligand was in a basal position of the square-pyramidal environment. Thus, the complex [Cu(cyclops)py]$^+$ exhibits an apical Cu–N(py) bond which is as strong as or stronger than that of most other "normal" square-pyramidal copper(II) complexes involving pyridine as the apical ligand but which is not foreshortened to the degree necessary to make it comparable to the above-mentioned cyanato-*N* and iodo complexes, where the apical bonds were almost as short as basal bonds would be expected to be.

Due to the expected interaction between the fluorine atom (F1) which is farthest out of the basal plane and the carbon and hydrogen atoms adjacent to the nitrogen in the pyridine ligand, the orientation of the pyridyl ligand is such that the plane of this ligand is approximately perpendicular to the F1–C4 line. The py ligand is highly planar (Table IV), as expected, and this ligand plane is perpendicular to the basal plane of four nitrogen atoms (dihedral angle 89°). Bond lengths and angles within the pyridine ligand are very similar to those found in earlier studies.[20–23]

The purpose of this study, as stated in the Introduction, was to verify the simultaneous variation of apical bond strength and apical displacement of the metal ion invoked by Addison and Wicholas[1] in explaining the spectrochemical series of the apical ligands. The results obtained in this series of studies (see Table V) confirm without question both the unusually high degree of metal ion apical displacement and the variability of this displacement suggested by these previous authors. The collected structural results also support these authors' contention that abnormally strong bonds to anionic apical ligands would be found to be the cause of the unusual ordering of the anionic vs. the neutral ligands in the apical spectrochemical series. As was argued above, neutral apical ligands such as water and pyridine form strong apical bonds which lie within the normal observed range for such species, while the bond lengths observed for the anionic apical species I^- and NCO^- were nearly as short as would be expected for these same ligands in basal positions.

The results presented here indicate that the two structural parameters of importance in determining the position of a ligand within the apical spectrochemical series, namely the apical bond strength and the apical copper(II) displacement, do not vary simultaneously as one moves through the given series of apical ligands. Despite the difference of almost 40 nm in the wavelength of maximum visible absorption,[1] the pyridine- and iodo–copper(II) complexes of cyclops exhibit essentially identical metal ion apical displacements. The reason, then, for the spectroscopic difference seen for these two complexes must lie solely in the d_{z^2}–$d_{x^2-y^2}$ orbital energy compression which results from formation of the extraordinarily short, strong Cu–I^- bond as compared to the Cu–N(py) apical bond of normal strength in the present work.

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Supplementary Material Available: Table VI, a listing of observed and calculated structure factor amplitudes (×10) for [Cu(cyclops)py]ClO$_4$ (8 pages). Ordering information is given on any current masthead page.

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