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Structural Variations in Macrocyclic Copper(II) Complexes: Crystal and Molecular Structure of Cyano(difluoro-3,3'-(trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II)–Methanol, [Cu(cyclops)CN]·CH₃OH

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The crystal and molecular structure of the compound cyano(difluoro-3,3'-(trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II)–methanol, [Cu(cyclops)CN]·CH₃OH, has been determined by a single-crystal X-ray diffraction study. The deep green crystals are monoclinic, of space group $P2_1/c$ (No. 14), with four formula units in the unit cell (a = 12.61 (1) Å, b = 7.674 (7) Å, c = 19.46 (1) Å, β = 106.38 (2)°). The structure has been refined by full-matrix least-squares methods to R = 0.055 (R_w = 0.071) for 2048 independent reflections for which $F^2 > 3\sigma(F^2)$. The complex exhibits square-pyramidal coordination geometry about the copper(II) ion, with the cyanide ligand occupying the apical coordination site. The copper(II) atom is displaced to a very large degree (0.56 Å) from the plane of the four coordinating nitrogen atoms of the macrocycle and forms a strong bond (Cu–C = 2.042 (8) Å) to the apical cyanide ligand. This strong apical bond is in keeping with the cyclops macrocycle's ability to allow unusually strong bonding between copper(II) and apical anionic ligands. The methanol molecule found in the lattice does not interact with the copper atom but instead forms a hydrogen bond to the nitrogen atom of the apical cyanide ligand.

Introduction

In a series of structural studies in this laboratory, two aspects of the coordination chemistry of copper(II) have been investigated. First, while it is known that "soft" ligands of sufficiently high oxidation potential (such as cyanide ion, iodide ion, thiols, etc.) can reduce copper(II) to the cuprous state when placed in binary combination with the metal,[1] it is possible to prevent this metal reduction and to form stable copper(II) complexes containing cyanide and iodide ligands if the metal is bound to a "stabilizing" ligand (typically an aliphatic or aromatic amine) before introduction of the soft reducing species into the coordination sphere.[2–13] Introduction of an aliphatic thiolate sulfur into the coordination sphere of a copper(II) ion has proven to be more difficult, and only mixed-valence copper(I)–copper(II) clusters[14,15] and a substituted thiophenol complex[16] have shown well-characterized stable Cu(II)–S(thiolate) binding. The synthesis of copper(II)–thiolate complexes remains a goal of significance due to the known Cu(II)–S(thiolate) binding in two "blue" copper proteins,[17,18] and one of the common suppositions is that the overall structure of the copper(II)–thiolate complex would be of importance in determining stability. Because of this, we have engaged in a systematic investigation of the structures of cyano and iodo complexes of copper(II), in order to ascertain whether there is, in fact, any preferred structure or coordination position which is especially favorable for redox stability in these species. The structure of the title compound, cyano(difluoro-3,3'-(trimethylenedinitrilo)bis(2-butanone oximato)borato)copper(II)–methanol (the macrocyclic ligand difluoro-3,3'-(trimethylenedinitrilo)bis(2-butanone oximato)borate will hereafter be referred to as cyclops), [Cu(cyclops)CN]·CH₃OH, which is presented in this paper, is the final study in our series of structures of monomeric complexes involving Cu(II)–CN⁻ bonding.

The structure of the complex [Cu(cyclops)CN]·CH₃OH is also of interest relative to our systematic study of structural variations in the series of five-coordinate macrocyclic complexes [Cu(cyclops)X] and [Cu(cyclops)L]⁺ (X⁻ = cyanate,[19] iodide;[8] L = H₂O,[20] pyridine[21]). On the basis of spectroscopic evidence, it had been suggested[13] that, in this type of complex large, variable displacements of the copper(II) ion from the plane of the coordinating macrocyclic nitrogen atoms would be seen and that anionic apical ligands would be found to bind unusually strongly to the central metal atom. Our previous structural investigations have confirmed these very interesting suggestions, and we have also investigated the influence of macrocyclic cavity size[20] and the unpaired electron of the Cu(II) d⁹ configuration[22] (by comparing the structure of [Ni(cyclops)I] with its Cu(II) counterpart) on these unusual structural features. Since CN⁻ and NCO⁻ were surprisingly similar in their visible spectroscopic parameters and in their resultant position in the apical ligand "spectrochemical series" for [Cu(cyclops)X] and [Cu(cyclops)L]⁺, it was suggested[13] that the complexes [Cu(cyclops)NCO] and [Cu(cyclops)CN] should show very similar apical displacements of the metal ion and similarly strong Cu(II)–apical ligand bonds. Since the apical displacement of 0.58 Å for Cu(II) in the cyanato-N complex was the largest such displacement yet seen, it was decided to verify these spectroscopically based structural

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predictions concerning the relative apical ligand strengths of CN^- and NCO^- by a study of the structure of the cyano complex.

Experimental Section

Synthesis. The title compound was prepared by the method of Addison and Wicholas[13] by adding a solution containing cyanide ion to a warm solution of the aquo complex $[Cu(cyclops)H_2O](ClO_4)$. Slow cooling of this reaction mixture to refrigerator temperature yielded crystals of the title compound which were suitable for single-crystal X-ray diffraction studies. Although the compound obtained in this way was formulated by the original synthetic workers as $[Cu(cyclops)CN] \cdot H_2O$,[13] the X-ray structural investigation clearly shows the lattice solvent molecule to be a methanol molecule rather than a water molecule (see below). Accordingly, the compound has been formulated as $[Cu(cyclops)CN] \cdot CH_3OH$.

Crystal Data. For $[Cu(C_{13}H_{22}BF_2N_5O_3)]$ (mol wt 408.70): $a = 12.61$ (1) Å, $b = 7.674$ (7) Å, $c = 19.46$ (1) Å, $\beta = 106.38$ (2)°, $V = 1806.7$ Å^3, $\rho_{calcd} = 1.50$ g cm^{-3} (for $Z = 4$), $F(000) = 844$, 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) = 13.0 cm^{-1}.

Data Collection and Reduction. Preliminary precession and Weissenberg photographs revealed Laue symmetry $2/m$ and the systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. As a consequence of these observations, the space group $P2_1/c$ (No. 14)[23] was assigned.

The crystal chosen for data collection was mounted on the Enraf-Nonius CAD-3 diffractometer, with the crystal's b axis nearly aligned 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[24] on the automatically determined[25] angular settings of 24 reflections (at 20 (± 1) °C) for which $18° < 2\theta < 22°$.

The intensities of 2983 independent reflections for which $h \geq 0$, $k \geq 0$, and $4.5° < \theta < 25.0°$ were measured by θ–2θ scans, employing Zr-filtered Mo Kα radiation. The total scan range was 1.0° for all reflections, and other details of intensity data collection followed the usual practice in this laboratory.[20]

The intensity of one of three control reflections (233, 600, 40$\bar{8}$) was measured every 25 reflections during data collection. On examination of the data for these very intense control reflections, their intensities were found to have increased by approximately 15% during the data collection process. This intensity change was attributed to a change in the mosaicity of the crystal (with resultant change in extinction properties) due to loss of methanol lattice solvent during the data collection period. Since for this type of extinction-dependent process the very intense control reflections used do not provide a good indication of the behavior of weaker reflections, it was decided not to make any correction to the intensities of the data based on this observed trend. Since the final structural results obtained (see below) appeared to be of acceptable quality, we believe that this decision was justified.

Lorentz and polarization corrections were applied to the observed data. The data were not corrected for absorption, due to the small absorption coefficient for Mo Kα radiation reported above. The uncertainty parameter, g,[7,26] was taken as 0.04. The 2048 unique reflections for which $F^2 > 3\sigma(F^2)$ were employed in the subsequent solution and refinement of the structure.

Solution and Refinement of the Structure. The position of the copper(II) ion was assigned from the double-intensity peaks in the Harker sections of the Patterson map. Initial positions for all non-hydrogen atoms of the [Cu(cyclops)CN] unit were then obtained from a Fourier synthesis for which the copper(II) atom provided phase

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

(24) The following programs were used in this structure determination: Zalkin's FORDAP Fourier program; Ibers' NUCLS, a 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. The program for data reduction and Lp correction was locally written for the CDC Cyber 171/172 computers at Colorado State University.

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

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Table I. Fractional Atomic Coordinates[a] for $[Cu(cyclops)CN] \cdot CH_3OH$

atom	x	y	z
Cu(II)	−0.26052 (6)	0.1518 (1)	0.18499 (4)
C1	−0.3201 (6)	−0.0972 (10)	0.1732 (4)
N1	−0.3532 (6)	−0.2344 (11)	0.1597 (4)
N2	−0.2948 (4)	0.2749 (8)	0.2658 (3)
N3	−0.3914 (4)	0.2889 (8)	0.1315 (3)
N4	−0.1879 (4)	0.1657 (8)	0.1066 (3)
N5	−0.1037 (4)	0.1414 (8)	0.2417 (3)
B1	−0.1473 (7)	0.1334 (14)	0.3537 (4)
F1	−0.2015 (3)	−0.0246 (6)	0.3400 (2)
F2	−0.0924 (3)	0.1576 (8)	0.4240 (2)
O1	−0.0634 (3)	0.1442 (8)	0.3144 (2)
O2	−0.2313 (4)	0.2779 (7)	0.3347 (3)
C2	−0.3772 (6)	0.3859 (9)	0.2484 (4)
C3	−0.4386 (5)	0.3800 (9)	0.1700 (4)
C4	−0.4352 (6)	0.2816 (11)	0.0532 (4)
C5	−0.3748 (6)	0.1474 (12)	0.0203 (4)
C6	−0.2512 (6)	0.1891 (12)	0.0288 (4)
C7	−0.0834 (6)	0.1537 (10)	0.1267 (4)
C8	−0.0317 (5)	0.1410 (10)	0.2054 (3)
C9	−0.4058 (7)	0.5107 (11)	0.3010 (5)
C10	−0.5454 (6)	0.4764 (11)	0.1442 (5)
C11	−0.0037 (6)	0.1542 (13)	0.0795 (4)
C12	0.0921 (5)	0.1334 (12)	0.2394 (5)
O3	0.2914 (6)	0.1569 (12)	0.4674 (4)
C13	0.1809 (8)	0.1869 (14)	0.4655 (7)

[a] Estimated standard deviations in the least significant digit(s) are given in parentheses.

Table II. Anisotropic Thermal Parameters[a] for $[Cu(cyclops)CN] \cdot CH_3OH$

atom	$10^3 U_{11}$	$10^3 U_{22}$	$10^3 U_{33}$	$10^3 U_{12}$	$10^3 U_{13}$	$10^3 U_{23}$
Cu(II)	24.6 (4)	40.8 (5)	37.9 (5)	1.7 (4)	8.9 (3)	0.4 (4)
C1	35 (4)	40 (5)	61 (5)	−2 (3)	18 (3)	5 (4)
N1	58 (5)	63 (5)	106 (7)	−10 (4)	28 (4)	3 (5)
N2	27 (3)	45 (4)	41 (3)	0 (3)	10 (3)	−4 (3)
N3	25 (3)	41 (4)	53 (4)	0 (3)	5 (3)	3 (4)
N4	34 (3)	47 (4)	39 (3)	−3 (3)	9 (2)	0 (3)
N5	24 (3)	55 (4)	38 (3)	−1 (3)	12 (2)	−5 (3)
B1	46 (5)	62 (6)	38 (5)	11 (5)	15 (4)	2 (4)
F1	56 (3)	63 (3)	60 (3)	9 (2)	24 (2)	10 (3)
F2	54 (3)	124 (4)	36 (2)	12 (3)	7 (2)	−3 (3)
O1	26 (2)	90 (4)	31 (2)	3 (3)	7 (2)	−4 (3)
O2	46 (3)	66 (4)	41 (3)	7 (3)	19 (3)	−4 (2)
C2	42 (4)	30 (4)	70 (5)	−1 (4)	32 (4)	5 (3)
C3	26 (3)	33 (4)	59 (5)	−3 (3)	10 (3)	7 (4)
C4	41 (4)	69 (6)	45 (5)	9 (4)	−9 (3)	2 (6)
C5	43 (4)	83 (6)	45 (4)	2 (5)	−5 (3)	−8 (5)
C6	52 (5)	85 (7)	34 (4)	−2 (4)	5 (3)	−1 (5)
C7	46 (4)	40 (4)	42 (4)	−5 (4)	20 (3)	−9 (4)
C8	35 (3)	44 (4)	36 (4)	−7 (3)	8 (3)	−8 (4)
C9	82 (6)	51 (5)	78 (6)	18 (5)	49 (5)	−9 (5)
C10	34 (4)	50 (5)	97 (7)	17 (4)	16 (4)	19 (5)
C11	57 (5)	99 (7)	49 (5)	−2 (5)	37 (4)	5 (6)
C12	22 (3)	92 (7)	71 (5)	1 (3)	17 (4)	−1 (4)
O3	60 (4)	145 (8)	94 (6)	9 (5)	11 (4)	50 (6)
C13	46 (5)	84 (9)	121 (9)	14 (6)	26 (6)	33 (7)

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

information. Scattering factors for copper(II), nitrogen, carbon, fluorine, and oxygen were taken from ref 27, as were terms $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to copper.

Three cycles of full-matrix least-squares refinement (on F), in which anisotropic thermal parameters were assigned to all atoms of the [Cu(cyclops)CN] unit, lowered R $(= \sum ||F_o| - |F_c|| / \sum |F_o|)$ to 0.110 and R_w $(= [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2})$ to 0.154. A difference Fourier map calculated at this point clearly showed the presence of two additional atoms, which were assigned (on the basis of peak intensity

(27) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
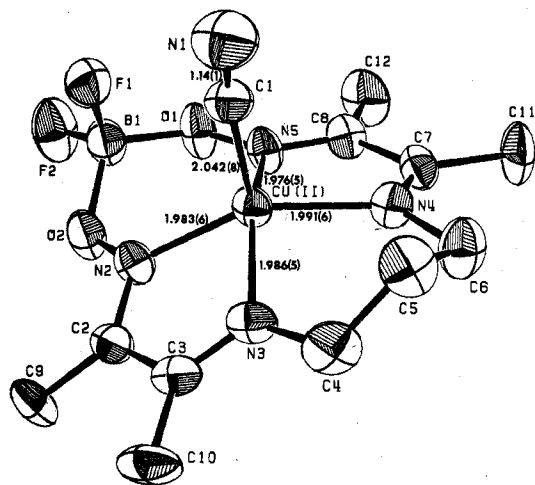
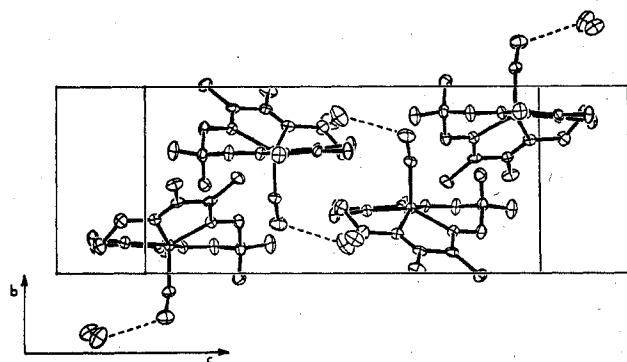**Figure 1.** View of the [Cu(cyclops)CN] complex unit.

Figure 2. View (*c* horizontal, *b* vertical) of one unit cell for the compound [Cu(cyclops)CN]·CH₃OH. Hydrogen bonding between cyanide nitrogen and methanol oxygen is represented by dashed lines.

Table III. Bond Lengths and Angles[a] for [Cu(cyclops)CN]·CH₃OH

(a) Bond Lengths (Å)

Cu(II)–C1	2.042 (8)	C2–C9	1.52 (1)
Cu(II)–N2	1.983 (6)	C8–C12	1.51 (1)
Cu(II)–N3	1.986 (5)	C2–C3	1.51 (1)
Cu(II)–N4	1.991 (6)	C8–C7	1.49 (1)
Cu(II)–N5	1.976 (5)	C3–C10	1.49 (1)
C1–N1	1.14 (1)	C7–C11	1.54 (1)
N2–O2	1.355 (7)	C3–N3	1.29 (1)
N5–O1	1.362 (7)	C7–N4	1.27 (1)
B1–O1	1.47 (1)	N3–C4	1.47 (1)
B1–O2	1.51 (1)	N4–C6	1.510 (8)
B1–F1	1.38 (1)	C4–C5	1.52 (1)
B1–F2	1.36 (1)	C6–C5	1.55 (1)
N2–C2	1.312 (9)	C13–O3	1.40 (1)
N5–C8	1.299 (9)		

(b) Bond Angles (Deg)

Cu(II)–C1–N1	173.2 (8)	O2–B1–F1	108.9 (6)
C1–Cu(II)–N2	112.3 (3)	O2–B1–F2	105.6 (7)
C1–Cu(II)–N3	102.2 (3)	O2–B1–O1	113.0 (7)
C1–Cu(II)–N4	101.4 (3)	O1–B1–F1	109.8 (7)
C1–Cu(II)–N5	107.7 (3)	O1–B1–F2	106.1 (6)
N2–Cu(II)–N3	80.1 (2)	F1–B1–F2	113.4 (7)
N2–Cu(II)–N4	146.3 (2)	N2–C2–C9	123.9 (6)
N2–Cu(II)–N5	89.1 (2)	N5–C8–C12	123.7 (6)
N3–Cu(II)–N4	93.6 (2)	N2–C2–C3	112.7 (7)
N3–Cu(II)–N5	150.1 (2)	N5–C8–C7	112.9 (5)
N4–Cu(II)–N5	80.0 (2)	C9–C2–C3	123.4 (6)
Cu(II)–N2–O2	126.4 (4)	C12–C8–C7	123.5 (7)
Cu(II)–N5–O1	127.0 (4)	C2–C3–C10	118.9 (7)
Cu(II)–N2–C2	116.1 (5)	C8–C7–C11	116.3 (6)
Cu(II)–N5–C8	116.1 (4)	C2–C3–N3	114.6 (6)
Cu(II)–N3–C3	115.8 (5)	C8–C7–N4	116.0 (7)
Cu(II)–N4–C7	115.0 (5)	C10–C3–N3	126.6 (7)
Cu(II)–N3–C4	122.6 (5)	C11–C7–N4	127.7 (6)
Cu(II)–N4–C6	123.2 (5)	C3–N3–C4	121.6 (6)
O2–N2–C2	116.6 (6)	C7–N4–C6	121.9 (6)
O1–N5–C8	116.9 (5)	N3–C4–C5	112.0 (6)
N2–O2–B1	114.1 (5)	N4–C6–C5	108.2 (6)
N5–O1–B1	115.2 (5)	C4–C5–C6	114.9 (7)

[a] Standard deviations in the least significant digit(s) are given in parentheses.

and proximity to the cyanide nitrogen (see below)) as carbon and oxygen of a methanol molecule. Due to the apparent changes in the crystal during data collection, it was felt to be unreasonable to assign unit populations to these two atoms. Consequently, the positional, thermal, and population parameters (the latter constrained to equality) for these two atoms were allowed to vary through four cycles of least-squares refinement. At the end of this process, the population parameters had converged to a value of 0.888, and the population parameters for C13 and O3 were fixed at this value for the remainder of the calculations. Three subsequent cycles of full-matrix least-squares refinement, with all atoms assigned anisotropic thermal parameters, lowered *R* to its final value of 0.055 and *R*ᵥᵥ to 0.070. The error in an observation of unit weight was 2.02, and the final data/parameter ratio was 9.1. On the final refinement cycle, all calculated parameter shifts were less than 10% of the corresponding standard deviations. Weight assignment and minimization were as described previously. No correction for secondary extinction was deemed necessary. The final difference Fourier map revealed no peaks above 0.5 e Å⁻³.

Final atomic positional parameters for [Cu(cyclops)CN]·CH₃OH are listed in Table I, while final values of the anisotropic thermal parameters are listed in Table II. Table V, included as supplementary material, contains a listing of the observed and calculated structure factor amplitudes.

Results and Discussion

The structure of the [Cu(cyclops)CN] complex unit is depicted in Figure 1, and Table III lists the bond lengths and angles exhibited by this species. As can be seen, the copper(II) ion is surrounded by a distorted square-pyramidal ligand array, with the apical position occupied by the carbon atom of the cyanide ligand and the basal positions occupied by the four nitrogen atoms of the macrocyclic cyclops ligand. The copper(II)–nitrogen bond lengths (Cu–N(av) = 1.984 (3) Å) are best considered equal within experimental error. This has been

the usual case in our studies of [Cu(cyclops)X] and [Cu(cyclops)L]⁺ structures,[8,19-21] although other studies employing similar ligands or different metal ions have often shown small, significant differences between metal–N(oxime) bond lengths (which are usually slightly shorter) and the metal–N(imine or amine) bond lengths.[22,28-35] In the present case, in fact, there is a very weak suggestion of such a difference between the Cu–N(oxime) (1.983 (6), 1.976 (5) Å) and Cu–N(imine) (1.986 (5), 1.991 (6) Å) bond lengths. The structures of the copper(II)–cyclops complexes studied in this laboratory have shown that variations in Cu–N(macrocycle) bond lengths are closely associated with the strength of the bond between the apical ligand and copper(II) and with the degree of apical displacement of the metal atom. The Cu–N(av) bond length seen in the present case is only slightly shorter than Cu–N(av, macrocycle) of 2.001 (3) Å in [Cu(cyclops)NCO].[19] In other copper(II)–cyclops complexes,[8,20,21] where apical displacements of the metal atom are smaller than in the cyano and cyanato-*N*

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Table IV. Least-Squares Planes^a for [Cu(cyclops)CN]·CH$_3$OH

(a) Deviations from the Planes

plane 1 ($n = 4$): N2 (0.03), N3 (−0.07), N4 (0.01), N5 (−0.03),
  Cu(II) (−0.56), O1 (0.04), O2 (0.21), B1 (−0.48), C2 (0.48), C3
  (0.31), C4 (−0.18), C5 (−0.81), C6 (0.03), C7 (0.35), C8 (0.36)

plane 2 ($n = 6$): N2 (−0.11), C2 (0.00), C9 (0.11), C3 (0.05), C10
  (−0.06), N3 (0.19), Cu(II) (0.05)

plane 3 ($n = 6$): N5 (−0.01), C8 (0.00), C12 (0.05), C7 (0.01),
  C11 (0.01), N4 (0.00), Cu(II) (−0.08)

plane 4 ($n = 4$): N3 (0.08), N4 (−0.01), C4 (−0.01), C6 (0.05),
  C5 (−0.71), Cu(II) (−0.52)

plane 5 ($n = 4$): N2 (−0.02), N5 (0.02), O1 (−0.07), O2 (0.01),
  B1 (−0.70), Cu(II) (−0.40)

(b) Equations of the Planes^b

plane	A	B	C	D
1	4.489	7.171	−1.779	0.148
2	7.951	5.742	−7.305	−2.600
3	0.615	7.650	0.874	1.241
4	3.804	7.316	−1.666	0.326
5	4.664	7.078	−4.120	−0.503

(c) Dihedral Angles (Deg) between Planes

planes	angle	planes	angle
1-2	22.8	2-4	25.4
1-3	18.3	2-5	18.8
1-4	3.3	3-4	15.2
1-5	7.0	3-5	21.5
2-3	40.2	4-5	7.7

^{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 $Ax + By + Cz = D$.

cases, the observed Cu(II)−N(macrocycle) bonds were shorter than in these two cases of extreme apical displacement.

The cyanide ligand is bound to the copper(II) ion through a relatively strong (see Discussion below) apical bond, with Cu−C1 = 2.042 (8) Å. The C1−N1 bond length of 1.14 (1) Å is similar to other results involving the cyanide ion bound to copper(II)[2,5-7] or other transition metals.[36] The displacement of the copper(II) atom from the mean plane of the four nitrogen atoms of the cyclops macrocycle toward the apical cyanide ligand is 0.56 Å (see Table IV). This apical displacement is, as was predicted from spectroscopic parameters,[13] equivalent to the very large displacement of 0.58 Å seen in the complex [Cu(cyclops)NCO].[19] Thus, the present results confirm the structural predictions made regarding the complexes of these two high-field apical ligands on the basis of the spectroscopic results.

Bond lengths within the macrocyclic ligand are similar to results obtained in previous studies.[8,19-22] The unsaturated portions of the macrocyclic ligand (planes 2 and 3 in Table IV) are planar to the usual degree, and the macrocycle "flexes" to accommodate the strong apical bonding of the metal atom. This "flexing" involves a downward tilt of the planes 2 and 3 to keep the copper(II) ion essentially in these planes (Cu(II) 0.05 Å above plane 2, 0.08 Å above plane 3) and to maintain a high degree of overlap between metal and ligand orbitals. Because of the high degree of apical displacement of the metal ion in [Cu(cyclops)CN], a large degree of flex is necessary to maintain this overlap, and this is reflected in the dihedral angles of approximately 20° between planes 2 and 3 of Table IV and the reference plane of the four coordinating macrocyclic nitrogen atoms. The corresponding dihedral angles were even larger at 27° in the [Cu(cyclops)NCO] complex,[19] where

the apical displacement of the metal was also large, and were considerably smaller (10−15°) in other complexes in this series for which observed apical displacements were smaller.[8,20-22]

The flexibility of the macrocycle is also underscored by the conformational changes which have occurred throughout this series of copper(II) complexes. If the chair/boat terminology is adopted to describe the relative positions of the six atoms B$_1$, N1−N4, and the central atom of the propylene linkage and if up/down is adopted to describe the position of the boron atom (up = the same side of the four-nitrogen reference plane as copper(II)), the conformations seen in this series of structures can be summarized as follows: [Cu(cyclops)NCO], boat (up); [Cu(cyclops)CN], boat (up); [Cu(cyclops)I], chair (up); [Cu(cyclops)py]$^+$, chair (up); [Cu(cyclops)H$_2$O]$^+$, chair/boat disordered mixture (up); [Ni(cyclops)I], chair/boat disordered mixture (down). Unfortunately, the correlation between these conformations and the obvious structural changes occurring about the metal atom in these complexes is difficult to discern, but the ease with which these conformational changes are made is evident.

The discovery that a methanol molecule from the original solvent engages in hydrogen bonding with the cyanide nitrogen atom of [Cu(cyclops)CN] is not surprising. In each of the cyanocopper(II) complex structures investigated to date, the propensity of the cyanide ligand toward bridging has led to hydrogen bonding,[2,6] to dimerization,[5,6] or to solid-state polymerization.[7,38] Hydrogen bonding between cyanide nitrogen and methanol oxygen in the present case is supported by the N1−O3 distance of 2.92 (1) Å and the N1−O3−C13 angle of 115.6 (7)°.[37]

With the completion of the present structure, structural parameters for copper(II)−cyanide bonding are available for the cyanide ion in all four of the possible coordination sites of the common five-coordinate ligand geometries about copper(II). In [Cu(phen)$_2$CN]NO$_3$·H$_2$O,[2] cyanide ion occupied an equatorial position of a trigonal-bipyramidal ligand array, with Cu(II)−C = 1.94 (1) Å. In [Cu$_2$(tren)$_2$(CN)$_2$](BPh$_4$)$_2$,[6] CN$^-$ was found in an axial position of the trigonal-bipyramidal geometry, with Cu−C = 1.97 Å. In [Cu(terpy)CN]NO$_3$·H$_2$O[7] and the cyano(diethylenetriamine)copper(II) complex ion,[38] CN$^-$ was found in a basal position of the square-pyramidal coordination geometry, with Cu−C = 1.92 (1) and 1.995 (4) Å in these two cases, respectively. Clearly, the Cu(II)−C1 distance of 2.042 (8) Å observed in the present study is the longest such bond in this series of complexes, as would be expected for the case of apical binding in a square-pyramidal array. However, the normally expected elongation for a bond length in this apical position is 0.2−0.6 Å,[39] which would lead one to expect a Cu(II)−C bond length of at least 2.12 Å, based on the above results in other copper(II) complexes. This abnormally short bond emphasizes the unusually strong binding to anionic apical ligands seen in the entire series of copper(II)−cyclops complexes.[8,19-21] The fact that redox-stable bonding of copper(II) to the cyanide ion has now been seen for a variety of substitution modes in the two most common five-coordinate geometries implies that coordination geometry is not as important a variable in preventing reduction of the metal atom by the soft cyanide ligand. Presumably, the ability of the stabilizing ligand(s) to increase the electron density of the metal ion through σ donation regardless of geometry is a much more important factor in this type of redox stabilization.

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Crystal and Molecular Structure of CuCo(fsa)₂en·6H₂O (H₄(fsa)₂en = N,N'-Bis(2-hydroxy-3-carboxybenzylidene)-1,2-diaminoethane): An Example of Close-Packed Association of Two Heterobinuclear Units through the Formation of a Water Molecule Network

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The crystal structure of CuCo(fsa)₂en·6H₂O, one member of the wide series MM'L·X (M, M' = transition element, L = H₄(fsa)₂en, X = H₂O, CH₃OH) was determined by the X-ray single-crystal diffraction method. It crystallizes in the orthorhombic space group *Pbca* with $a = 20.549$ (5) Å, $b = 15.948$ (4) Å, $c = 13.307$ (5) Å, $V = 4.360.9$ (1) Å³, $\rho_{exptl} = 1.76$ (1) g/cm³, and $Z = 8$. The structure was solved by direct methods and refined by full-matrix least squares to a conventional R of 0.050 for 3623 reflections with $I > 2.5\sigma(I)$. The copper atom, coordinated by two nitrogen atoms and two phenolic oxygen atoms in a square-planar manner, occupies the "inside" site of the molecule, a water molecule being above at 2.784 Å; the cobalt atom in the "outside" site, coordinated to four oxygen atoms and one water molecule, has square-pyramidal coordination. Two molecules related by a symmetry center are packed together, forming a tetramer [CuCo(fsa)₂en·H₂O]₂ in which the two transition metals occupy the center of octahedra sharing edges and corners. Such units are encapsulated in a three-dimensional network of water molecules. The title complex exhibits some unusual structural features in the series MM'L·X.

Introduction

Whereas the study of homobinuclear complexes with paramagnetic metallic centers is still a very active field in inorganic chemistry, the study of heterobinuclear complexes takes on increasing importance. Such complexes have already led to a more advanced understanding of the mechanism of exchange interaction. In this respect, the most striking result is likely the strict orthogonality of the magnetic orbitals centered on the metallic centers, which was realized in a Cu^{II}VO^{II} complex.[2] An identical situation was obtained in a Co^{II}Cu^{II} complex.[3] Among the bichelating ligands used to obtain heterobinuclear complexes,[4-6] the ligand noted (fsa)₂en⁴⁻ derived from the Schiff base N,N'-bis(2-hydroxy-3-carbobenzylidene)-1,2-diaminoethane seems to be the one having the greatest versatility. This ligand was used for the first time by Okawa et al.[7] and was used since by several groups.[8-16]

The synthesis of new heterobinuclear complexes, the determination of their crystal and molecular structure, and then the investigation of their magnetic properties are the three cornerstones of the study of the *interaction in heterobinuclear complexes.* The knowledge of the structure is often necessary and always useful to interpret the magnetic properties; it can also sometimes have a great importance in itself when this structure reveals some quite unusual features. Such is the case for the structure described in this paper. Attempting to recrystallize from a methanolic solution the complex CoCu-(fsa)₂en·3H₂O, the structure of which was recently published,[17] we noticed that in some specific conditions, in addition to the starting material, a new compound of formula CuCo-(fsa)₂en·6H₂O was obtained. It was of interest to compare its structure to that of CuCo(fsa)₂en·3H₂O. These two structures appeared to be very different. The Co(II) ion in the outside site of the new complex has a fivefold coordination

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