(bond length)–(bond order) curves are only approximate, they demonstrate that equal bond lengths may correspond to considerably different valence bond orders for different elements (e.g., N vs. C, S vs. P, or Se vs. As). These curves suggest that the observed X–X bond lengths for the $M_2(CO)_6(\mu\text{-}X_2)$ complexes correspond to approximate X–X bond orders of 1.4 for the iron dimers and 1.9 for the cobalt dimers.

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Registry No. $Fe_2(CO)_6(\mu\text{-}Se_2)$, 71341-69-0.

Supplementary Material Available: Observed and calculated structure factors for $Fe_2(CO)_6(\mu\text{-}Se_2)$ (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Presented in part at the National Meeting of the American Crystallographic Association, Norman, OK, March 1978. (b) Based in part upon a dissertation submitted by C.F.C. to the Graduate School of the University of Wisconsin, Madison, in partial fulfillment of the requirements for the Ph.D. degree, December 1975.

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Structural Variations in Macrocyclic Copper(II) Complexes. Crystal and Molecular Structure of Iodo[difluoro[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]borato]copper(II), [Cu(cyclops)I]

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The crystal and molecular structure of [Cu(cyclops)I] (**1**, cyclops = difluoro[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]borate) has been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The dark green crystals of **1** were monoclinic, space group $P2_1/c$ (No. 14), with four formula units in the unit cell ($a = 10.036$ (3) Å, $b = 7.399$ (3) Å, $c = 24.982$ (8) Å, $\beta = 106.67$ (1)°). The structure of **1** was refined to $R = 0.046$ ($R_w = 0.047$) for 1488 independent reflections with $F^2 > 3\sigma(F^2)$. The discrete, monomeric complex ions exhibited square-pyramidal coordination geometry about the central copper(II) ion, with iodide occupying the apical position and the four basal coordination sites being occupied by the nitrogen atoms of the quadridentate macrocyclic cyclops ligand. The flexible macrocyclic ligand allows a large displacement (0.38 Å) of the copper(II) ion out of the basal plane of four nitrogen atoms in the direction of the apical iodo ligand; while simultaneously maintaining strong copper(II)–nitrogen bonding (Cu–N(av) = 1.956 (7) Å). A very short, strong bond is observed between the metal atom and the apical iodo ligand (Cu–I = 2.742 (2) Å), which underscores the ability of the cyclops macrocycle to allow very strong bonds to be formed to ligands in the apical position of a square-pyramidal coordination environment about copper(II).

Introduction

Our interest in the structures of copper(II) complexes of the macrocycle difluoro[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]borate (**2**, hereafter referred to as cyclops) became great when the structure of the square-pyramidal cyanato-*N* adduct [Cu(cyclops)(NCO)] was found to exhibit a striking degree of metal displacement (0.58 Å) out of the basal plane of nitrogen atoms and an extremely short Cu–

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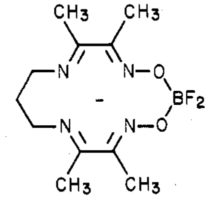

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N(cyanato) bond length of 2.038 (6) Å to the apical cyanato-*N* ligand.[1] While the apical bond length observed in that study was unprecedentedly short, the bond length to the apical water molecule in [Cu(cyclops)H_2O](ClO_4) was found to lie at the low end of the range of values that had been previously observed.[2]

Addison and co-workers[3] argued, on the basis of spectroscopic evidence, that the "abnormal" spectrochemical series observed for a range of apical ligands in the cationic and neutral complexes $[Cu(cyclops)L]^+$ and [Cu(cyclops)X] represented a combination of two effects. The first, a strongly variable apical displacement of the copper(II) ion out of the basal plane of the coordinating nitrogen atoms of the quadridentate macrocycle, has been demonstrated to hold in these complexes by our earlier studies.[1,2] The second effect, an unusually strong interaction of the copper(II) ion with anionic ligands in the apical position, was (according to Addison and Wicholas) responsible for the reversal of normal positions in the observed spectrochemical series for apical ligands such as the halide ions when compared with neutral ligands such as water and pyridine. While the structure of the cyanato-*N* adduct did show just this sort of extremely strong apical bonding interaction (see above), the position of the cyanato ligand at the extreme end of the observed spectrochemical series of apical ligands does not allow ready comparison of the strength of the apical interaction to those for neutral ligands positioned similarly in the spectrochemical series. We therefore chose to determine the structure of the complex [Cu(cyclops)I], since the iodo ligand lies toward the center of the observed spectrochemical series,[3] close to the position of pyridine (py). Our structural study of the complex [Cu(cyclops)py](ClO_4), which will be reported at a later date, will allow comparison of the apical interactions and metal displacements in these compounds which are so surprisingly similar in their spectroscopic properties.

The structure of the iodo complex [Cu(cyclops)I] was doubly interesting, due to our past studies of the structures of complexes of copper(II) with soft ligands of high reducing power.[4,5] The presence of the soft halide ion (which normally reduces copper(II) to copper(I)[6] in the absence of a good "stabilizing" ligand such as cyclops) in the coordination sphere of copper(II) is not common.[7-10] Therefore, we wished to expand the range of structural types for which stable Cu(II)–I^- binding had been seen by study of the title compound. Details of the results of the structural determination for [Cu(cyclops)I] are found below.

Experimental Section

Synthesis. Iodo[difluoro[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]borato]copper(II), [Cu(cyclops)I] (1). The compound was prepared by adding tetraethylammonium iodide (102.9 mg, 0.4 mmol) to a boiling solution of mono(dioxane)bis{[difluoro[3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)]borato]copper(II) perchlorate} ({(Cu(cyclops))$_2C_4H_8O_2$}(ClO_4)$_2$, 103.8 mg, 0.21 mmol) in 10 mL of methanol. The dioxane-bridged dimer had been previously prepared by the method reported by Gagné.[11] The resulting dark green solution was slowly cooled to room temperature and allowed to stand overnight. Crystals suitable for single-crystal X-ray diffraction studies were isolated by vacuum filtration.

Crystal Data. For [$CuC_{11}H_{18}N_4O_2BF_2I$]: mol wt 477.55, monoclinic, a = 10.036 (3) Å, b = 7.399 (3) Å, c = 24.982 (8) Å, β = 106.67 (1)°, V = 1777.1 Å^3; ρ_{obsd} = 1.79 g cm^{-3} (by neutral buoyancy in 1,2-dibromoethane/chloroform), ρ_{calcd} = 1.79 g cm^{-3}, Z = 4, $F(000)$ = 932, space group $P2_1/c$ (No. 14), Mo Kα radiation, λ_1 0.709 30 Å, λ_2 0.713 59 Å, μ(Mo Kα) = 30.6 cm^{-1}.

Data Collection and Reduction. Preliminary Weissenberg and precession photographs revealed only Laue symmetry $2/m$, consistent with the monoclinic crystal system. These photographs also exhibited the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, which are consistent only with the space group $P2_1/c$ (No. 14).[12]

The small, dark green crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the crystal's b axis approximately coincident with the diffractometer ϕ axis. After centering of the crystal, the orientation matrix for data collection and the unit cell parameters reported above were obtained from least-squares calculations[13] on the automatically determined[14] angular settings of 25 reflections (at 20 (±1) °C) with $18° < 2\theta < 22°$.

The intensities of 3078 reflections (with some duplication in the zero layer on k and with $h \geq 0$, $k \geq 0$) with $4.5° < \theta < 25°$ 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 attenuators were inserted for strong reflections to keep the counting rate at the reflection maximum below 2500 counts s^{-1} and thus avoid coincidence losses.

The intensity of one of three control reflections ($\bar{2}06$, $23\bar{3}$, and 226) was measured every 25 reflections. No significant changes were noted in the intensities of the control reflections during data collection. Lorentz and polarization corrections were applied to the observed data, and the data were also corrected for absorption by a numerical Gaussian integration technique (2 × 4 × 8 sampling grid).[13] The dimensions of the data collection crystal were 0.05 mm ($\{100\} \rightarrow \{\bar{1}00\}$) × 0.15 mm ($\{001\} \rightarrow \{00\bar{1}\}$) × 0.40 mm ($\{011\} \rightarrow \{0\bar{1}\bar{1}\}$) × 0.32 mm ($\{0\bar{1}1\} \rightarrow \{01\bar{1}\}$). Extrema in the calculated transmission coefficients were 0.625 and 0.863. The uncertainty parameter, g, in the formula used for the calculation of the standard deviation in the intensity[5,15] was taken as 0.04. Reflections for which $F^2 > 3\sigma(F^2)$ were taken to be observed and the 1488 unique reflections which met this criterion were used in the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure. The position of the iodide ion was assigned from the Patterson map, and initial positions for all nonhydrogen atoms were then obtained from Fourier syntheses for which atoms in known positions provided phase information. Scattering factors for copper(II), iodide, fluorine, oxygen, nitrogen, carbon, boron, and spherical bonded hydrogen[16] were taken from ref 17, as were correction terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper and iodine.

All atomic positional and thermal parameters refined satisfactorily through two cycles of refinement in which isotropic thermal parameters were assigned to each atom. In the final full-matrix least-squares refinement cycles, all nonhydrogen atoms of the model were given anisotropic thermal parameters, and hydrogen atoms were included in the model in calculated idealized positions 0.95 Å from carbon. Isotropic thermal parameters 1.0 Å^2 larger than that for the atom to which they were attached were assigned to the hydrogen atoms. Refinement continued until all shifts in parameters were less than 5% of the estimated standard deviation for that parameter.

The final R $(=[\sum||F_o| - |F_c||/\sum|F_o|])$ value was 0.046 (unobserved reflections not included), while the final R_w $(=[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2})$ value was 0.047. The error in an observation of unit weight was 1.32. The NUCLS refinement program minimizes $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively, and w is the weight for each reflection $(=4F_o^2/\sigma^2(F_o^2))$. No correction for secondary extinction was undertaken, and the final difference Fourier map revealed one peak (0.8 e Å^{-3}) in the immediate vicinity of the iodide ligand, while all other peaks were lower than 0.6 e Å^{-3}.

Final atomic positional parameters for **1** are listed in Table I, while the final values of the anisotropic thermal parameters for **1** are listed in Table II.

Results and Discussion

The crystals of **1** consist of discrete, neutral, monomeric complexes, [Cu(cyclops)I]. The structure of one of these complex units is displayed in Figure 1, and Table III lists the

Table I. Atomic Coordinates (Fractional)[a] for Cu(cyclops)I

atom	*x*	*y*	*z*
Cu	−0.15464 (13)	0.15730 (17)	0.37722 (5)
I	−0.25349 (10)	0.47988 (10)	0.32751 (3)
F1	0.3129 (7)	0.2297 (11)	0.4390 (3)
F2	0.1311 (8)	0.3983 (9)	0.3869 (3)
O1	0.1143 (7)	0.2245 (10)	0.4637 (3)
O2	0.1361 (9)	0.0834 (10)	0.3771 (3)
N1	−0.0273 (9)	0.2169 (10)	0.4505 (3)
N2	−0.2856 (9)	0.1460 (12)	0.4225 (4)
N3	−0.2618 (11)	0.0088 (11)	0.3162 (3)
N4	−0.0026 (11)	0.0704 (11)	0.3489 (4)
C1	−0.0834 (11)	0.2297 (12)	0.4912 (4)
C2	−0.2363 (11)	0.2047 (13)	0.4726 (5)
C3	−0.4338 (13)	0.1129 (20)	0.3956 (6)
C4	−0.4570 (13)	−0.0399 (19)	0.3540 (7)
C5	−0.4135 (14)	−0.0002 (18)	0.3023 (6)
C6	−0.1937 (16)	−0.0539 (14)	0.2844 (5)
C7	−0.0382 (16)	−0.0433 (14)	0.3078 (5)
C8	−0.0036 (13)	0.2692 (15)	0.5491 (5)
C9	−0.3164 (14)	0.2441 (19)	0.5137 (6)
C10	−0.2505 (17)	−0.1354 (18)	0.2264 (5)
C11	0.0623 (16)	−0.1557 (17)	0.2887 (6)
B1	0.1744 (15)	0.2366 (23)	0.4169 (7)
H1(C3)	−0.4775	0.0838	0.4235
H2(C3)	−0.4744	0.2198	0.3767
H1(C4)	−0.4057	−0.1417	0.3721
H2(C4)	−0.5533	−0.0684	0.3428
H1(C5)	−0.4468	−0.0932	0.2756
H2(C5)	−0.4521	0.1122	0.2870
H1(C8)	−0.0391	0.1989	0.5738
H2(C8)	0.0914	0.2399	0.5542
H3(C8)	−0.0120	0.3940	0.5564
H1(C9)	−0.3133	0.3702	0.5212
H2(C9)	−0.4103	0.2070	0.4984
H3(C9)	−0.2759	0.1798	0.5474
H1(C10)	−0.3357	−0.0777	0.2076
H2(C10)	−0.1850	−0.1177	0.2059
H3(C10)	−0.2659	−0.2610	0.2297
H1(C11)	0.0687	−0.2718	0.3055
H2(C11)	0.0309	−0.1673	0.2492
H3(C11)	0.1510	−0.0990	0.2994

[a] Estimated standard deviations are given in parentheses. If no standard deviation is given, the parameter was not refined.

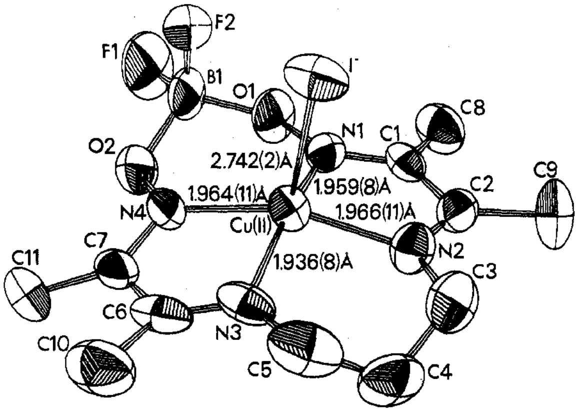

Figure 1. A view of the neutral [Cu(cyclops)I] molecule. Hydrogen atoms have been omitted, and 50% probability ellipsoids are depicted.

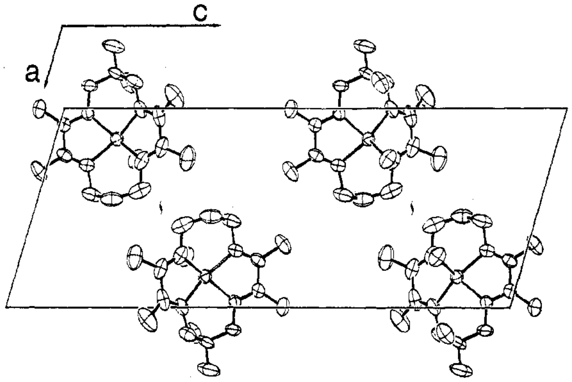

Figure 2. A view (down *b*) of the unit cell contents for [Cu(cyclops)I]. No hydrogen atoms are included.

bond lengths and angles which characterize this species. Table IV presents the results of various tests of the planarity of different portions of the complex unit. Finally, Figure 2 shows the manner in which the contents of the unit cell are arrayed and related by some of the symmetry elements present. The only significant intermolecular interactions involve van der Waals contacts between molecules, as neither the copper(II) ion nor the iodo ligand engages in any chemically significant intermolecular contacts.

The coordination geometry about the copper(II) ion corresponds to a tetragonally distorted square pyramid. The Cu–N bond lengths observed are best regarded as equal, given the magnitude of the experimental errors in these parameters.

Table II. Anisotropic Thermal Parameters[a] for Cu(cyclops)I

atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{13}	10^3U_{23}
Cu	45.5 (8)	45.5 (8)	43.2 (7)	2.6 (7)	11.5 (6)	−4.7 (6)
I	87.3 (7)	44.7 (5)	63.1 (5)	−7.3 (5)	3.8 (4)	−5.2 (4)
F1	41 (4)	128 (7)	140 (7)	−8 (5)	35 (4)	−41 (6)
F2	104 (6)	56 (4)	102 (5)	−26 (5)	62 (5)	−20 (4)
O1	30 (5)	78 (5)	67 (5)	1 (4)	12 (4)	−11 (4)
O2	52 (5)	58 (5)	86 (6)	1 (4)	34 (5)	−13 (4)
N1	42 (6)	42 (5)	42 (6)	−7 (4)	14 (4)	−4 (4)
N2	38 (6)	63 (6)	61 (6)	0 (5)	15 (5)	0 (5)
N3	81 (8)	29 (5)	45 (6)	6 (6)	1 (5)	3 (5)
N4	69 (7)	32 (5)	57 (6)	2 (5)	34 (5)	−3 (4)
C1	50 (7)	28 (5)	44 (7)	9 (5)	13 (6)	−2 (5)
C2	45 (7)	40 (6)	65 (8)	5 (6)	24 (6)	5 (6)
C3	44 (8)	92 (10)	114 (11)	−2 (8)	31 (8)	−12 (9)
C4	48 (8)	79 (10)	123 (12)	−21 (8)	13 (8)	−8 (9)
C5	65 (10)	62 (9)	105 (11)	3 (8)	−15 (8)	−8 (8)
C6	101 (12)	34 (7)	39 (7)	−17 (7)	5 (7)	0 (5)
C7	110 (12)	33 (6)	60 (7)	−12 (7)	51 (8)	−5 (6)
C8	82 (9)	62 (8)	46 (8)	−1 (7)	16 (6)	−9 (6)
C9	91 (10)	108 (6)	86 (10)	11 (9)	59 (8)	−12 (9)
C10	151 (14)	78 (9)	63 (9)	−32 (11)	27 (9)	−18 (8)
C11	136 (14)	66 (8)	132 (12)	−15 (10)	90 (11)	−44 (9)
B1	38 (10)	79 (11)	90 (12)	−8 (9)	37 (9)	−22 (10)

[a] Estimated standard deviations are given in parentheses. The form of the anisotropic thermal ellipsoid is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

Table III. Bond Lengths and Angles[a] for Cu(cyclops)I

(a) Bond Lengths (Å)

Cu-I	2.742 (2)	O1-B1	1.465 (20)
Cu-N1	1.959 (8)	O2-B1	1.485 (18)
Cu-N2	1.966 (11)	C1-C2	1.481 (15)
Cu-N3	1.936 (8)	C1-C8	1.466 (14)
Cu-N4	1.964 (11)	C2-C9	1.504 (21)
N1-O1	1.365 (11)	C3-C4	1.508 (21)
N1-C1	1.301 (16)	C4-C5	1.506 (25)
N2-C2	1.283 (14)	C6-C7	1.503 (21)
N2-C3	1.466 (15)	C6-C10	1.522 (16)
N3-C5	1.463 (18)	C7-C11	1.488 (22)
N3-C6	1.274 (18)	B1-F1	1.341 (16)
N4-O2	1.371 (12)	B1-F2	1.413 (18)
N4-C7	1.297 (14)		

(b) Bond Angles (deg)

I-Cu-N1	106.4 (2)	N1-C1-C2	112.7 (9)
I-Cu-N2	94.7 (3)	N1-C1-C8	123.3 (10)
I-Cu-N3	95.2 (2)	C2-C1-C8	123.9 (11)
I-Cu-N4	109.8 (3)	N2-C2-C1	115.1 (11)
N1-Cu-N2	80.6 (4)	N2-C2-C9	126.9 (10)
N1-Cu-N3	158.4 (3)	C1-C2-C9	118.0 (10)
N1-Cu-N4	92.5 (4)	N2-C3-C4	112.1 (11)
N2-Cu-N3	96.7 (4)	C3-C4-C5	114.8 (12)
N2-Cu-N4	155.4 (4)	N3-C5-C4	110.1 (10)
N3-Cu-N4	81.0 (4)	N3-C6-C7	115.0 (10)
Cu-N1-O1	126.2 (7)	N3-C6-C10	128.0 (13)
Cu-N1-C1	115.8 (7)	C7-C6-C10	117.0 (13)
Cu-N2-C2	114.4 (8)	N4-C7-C6	111.2 (12)
Cu-N2-C3	120.1 (8)	N4-C7-C11	124.0 (12)
Cu-N3-C5	121.2 (8)	C6-C7-C11	124.8 (10)
Cu-N3-C6	114.9 (9)	O1-B1-O2	113.6 (12)
Cu-N4-O2	124.9 (7)	O1-B1-F1	106.6 (11)
Cu-N4-C7	115.6 (9)	O1-B1-F2	110.0 (12)
N1-O1-B1	116.6 (8)	O2-B1-F1	106.6 (12)
N4-O2-B1	115.3 (9)	O2-B1-F2	108.0 (11)
O1-N1-C1	117.5 (8)	F1-B1-F2	112.0 (13)
C2-N2-C3	124.1 (11)		
C5-N3-C6	123.0 (10)		
O2-N4-C7	117.4 (11)		

[a] Estimated standard deviations are given in parentheses.

Table IV. Least-Squares Planes[a] for Cu(cyclops)I

(a) Deviations from the Planes

plane 1 ($n = 4$): N1 (0.017), N2 (−0.068), N3 (0.010), N4 (−0.012), Cu (0.376), O1 (−0.126), O2 (−0.260), C1 (−0.257), C2 (−0.175), C3 (0.037), C4 (−0.584), C5 (0.155), C6 (−0.142), C7 (−0.368), B1 (0.374)
plane 2 ($n = 4$): N1 (0.020), N2 (−0.092), C1 (−0.057), C2 (0.008), Cu (0.112), O1 (−0.130), C3 (−0.043), C8 (−0.164), C9 (0.142)
plane 3 ($n = 4$): N2 (0.038), N3 (−0.005), C3 (−0.009), C5 (0.004), Cu (0.541), C2 (0.035), C4 (−0.724), C6 (−0.149)
plane 4 ($n = 4$): N3 (−0.040), N4 (0.024), C6 (0.048), C7 (−0.127), Cu (0.089), O2 (−0.210), C5 (0.016), C10 (0.315), C11 (−0.501)
plane 5 ($n = 4$): O1 (0.000), O2 (−0.002), N1 (−0.073), N4 (0.051), Cu (0.158), C1 (−0.483), C7 (−0.317), B1 (0.647)

(b) Equations of the Planes[b]

plane	A	B	C	D
1	0.481	−6.730	9.532	−2.839
2	0.934	−7.123	5.419	−0.891
3	−0.308	−6.940	8.486	−2.698
4	−0.524	−6.129	13.724	−4.383
5	−1.149	−6.700	10.599	−3.280

(c) Dihedral Angles between the Planes

planes	angle, deg	planes	angle, deg
1-2	9.9	2-4	20.9
1-3	8.9	2-5	15.2
1-4	11.1	3-4	13.8
1-5	9.3	3-5	6.3
2-3	8.9	4-5	10.3

[a] In section 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 $Ax + By + Cz = D$.

The average bond length of 1.956 (7) Å for the four Cu-N bonds in [Cu(cyclops)I] may be slightly longer than the corresponding average bond length seen in the complex ion $[Cu(cyclops)H_2O]^+$ (where Cu–N(av) = 1.940 (8) Å)[2] but is significantly shorter than the Cu–N(av) of 2.001 (4) Å seen in the cyanato-*N* adduct, [Cu(cyclops)NCO].[1]

These observed changes in Cu–N bond lengths between these three cyclops complexes follow the changes in the apical displacement of the metal ion. The complexes [Cu(cyclops)I] and $[Cu(cyclops)H_2O]^+$ have very similar Cu–N(av) distances, as mentioned above, and the apical displacements (relative to the plane of the four basal nitrogen atoms) of the copper(II) ions in the two cases are also comparable (0.38 and 0.32 Å, respectively). Both of these displacements are much smaller than the corresponding displacement of 0.58 Å seen in the highly distorted cyanato-*N* adduct referred to above. This degree of apical displacement of the metal ion is quite large, compared to the normal 0.1–0.2 Å displacement seen in square-pyramidal copper(II) complexes,[18] and is achieved by "flexing" of the cyclops macrocycle instead of a dramatic lengthening of the Cu–N bonds. The degree of this "flexing" of the macrocycle is reflected in the dihedral angles between the basal plane of the four coordinating nitrogen atoms and the planes of the unsaturated portions of the ligand (N1–C1–C2–N2 and N3–C6–C7–N4). In [Cu(cyclops)I] these dihedral angles are 9.9 and 11.1°, which are similar to the corresponding values of 10.8 and 19.8° observed for the cationic complex $[Cu(cyclops)H_2O]^+$[2] but considerably less than the dihedral angles of 28.0 and 25.7° observed for the same planes in the much more highly distorted complex [Cu(cyclops)NCO].[1] With respect to the atoms B1, N1–N4, and C4, the cyclops macrocycle may be described as in a "chair" conformation, as was the case for [Cu(cyclops)NCO],[1] but the energy separating the "boat" and "chair" conformations is not great, as was shown by the presence of both conformations (due to observed disorder at C4) in the structure of $[Cu(cyclops)H_2O]^+$.[2]

The primary purpose of this structural determination was to test the prediction of Addison and Wicholas[3] that remarkably strong bonds might be formed between the copper(II) ion and anionic apical ligands. The complexes [Cu(cyclops)I] and $[Cu(cyclops)H_2O]^+$ were not close together in these authors' observed spectrochemical series for apical ligands, where position in the spectrochemical series was determined by the relative energies of the $d_{x^2-y^2}$ orbital (strongly influenced by the apical metal ion displacement) and the d_{z^2} orbital (strongly influenced by the strength of the metal–apical ligand bond). Since the structural evidence already presented shows that there is not a large difference between the metal ion displacements in the iodo and aquo complexes, the copper(II)–iodide bond must be exceedingly short and strong in order to account for the observed position of the iodide ion relative to water in the apical spectrochemical series.

In fact, this is exactly what is found, as the observed Cu(II)–I bond length is only 2.742 (2) Å. Due to the reduction which normally accompanies attempts to bind the iodide ion to copper(II),[6] only three structures of copper(II) complexes are available for comparison.[7-10] These earlier structures involved very similar trigonal-bipyramidal coordination environments about copper(II), in which the iodo ligand occupied equatorial positions 2.71,[7,8] 2.679 (3),[9] and 2.672 (3) Å[10] from the copper(II) atom. These previously obtained Cu–I distances are slightly, but significantly, shorter than the Cu–I distance observed in the present study. The normal expectation, however, would have been that they should have been much shorter, due to the magnitude of the difference usually found when comparing copper(II) binding to a ligand in an equatorial position (tbp geometry) vs. an apical position (spy geometry).

For example, Hathaway's compilation[18] of copper–ligand bond lengths for square-pyramidal complexes shows that apical bromide ion–copper(II) bond lengths range from 3.08 to 3.19 Å, with an average of 3.15 Å. Comparison of the ionic radii of the bromide (1.95 Å[19]) and iodide (2.16 Å[19]) ions would lead to an expected Cu(II)–I (apical) bond length of approximately 3.35 Å, fully 0.6 Å longer than the 2.742 (2) Å observed in the present study. This extremely short Cu–I (apical) bond length confirms the prediction made by Addison and Wicholas[3] concerning the strength of interactions between the copper(II) ion and anionic apical ligands in the [Cu(cyclops)X] system. The relatively high position of the iodide ion in their observed spectrochemical series must then be due to the high energy of the d_{z^2} orbital of the metal ion as a result of this exceptionally strong interaction with the apical ligand.

The electronic origins of this dramatic effect, first seen in the structure of the [Cu(cyclops)NCO] complex[1] and now again for the [Cu(cyclops)I] case, are not clear, and ESR studies of these complexes might do much to sort out the contributions to the unusual bonding patterns observed in the copper(II)–cyclops system. It will be of interest to compare the metal ion apical displacement and the strength of the apical interaction observed in the present study with the corresponding structural parameters for a neutral apical ligand which is close to the iodo ligand in the observed apical spectrochemical series, and the structure of the [Cu(cyclops)py]$^+$ complex cation (py = pyridine) will be the next structure to be reported in this series.

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Registry No. 1, 66070-10-8; {(Cu(cyclops))$_2$C$_4$H$_8$O$_2$}(ClO$_4$)$_2$, 61128-85-6.

Supplementary Material Available: Table V, a listing of observed and calculated structure factor amplitudes (×10) for [Cu(cyclops)I] (11 pages). Ordering information is given on any current masthead page.

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