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Structure Determination, Spectroscopic Characterization, and Magnetic Properties of a Novel Dinuclear Copper(II) Crown Ether Bipyridine Complex

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Received November 13, 1992

The synthesis of a novel ligand system (**1**) composed of two bipyridine units linked by a crown ether moiety is described. Addition of 2 equiv of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ to **1** and subsequent oxidation yield a dinuclear μ -hydroxo-bridged copper(II) complex, $[(\mathbf{1})\text{Cu}_2(\text{OH})_2\text{BF}_4] \cdot 2\text{H}_2\text{O}$ (**2**). The structure of this complex has been determined by X-ray crystallographic methods. Crystal data: triclinic, space group $P\bar{1}$ (No. 2), $a = 10.060(1)$ Å, $b = 12.747(2)$ Å, $c = 16.787(1)$ Å, $\alpha = 92.01(1)$ °, $\beta = 103.01(2)$ °, $\gamma = 104.01(2)$ °. The Cu–O–Cu angles in complex **2** are nonequivalent (94.8 and 98.4°). One of the coppers is pentacoordinated; the other is hexacoordinated. Two molecules of **2** are linked by hydroxo ligands, forming a tetranuclear complex in which the $\text{Cu}_2(\text{OH})_2$ units have parallel but shifted positions. Magnetic susceptibility and EPR measurements suggest that complex **2** has a triplet ground state, with a triplet–singlet energy gap of 16 cm⁻¹.

Introduction

During the past two decades, interest in the coordination chemistry of dinuclear copper complexes has grown steadily.² Part of this stems from the fact that dinuclear copper centers are found in the active sites of metalloproteins.³ Current research is aimed at gaining insight into the factors governing the redox chemistry⁴ and magnetic properties⁵ of such complexes and at the binding and/or activation of molecular oxygen.^{2,3} As part of our program aimed at the development of metallo hosts,⁶ we describe here the synthesis, X-ray structure, and magnetic properties of a new copper complex (**2**) combining a dinuclear redox center and a potential crown ether binding site.

Experimental Section

Materials. Analytical grade reagents were used. CH_2Cl_2 , Et_2O , and triethylamine were distilled from CaH_2 . Acetonitrile was stored over 3-Å molecular sieves.

Syntheses. 5-Methyl-2,2'-bipyridine. This compound was synthesized by following Kröhnke's procedure.⁷

5-Carboxy-2,2'-bipyridine. This compound was synthesized according to the procedure described by Case for the preparation of 5,5'-dicarboxy-2,2'-bipyridine.⁸

5-(Chlorocarbonyl)-2,2'-bipyridine. A suspension of 0.3 g (1.5 mmol) of 5-carboxy-2,2'-bipyridine in 15 mL of SOCl_2 was refluxed under a dinitrogen atmosphere. The solid material dissolved completely after 30 min of refluxing, and the solution remained homogeneous throughout. After 15 h, SOCl_2 was evaporated. The product was characterized by the fact that the OH vibration at 3500 cm⁻¹ had disappeared.

1,10-Bis(2,2'-bipyridyl-5-ylcarbonyl)-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (1). To a solution of 0.162 g (0.62 mmol) of 1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (2,2'-Kryptofix) in 10 mL of dichloromethane were added 0.270 g (1.24 mmol) of 5-(chlorocarbonyl)-2,2'-bipyridine and 0.25 g (2.47 mmol) of triethylamine. This solution was stirred for 12 h, after which the solvent was removed in vacuo. The residue was purified by column chromatography over silica using chloroform/methanol (98/2, v/v) as eluent, to afford 0.217 g (0.35 mmol, 56%) of **1** as an oil. ^1H NMR (CDCl_3 , 298 K): δ 3.6 and 3.8 (2 \times s, 24H, $\text{NCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}$), 7.4 (m, 2H, py H), 7.9 (m, 4H, py H), 8.4 (m, 4H, py H), 8.7 (m, 4H, py H).

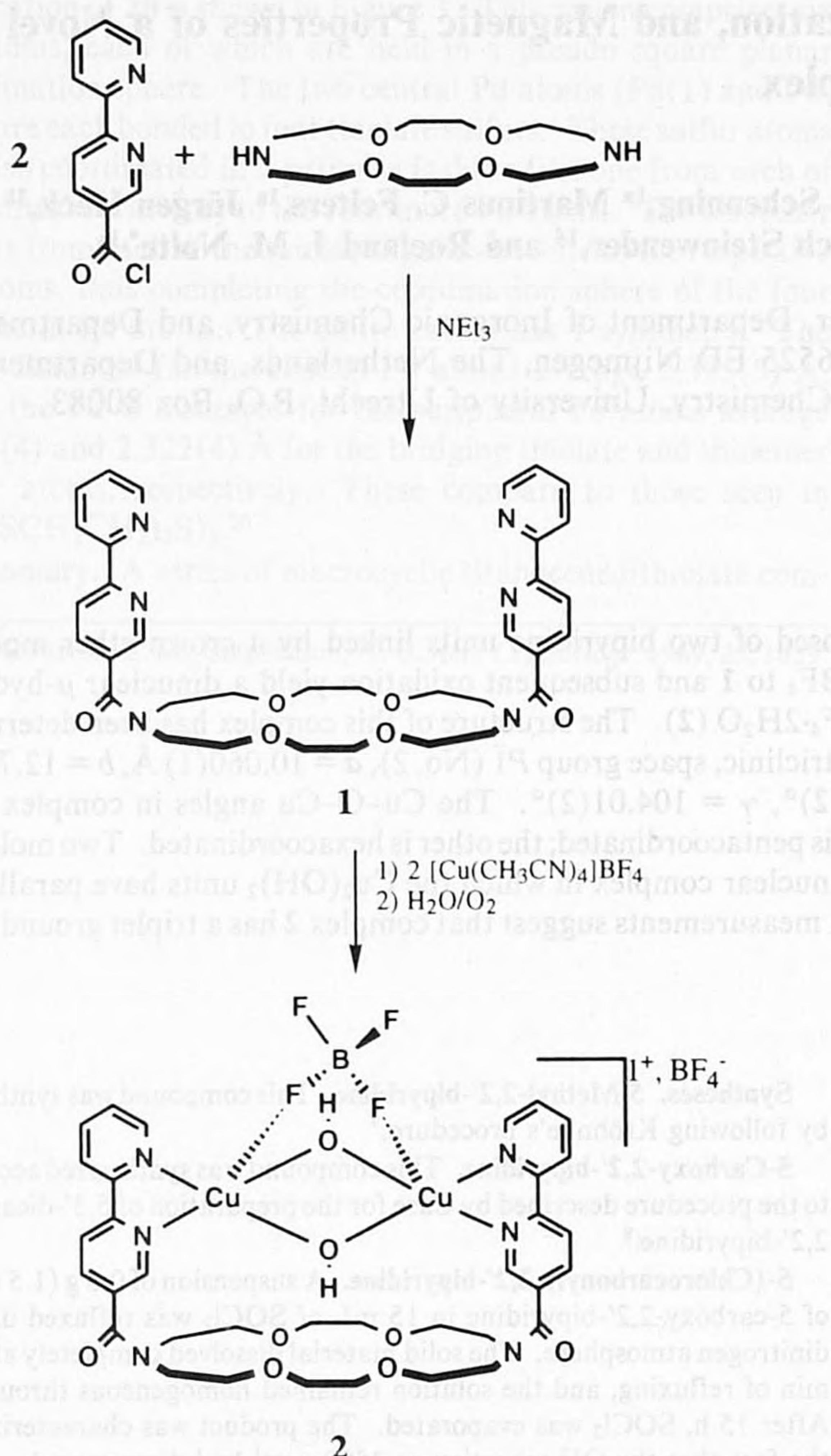
$[(\mathbf{1})\text{Cu}_2(\text{OH})_2\text{BF}_4] \cdot 2\text{H}_2\text{O}$ (2). In order to avoid the possible formation of mononuclear Cu^{II} species, we first prepared the dinuclear Cu^{I} complex of **1**, which was subsequently oxidized to the dinuclear, bis(μ -hydroxo)-bridged Cu^{II} complex. To a solution of 0.1 g (0.16 mmol) of **1** in 10 mL of thoroughly degassed acetonitrile was added 0.1 g (0.32 mmol) of $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$.⁹ After the solution had been stirred for 2 h, a small amount of water was added. The solution was subsequently stirred open to air for 30 min. After evaporation of the solvent and recrystallization from acetonitrile/ether, compound **2** was obtained as green cubic crystals, suitable for X-ray analysis. Yield: ~100%. Mp: dec > 180 °C. The physical characterization of **2** is given in the Results and Discussion.

Physical Measurements. The FT-IR spectra were recorded on a Mattson 5020 connected to a personal computer at a resolution of 2 cm⁻¹ over the range 4000–500 cm⁻¹. An RIIC-VLT-2 variable-temperature unit equipped with KBr windows was connected to a West M2071

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Scheme I



microprocessor-based controller. Liquid nitrogen was used as coolant, enabling us to obtain Nujol mull spectra over a temperature range of 300–150 K. Second-derivative spectra were calculated using the standard Mattson First software. Variable-temperature magnetic susceptibility data were collected in the temperature range 4.2–270 K by using a Oxford Instruments Foner-type magnetometer, calibrated with a Ni sample. A main solenoid field of 12 000 G was employed. Temperatures were recorded with calibrated resistance thermocouples. EPR spectra were recorded at X-band frequency in the temperature range 10–40 K using a Bruker ESP 300, equipped with a helium continuous flow cryostat. ^1H NMR spectra were recorded on a Bruker WH-90.

X-ray Structure Determination of $[(1)\text{Cu}_2(\text{OH})_2\text{BF}_4]\text{BF}_4 \cdot 2\text{H}_2\text{O}$. Collection and Reduction of Crystallographic Data. A crystal ($0.17 \times 0.27 \times 0.38$ mm) was mounted in a capillary. X-ray data were measured on a Nonius CAD4 diffractometer. Standard experimental and computational details are given elsewhere.¹⁰ The crystal data are listed in Table I.

Solution and Refinement of the Structure. The positions of the copper atoms were found by Patterson interpretation and those of the remaining non-hydrogen atoms by direct-methods fragment expansion (DIRDIF¹¹). The structure was refined by full-matrix least-squares techniques using SHELX.¹¹ Anisotropic temperature parameters were used for the non-hydrogen atoms except for those of the bipyridyl groups. The temperature factors of the H atoms of the bipyridyl groups were kept 0.01 \AA^2 larger than the temperature factors of their C atoms. The H atoms on O(19) and O(20) were taken from a difference Fourier map, and their temperature factors were refined. The H atoms of the crown ether were placed on the calculated positions and refined in a riding mode (C–H = 1.00 \AA) using one overall temperature factor. To compensate for local

Table I. Crystal Data for $[(1)\text{Cu}_2(\text{OH})_2\text{BF}_4]\text{BF}_4 \cdot 2\text{H}_2\text{O}$

chem formula	$\text{C}_{34}\text{H}_{40}\text{N}_6\text{O}_8\text{B}_2\text{F}_8\text{Cu}_2 \cdot 2\text{H}_2\text{O}$
system	triclinic
space group	$P\bar{1}$ (No. 2)
fw	997.4
cell dimens ^a	
<i>a</i> , Å	10.060(1)
<i>b</i> , Å	12.747(2)
<i>c</i> , Å	16.787(1)
α , deg	92.01(1)
β , deg	103.01(2)
γ , deg	104.01(2)
<i>V</i> , Å ³	2026.0(4)
<i>Z</i>	2
$\lambda(\text{Mo K}\alpha)$, Å	0.71073
<i>F</i> (000)	1020
<i>T</i> , K	298
ρ_{calc} , g cm ⁻³	1.64
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	11.48
<i>R</i> ^b	0.053
<i>R</i> _w ^c	0.056

^a From 25 reflections, $19 < 2\theta < 28^\circ$. ^b $R = \sum |F_o - |F_c|| / \sum F_o$. ^c $R_w = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

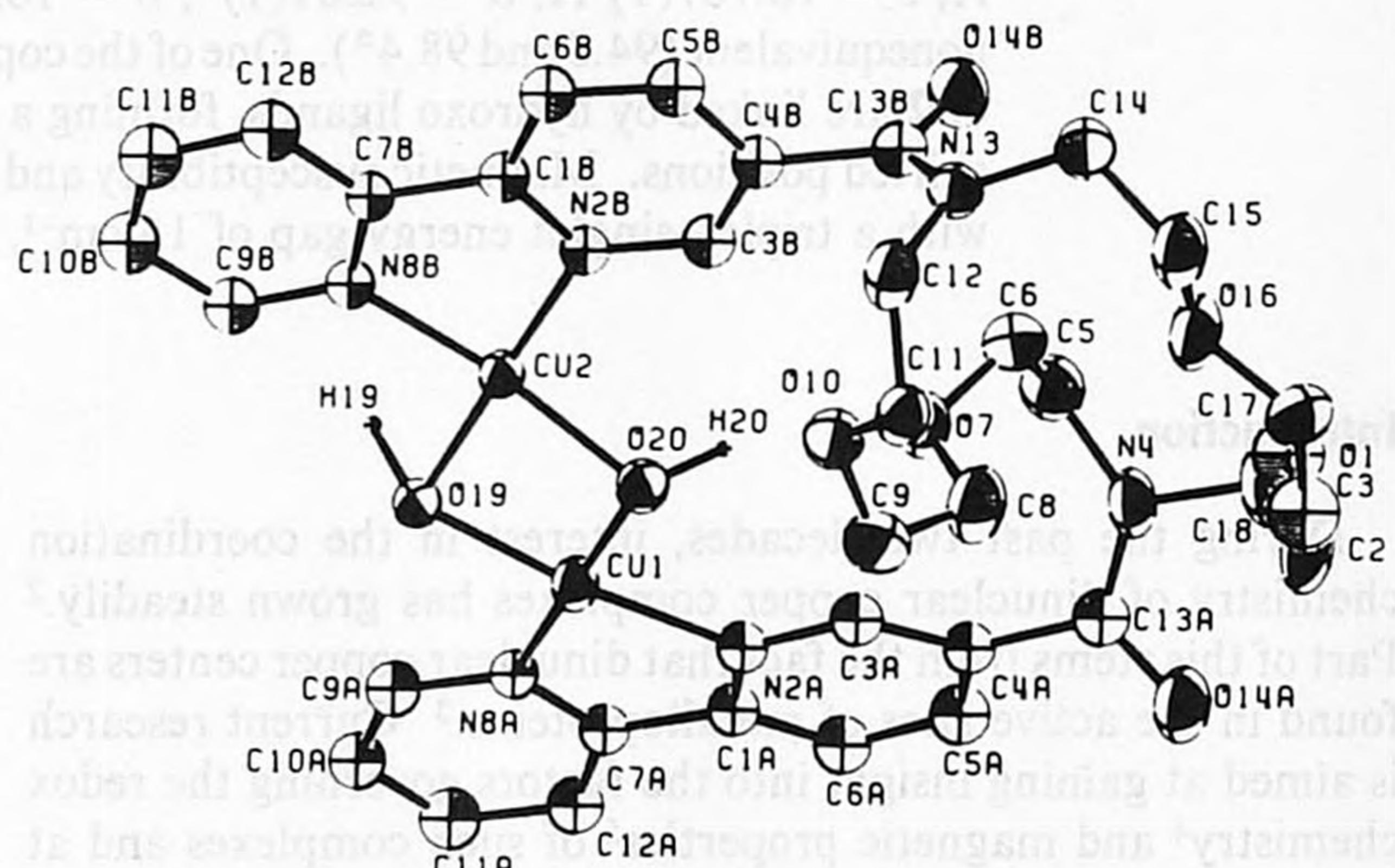


Figure 1. Ortep II¹² drawing of **2** with 50% probability anisotropic displacement ellipsoids for the non-hydrogen atoms.

disorder in the crown ether we split the atoms O(1) and C(18) into a ratio which refined to 0.8, whereas the neighboring atoms could not be split but led to large anisotropic temperature factors. In the difference electron density map, a region of electron density was observed in the neighborhood of the BF_4 anions near a center of symmetry (0.5, 0.5, 0.5). A channel of width 4.2 Å (H(51)...H(51')) distance connects two symmetry-related regions. To match for the observed electron density, we put in two oxygen atoms, O(99) and O(100), for the following reasons, O(99) was found with a peak height of $3.0 \text{ e } \text{\AA}^{-3}$, at suitable distances to the neighboring fluorine atoms (F(2), F(4), F(6'), and F(7')), distances of 3.38, 3.16, 3.39, and 3.17 Å. O(100) was found with a peak height of only $0.9 \text{ e } \text{\AA}^{-3}$, at a hydrogen-bonding distance O(99)...O(100) of 2.55 Å, and no other contacts with non-hydrogen atoms less than 3.43 Å were found; its electron density is smeared out and passes over the center of symmetry (0.5, 0.5, 0.5), which explains the very large anisotropic temperature factor and suggests some degree of disorder. The presence of water molecules is supported as well by the IR measurements (see below). Final convergence was reached at $R = 0.053$. The function minimized was $\sum w(F_o - |F_c|)^2$ with $w = 1 / [\sigma^2(F_o) + 0.0004F_o^2]$; maximum residual electron density was $0.4 \text{ e } \text{\AA}^{-3}$.

The molecular structure of the complex with the crystallographic numbering of its atoms is given in Figure 1.¹² The coordination of the copper centers and the numbering of the involved atoms are given in Figure 2. The atomic numbering of the second BF_4 anion (B(2), F(5), F(6), F(7), F(8)) and of the two water molecules (O(99), O(100)) is omitted from the figures for clarity. Positional and thermal atomic parameters are given in Table II, and selected interatomic distances and angles, in Table III.

Results and Discussion

Description of the Structure. The X-ray structure of complex **2** shows two molecules around a crystallographic center of

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Table II. Fractional Positional Parameters and U_{eq} Values with Eds's

	x	y	z	$10^2 U_{\text{eq}}, \text{\AA}^2$		x	y	z	$10^2 U_{\text{eq}}, \text{\AA}^2$
Cu(1)	0.14590(10)	0.05354(8)	0.08432(6)	2.95(4)	C(3)	0.3093(12)	0.2025(9)	0.5298(6)	6.9(5)
Cu(2)	0.00698(10)	0.22344(8)	0.03390(6)	2.70(4)	N(4)	0.3039(8)	0.1734(6)	0.4434(4)	4.5(3)
C(1A)	0.3467(8)	-0.0377(6)	0.1890(5)	3.0(2)	C(5)	0.3141(9)	0.2629(7)	0.3904(6)	5.0(4)
N(2A)	0.2461(7)	0.0157(5)	0.1939(4)	3.0(2)	C(6)	0.1789(10)	0.2981(7)	0.3652(8)	4.9(4)
C(3A)	0.2356(8)	0.0502(6)	0.2677(5)	3.2(2)	O(7)	0.0702(6)	0.2203(5)	0.3081(3)	4.2(3)
C(4A)	0.3239(8)	0.0360(6)	0.3408(5)	3.0(2)	C(8)	-0.0366(10)	0.1576(8)	0.3433(6)	5.1(4)
C(5A)	0.4250(9)	-0.0211(7)	0.3356(5)	4.1(2)	C(9)	-0.1673(10)	0.1171(7)	0.2795(6)	5.2(4)
C(6A)	0.4349(9)	-0.0570(7)	0.2600(5)	3.8(2)	O(10)	-0.2325(6)	0.2007(5)	0.2502(3)	4.5(3)
C(7A)	0.3520(8)	-0.0669(6)	0.1056(5)	2.9(2)	C(11)	-0.3271(9)	0.2270(7)	0.2945(5)	4.0(4)
N(8A)	0.2691(6)	-0.0282(5)	0.0458(4)	2.7(2)	C(12)	-0.3275(9)	0.3443(7)	0.2851(5)	4.3(4)
C(9A)	0.2701(8)	-0.0518(6)	-0.0326(5)	3.5(2)	N(13)	-0.1961(7)	0.4207(5)	0.3250(4)	3.8(3)
C(10A)	0.3510(8)	-0.1159(6)	-0.0554(5)	3.7(2)	C(14)	-0.1834(10)	0.4675(7)	0.4082(5)	4.6(4)
C(11A)	0.4320(9)	-0.1564(7)	0.0059(5)	4.4(2)	C(15)	-0.2142(10)	0.3904(8)	0.4704(5)	5.0(4)
C(12A)	0.4350(8)	-0.1333(6)	0.0877(5)	3.6(2)	O(16)	-0.1198(7)	0.3230(5)	0.4819(4)	5.4(3)
C(13A)	0.3192(9)	0.0738(7)	0.4253(5)	3.7(2)	C(17)	-0.1274(11)	0.2631(8)	0.5498(6)	5.6(5)
O(14A)	0.3284(6)	0.0082(5)	0.4784(4)	5.2(3)	C(18)	-0.042(2)	0.1819(12)	0.5543(9)	6.00 ^b
C(1B)	-0.1375(8)	0.3903(6)	0.0326(5)	2.9(2)	C(18A)	0.001(6)	0.230(5)	0.584(4)	6.00 ^b
N(2B)	-0.0643(6)	0.3351(5)	0.0862(4)	2.8(2)	O(19)	0.0636(6)	0.1073(4)	-0.0195(3)	3.1(2)
C(3B)	-0.0526(8)	0.3547(6)	0.1662(5)	3.2(2)	O(20)	0.0432(6)	0.1420(4)	0.1265(3)	3.3(2)
C(4B)	-0.1165(8)	0.4268(6)	0.1970(5)	3.1(2)	B(1)	0.3495(11)	0.3315(9)	0.1250(7)	3.8(4)
C(5B)	-0.1913(9)	0.4813(7)	0.1426(5)	3.8(2)	B(2)	0.2186(13)	0.1908(11)	0.7953(8)	5.4(6)
C(6B)	-0.2028(9)	0.4640(7)	0.0597(5)	3.6(2)	F(1)	0.3845(6)	0.2378(5)	0.1211(4)	8.3(3)
C(7B)	-0.1425(8)	0.3620(6)	-0.0543(5)	2.7(2)	F(2)	0.3134(8)	0.3433(7)	0.2001(4)	11.4(4)
N(8B)	-0.0736(7)	0.2863(5)	-0.0664(4)	2.8(2)	F(3)	0.2410(5)	0.3381(4)	0.0632(3)	5.8(2)
C(9B)	-0.0701(8)	0.2577(7)	-0.1429(5)	3.5(2)	F(4)	0.4628(6)	0.4188(6)	0.1274(5)	11.3(4)
C(10B)	-0.1347(9)	0.3008(7)	-0.2106(6)	4.2(2)	F(5)	0.0898(8)	0.1161(6)	0.7623(5)	12.0(4)
C(11B)	-0.2061(9)	0.3756(7)	-0.1974(6)	4.6(2)	F(6)	0.3170(7)	0.1659(6)	0.7595(4)	9.6(4)
C(12B)	-0.2116(9)	0.4082(7)	-0.1199(5)	4.0(2)	F(7)	0.1936(8)	0.2854(6)	0.7696(5)	10.6(4)
C(13B)	-0.0873(9)	0.4509(7)	0.2889(5)	3.5(2)	F(8)	0.2485(7)	0.1905(7)	0.8756(4)	11.8(4)
O(14B)	0.0319(6)	0.5033(5)	0.3257(4)	5.1(3)	O(99)	0.5403(12)	0.5814(9)	0.2874(7)	15.5(7)
O(1)	0.0955(11)	0.2292(9)	0.5435(5)	6.00 ^b	O(100)	0.422(5)	0.550(2)	0.407(3)	72.0(5)
O(1A)	0.033(4)	0.165(4)	0.525(5)	6.00 ^b	H(19)	0.1213	0.1693	-0.0497	25.0(9) ^c
C(2)	0.1785(13)	0.1519(10)	0.5569(6)	7.2(6)	H(20)	0.0761	0.1815	0.1792	19.0(7) ^c

^a $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j a_i^* a_j^* a_j U_{ij}$. ^b To compensate for local disorder, the atoms O(1) and C(18) were split into O(1)/O(1A) and C(18)/C(18A) to a ratio which refined to 0.80(1). ^c H(19) and H(20) were taken from a difference Fourier map and their temperature factors are refined.

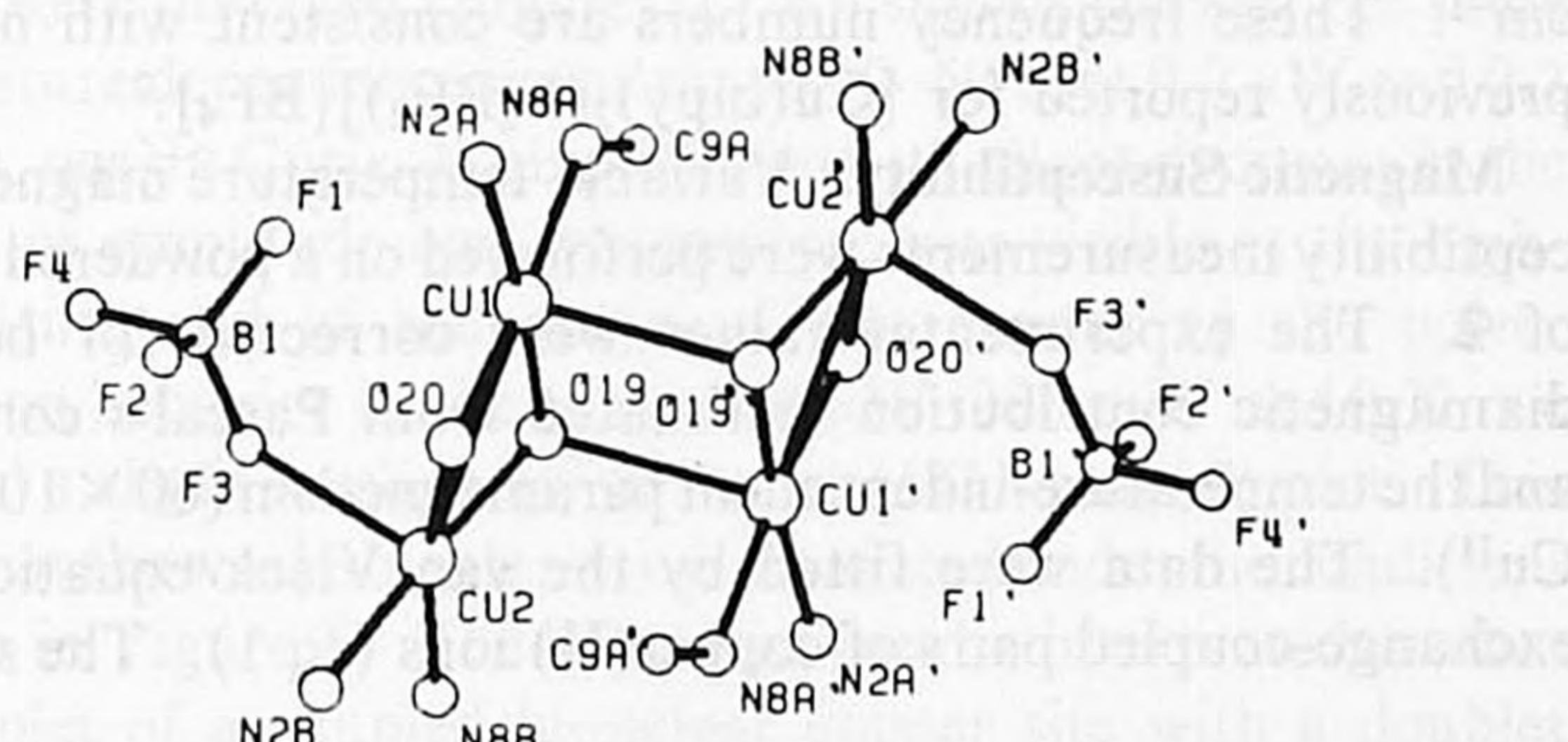


Figure 2. Pluto¹¹ drawing showing the coordination sphere of the copper centers and the connectivities between the dinuclear units.

Table III. Interatomic Distances (Å) and Angles (deg) Relevant to the Copper Coordination Spheres within the Tetranuclear Complex

Cu(1)-Cu(2)	2.902(2)	Cu(1)-F(1)	2.857(5)
Cu(1)-N(2A)	2.023(6)	Cu(2)-F(3)	2.384(5)
Cu(1)-N(8A)	1.995(7)	Cu(1)-Cu(1')	3.542(3)
Cu(1)-O(19)	1.975(5)	Cu(1)-Cu(2')	3.778(2)
Cu(1)-O(20)	1.918(6)	Cu(1)-O(19')	2.559(5)
Cu(2)-N(2B)	2.000(7)	Cu(1)-O(20')	4.051(6)
Cu(2)-N(8B)	1.982(6)	Cu(2)-Cu(2')	5.731(3)
Cu(2)-O(19)	1.966(6)	Cu(2)-O(19')	4.092(6)
Cu(2)-O(20)	1.915(6)	Cu(2)-O(20')	5.155(6)
Cu(1)-O(19)-Cu(2)	94.8(2)	O(19)-Cu(1)-N(8A)	100.4(2)
Cu(1)-O(20)-Cu(2)	98.4(3)	O(20)-Cu(1)-N(2A)	97.0(2)
N(2A)-Cu(1)-N(8A)	80.7(3)	O(19)-Cu(2)-N(8B)	98.1(2)
N(2B)-Cu(2)-N(8B)	81.2(3)	O(20)-Cu(2)-N(2B)	98.2(2)
O(19)-Cu(1)-O(20)	81.3(2)	Cu(1)-O(19)-Cu(1')	101.9(3)
O(19)-Cu(2)-O(20)	81.7(2)	Cu(1)-O(19')-Cu(2')	112.6(3)

symmetry. Each molecule of **2** (Figure 1) contains two copper atoms which are bridged by two hydroxo groups (OH19 and OH20). Each of the copper atoms has a square-planar coordination and is surrounded by two nitrogen atoms of a bipyridyl group and two oxygen atoms of the bridging hydroxo groups. The dihedral angle between the two basal planes is 17.6-(1)°. The geometry in the axial direction is different for the two

copper atoms, in contrast to the case of related complexes.¹³ Cu(1) has an elongated octahedral environment with apical positions occupied by a hydroxo oxygen of the neighboring molecule (Cu(1)...O(19') = 2.559 Å) and a fluorine atom (Cu(1)...F(1) = 2.857 Å) (see Figure 2). Cu(1) is displaced from its basal plane by 0.10 Å toward the oxygen atom. Cu(2) has a square-pyramidal environment with an apical fluorine atom (Cu(2)...F(3) = 2.384 Å) toward which the copper atom is displaced from its basal plane by 0.14 Å. Some other distances within the dimeric structure of Figure 2 are Cu(1)...Cu(1') = 3.542, Cu(1)...Cu(2') = 3.778, Cu(2)...Cu(2') = 5.731, Cu(2)...N(8A') = 3.232(5), and Cu(2)...C(9A') = 3.09(1) Å (see also Table III).

The two hydroxo groups that link the two Cu^{II} centers are different (Figure 2). One of them (O19) is hydrogen-bonded to a fluorine atom (F8) (not shown in Figure 2) of the BF₄ anion (O-H = 1.08, O...F = 2.89(1), H...F = 1.96 Å; O-H...F = 142°). The other hydroxo group (O20) weakly interacts with an oxygen atom (O7) of the crown ether moiety (O-H = 0.95, O...O = 3.11(1), H...O = 2.22 Å; O-H...O = 155°; indicating a distance which is presumed to be the geometrical limit of "linear" hydrogen bonds^{14,15}).

IR Spectroscopy. In order to gain more insight into the bonding pattern of the hydroxo groups as well as into the type of solvent molecules included in the crystals of compound **2**, we undertook a FT-IR variable-temperature investigation on crystals of the same batch as used for the X-ray diffraction measurements.

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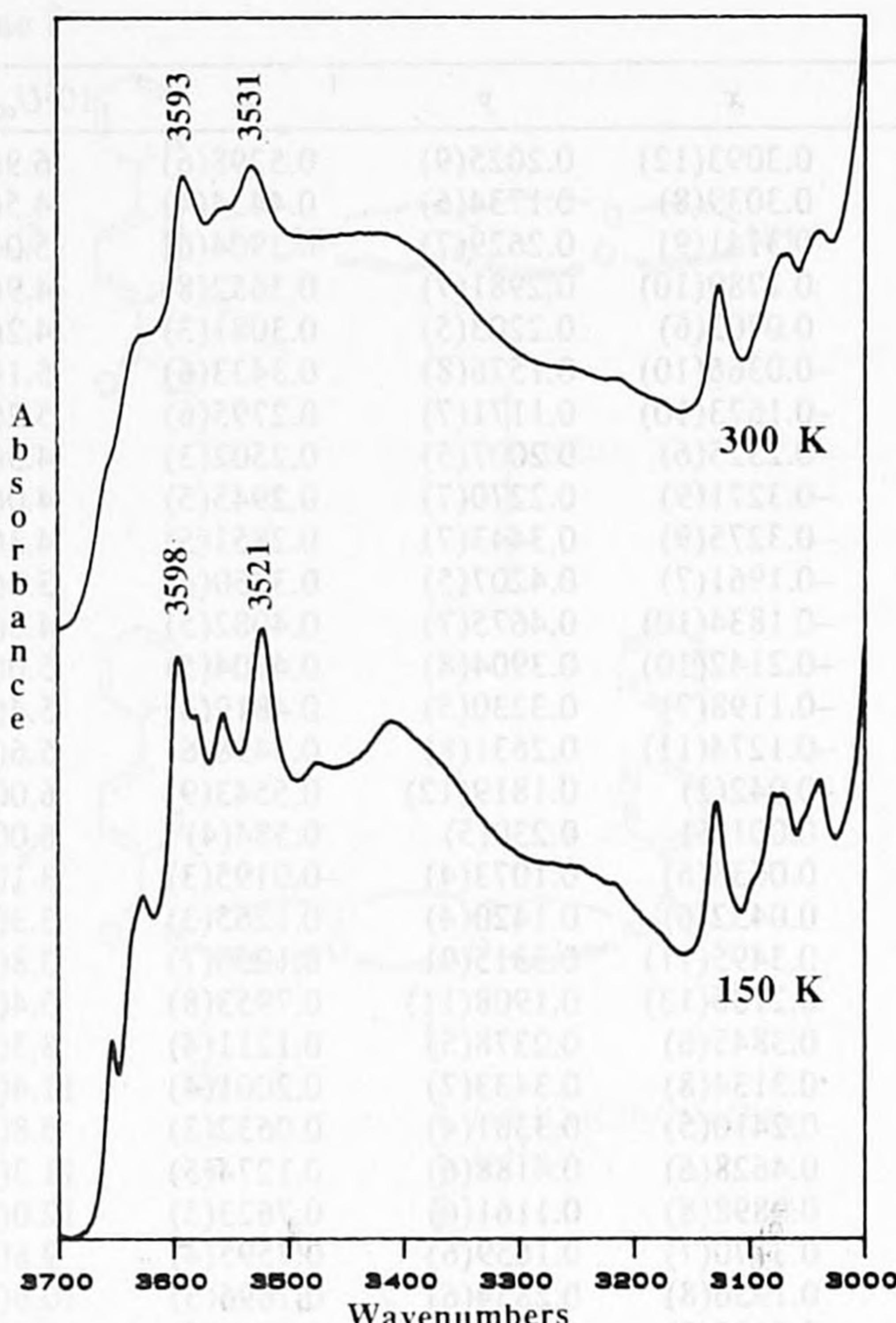


Figure 3. IR spectra of **2** in the 3000–3700-cm⁻¹ region at 300 K (top) and 150 K (bottom).

The Nujol mull IR spectrum at ambient temperature (Figure 3, upper trace) exhibited an intense broad band (3650–3100 cm⁻¹) centered at about 3430 cm⁻¹. On the high-frequency side of this absorption band we observed two narrow and intense bands at 3593 and 3531 cm⁻¹ and, furthermore, two shoulders at 3658 and 3634 cm⁻¹. Lutz et al.¹⁶ have shown that free or weakly bonded OH⁻ groups are characterized by rather intense bands with small half-bandwidth. Secco¹⁷ has assigned sharp peaks at 3596 and 3572 cm⁻¹ in the IR spectrum of Cu₄(OH)₆SO₄ to "free", non-hydrogen-bonded OH⁻ groups which are characterized by O...O distances of 3.14 and 2.96 Å, respectively. We assign the two above mentioned absorptions at 3593 and 3531 cm⁻¹ therefore to the two different OH⁻ groups in **2**. The underlying broad band is probably due to water molecules included in the crystal lattice. These molecules have different OH stretching vibrations because they have different association patterns with oxygen and fluorine atoms. This assumption is supported by the fact that the region between 1580 and 1650 cm⁻¹ exhibits several other absorption bands which are the result of H₂O deformations. Acetonitrile, another molecule possibly included in the crystal, could not be detected in the IR spectra. On the basis of these observations, we may therefore conclude that the region of electron density observed in the difference electron density map is due to water molecules.

IR spectra were recorded in 50 K steps from 300 to 150 K. Band maxima were located using the second-derivative technique. As can be seen in Figure 3, the overlapping absorption bands become more resolved at low temperature. The second-derivative spectra revealed that at all temperatures the same number of bands are present; only the band maxima shift on cooling. We have assigned the absorptions at 3593 and 3531 cm⁻¹ to the two OH⁻ groups bridging the Cu^{II} atoms. One of these groups, most likely OH(20), is not hydrogen-bonded, as was indicated by the large O...O distance. This group is spectroscopically characterized by a small negative temperature coefficient ($d\nu/dT = -0.036$ cm⁻¹/K) and can therefore be called a "free" OH⁻ group. The other hydroxyl group, OH(19), exhibits a weak O–H...F hydrogen

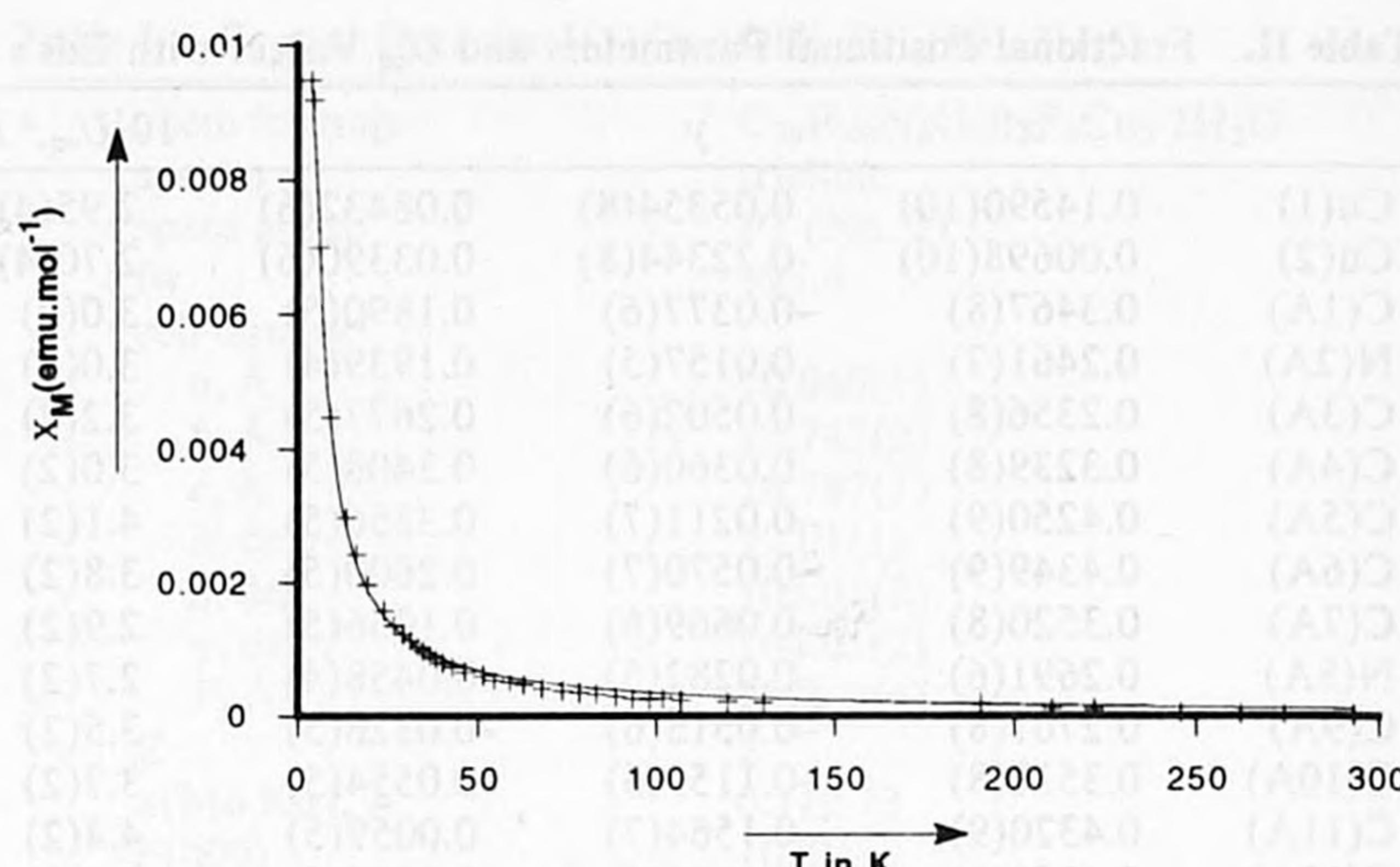


Figure 4. Corrected magnetic susceptibility versus temperature for **2**.

bond and is characterized by a positive temperature coefficient ($d\nu/dT + 0.064$ cm⁻¹/K) and a stretching frequency shift relative to the free OH⁻ of 62 cm⁻¹ at 300 K.

It is of interest to compare the OH stretching frequency of the "free" OH⁻ group in **2** (3593 cm⁻¹) and that of the structurally related compound Cu₄(OH)₆SO₄¹⁷ (3596 cm⁻¹) with the frequency of gaseous OH⁻ ions (3555 cm⁻¹).¹⁸ In the former two compounds, these frequencies have shifted by about 40 cm⁻¹ to higher wavenumbers. Lutz et al.¹⁹ have assigned this "hardening" of the intraionic OH⁻ bond to a strengthening effect caused by the interaction with the adjacent metal ions. In general, this effect is very pronounced with small, highly charged metal ions, like Li⁺ or Mg²⁺. In compound **2**, the frequency shift is comparable to that found in barium hydroxide or strontium hydroxide.^{16,20}

The ν₃ vibrational band of the BF₄⁻ ions is rather broad and structured. Because of lowering of the symmetry, this band is split into three modes at approximately 1020, 1060, and 1095 cm⁻¹. These frequency numbers are consistent with numbers previously reported for [Cu(bipy)₂(F₂BF₂)][BF₄].²¹

Magnetic Susceptibility. Variable-temperature magnetic susceptibility measurements were performed on a powdered sample of **2**. The experimental values were corrected for both the diamagnetic contribution (estimated from Pascal's constants) and the temperature-independent paramagnetism (60×10^{-6} emu/Cu^{II}). The data were fitted by the van Vleck equation²² for exchange-coupled pairs of copper(II) ions (eq 1). The symbols

$$\chi_m = \frac{g^2 N \beta^2}{3kT} \left[1 + \frac{1}{3} \exp\left(\frac{-2J}{kT}\right) \right]^{-1} + N\alpha + \rho \quad (1)$$

in eq 1 have their usual meaning, ρ accounts for the contribution of monomeric impurities present in the sample. In order to account for lattice effects, the temperature term in eq 1 was replaced by $(T - \Theta)$, Θ being a parameter that describes the interdimer interaction. The magnetic parameters that gave the best fit were $g = 2.16$, $J = +16$ cm⁻¹, and $\Theta = 1.2 \times 10^{-2}$ K (see Figure 4). This fit was obtained if it was assumed that approximately 1% monomeric impurities were present. The positive J value can be rationalized in terms of a triplet ground state and a higher lying singlet excited state, which are separated by 16 cm⁻¹. These findings are in agreement with the EPR spectrum of **2** (vide infra), which shows both triplet and doublet signals.

EPR. A frozen solution of **2** (1 mM) in acetonitrile gave a broad signal at $g = 2$ with an anisotropy and hyperfine splitting typical of Cu²⁺ in a ligand field of axial symmetry (not shown). The values of g_{\perp} , g_{\parallel} , and $A_{Cu\parallel}$ were 2.05, 2.26, and 165 G, respectively. No other signals were detected in the temperature

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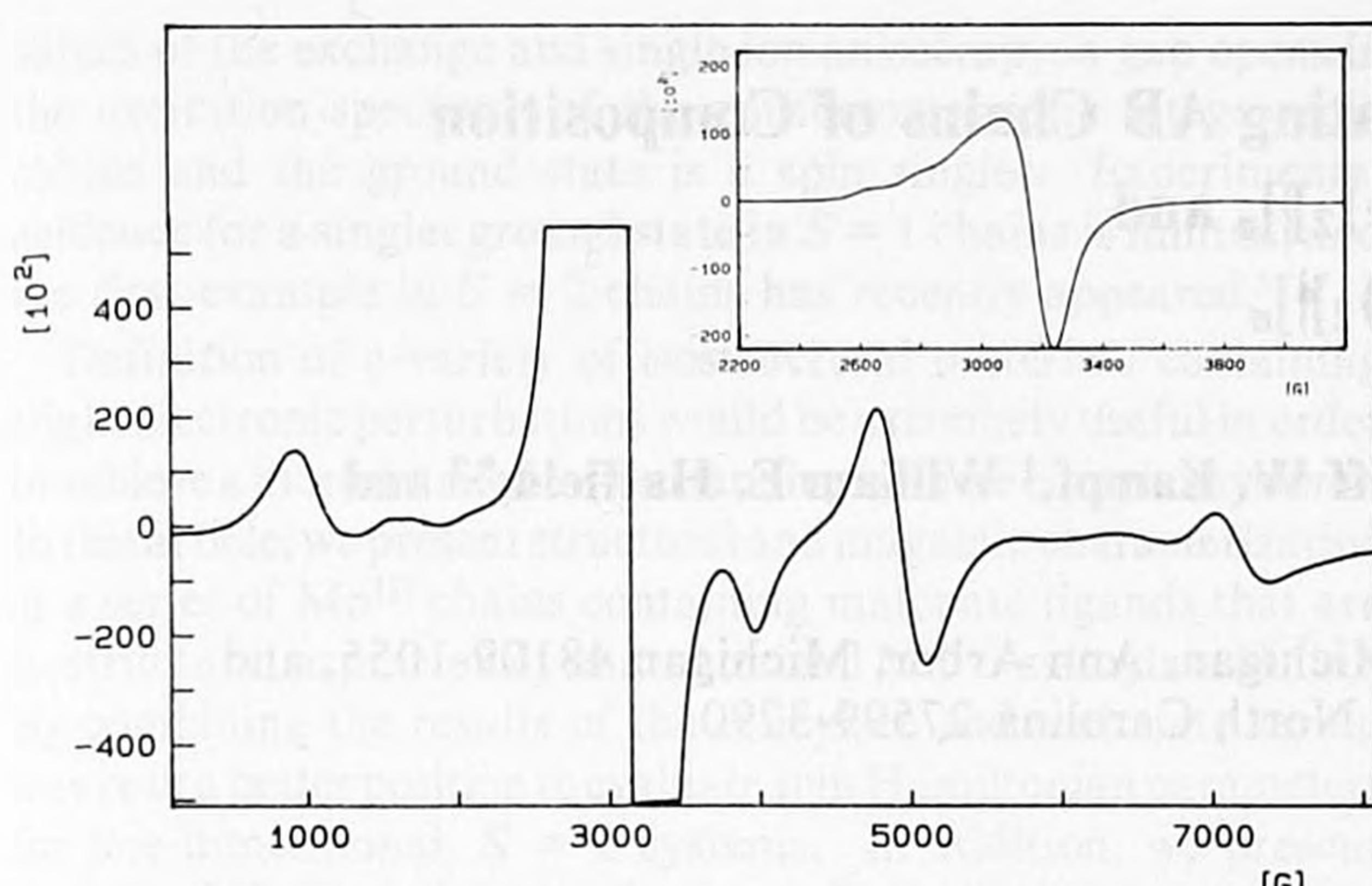


Figure 5. EPR spectrum of **2** in the solid state. Experimental parameters (Figure 5, inset): power 1 mW, 0.2 μ W; frequency 9.2062, 9.1973 GHz; modulator amplitude 5, 4 Gs; temperature 6.8, 6.4 K.

range 8–50 K and the power range 0.1–10 mW. The signal showed Curie–Weiss behavior in the temperature range indicated. The EPR spectrum was clearly not that of a triplet state. It represented monomeric copper which is magnetically undiluted, as judged from the poor resolution of the Cu hyperfine splitting. As the EPR and susceptibility experiments gave different results, which might be ascribed to the solvent, we also investigated the EPR spectrum of a solid sample of **2** in the temperature range 5–50 K.

This EPR spectrum was again dominated by a broad $g = 2$ signal typical of monomeric copper (Figure 5, inset), with the following values: $g_{\perp} = 2.06$, $g_{\parallel} = 2.31$, and $A_{Cu\parallel} = 145$ G. In addition to the $g = 2$ signal, weak signals at $g = 0.91$ (7200 G), $g = 1.31$ (5000 G), $g = 1.66$ (3960 G), and $g = 5.9$ – 8.3 (1100–800 G) were observed (Figure 5). All signals showed the same temperature dependence in the range 10–50 K at 0.2 μ W and 0.2 mW, i.e. nearly Curie–Weiss behavior. A slight decrease in the product of amplitude and temperature was visible at the high-temperature end of the range. Upon examining the power saturation behavior in the range 0.2 μ W–200 mW at 10 K, we observed a slight leveling off of the $\log(IT)$ vs $\log(P)$ plot. This shows that the weak signals are not saturated under the conditions as given in Figure 5. The spectrum can be interpreted as that of a triplet of a coupled binuclear copper site with a doublet contamination of monomeric copper. The outer lines at 7200 and 930 G may be assigned to the H_{z2} and H_{z1} transitions, respectively.²³ The difference in resonance positions between H_{z2} and H_{z1} was taken to correspond to twice the value of the zero-field-splitting constant D' , yielding 3135 G, or $D = 0.293$ cm⁻¹.²⁴ The dipolar part of D depends on the distance between the copper ions.²⁵ In the point-dipole approximation, D can be considered to be built up from a dipolar contribution D_{dip} and a pseudodipolar contribution D_{ex} :

$$D_{\text{dip}} = -(g_{\parallel}^2 + \frac{1}{4}g_{\perp}^2)\beta^2/r^3$$

$$D_{\text{ex}} = -\frac{1}{8}J[\frac{1}{4}(g_{\parallel}^2 - 2)^2 = (g_{\perp}^2 - 2)^2]$$

Neglecting the latter contribution to D in view of the small value of J (see section on magnetic susceptibility), a value of 2.25 Å can be derived for the copper–copper distance from the expression for D_{dip} . This value is much lower than the crystallographically obtained value of 2.90 Å (cf. Table I). It should be noted, however,

that difficulties may arise when this approach is applied to distances <3 Å.²⁶

Relationship between Structure and Magnetism. Both the magnetic susceptibility and the EPR techniques confirm that the exchange coupling in **2** is ferromagnetic. Crawford et al. have worked out a correlation between the Cu–O–Cu bridge angle (θ) and the nature of the exchange interaction.⁵ This correlation predicts that compounds with a bridge angle >97.5° will be antiferromagnetic, and compounds with $\theta < 97.5^\circ$, ferromagnetic. Since **2** possesses two asymmetric Cu–O–Cu units, one ($\theta = 98.4^\circ$) giving rise to antiferromagnetic interaction and the other ($\theta = 94.8^\circ$) to ferromagnetic interaction, it is difficult to predict the magnetic behavior on the basis of the above-mentioned relationship. The average value of θ in **2** is 96.6°. According to Crawford et al., this should lead to ferromagnetism with an exchange parameter J of 35.21 cm⁻¹. This value differs from the value calculated from the magnetic susceptibility measurements ($J = 16$ cm⁻¹). However, as noted before,²⁷ the value of J is very sensitive to small changes in the Cu–O–Cu bridge distance, deviations from planarity in the Cu(OH)₂Cu network, and variations in spin density. Since **2** has a roof structure (the dihedral angle between the two basal planes is 17.6°), it is not unlikely that deviations in J occur.

Concluding Remarks. The complex described in this paper is the second example of a bis(μ -hydroxo)-bridged copper(II) complex with bipyridine ligands that are linked through long out-of-plane Cu–O(H) bonds.²⁸ It does not have the cubane-like structure found by Sletten for a related bipyridine Cu^{II} complex without crown ethers.²⁸ Furthermore, our complex is the first example of a bis(μ -hydroxo)-bridged copper(II) compound with bipyridine ligands that possesses a dimeric structure with asymmetric Cu–O–Cu angles. Although one of the angles is expected to give rise to antiferromagnetic behavior, the overall susceptibility of **2** is ferromagnetic. Exchange interactions only take place within one dimer. For the explanation of the magnetic properties of **2**, it was not necessary to take into account any interaction between two dimers linked as in Figure 2. These findings parallel those reported by Haase²⁹ and Sletten²⁸ on tetrameric alkoxo/hydroxo-bridged Cu(II) clusters. These authors concluded that the exchange interaction between two dinuclear units is very small. Further investigations are under way and include the preparation and structural characterization of the mono(bipyridine) analogue of **2**.³⁰ The host–guest binding properties of complexes of type **2** will be described in a separate paper.³¹

Acknowledgment. We thank J. M. M. Smits for the crystallographic measurements, C. J. Beers for technical support and assistance during the magnetic measurements, and G. E. Janssen, A. A. K. Klaassen, and E. J. Reijerse for assistance in the EPR work.

Supplementary Material Available: Tables giving calculated hydrogen positions, anisotropic thermal parameters, bond distances, bond angles, and additional experimental crystallographic details (9 pages). Ordering information is given on any current masthead page. Structure factor tables may be obtained directly from the authors.

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