

not detected at room temperature.

Formation of $\text{Ni}^{\text{III}}(\text{H}_{-3}\text{G}_3\text{a})(\text{NH}_3)$ is exothermic and has a very small entropy change, in contrast with axial substitutions of anions in nickel(III) macrocyclic complexes, where $\Delta H^\circ > 0$ and the reaction is driven by a favorable entropy change brought about by charge neutralization.

Acknowledgment. We are grateful to Dr. Carl A. Koval for helpful discussions and to Arlene Hamburg for synthesis of the Aib-containing peptides. This investigation was supported by Public Health Service Grant Nos. GM-19775 and GM-12152 from the National Institute of General Medical Sciences.

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201

Oxygenation of [Tris(2-pyridyl)amine](trifluoromethanesulfonato)copper(I) in Nonaqueous Solvents. Synthesis and Structural Characterization of the Cubane-like Cluster $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2[\text{N}(\text{C}_5\text{H}_4\text{N})_3]_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$

PATRICIA L. DEDERT, THEOPHILUS SORRELL, TOBIN J. MARKS,*¹ and JAMES A. IBERS*

Received December 29, 1981

A product of the reaction of molecular oxygen with [tris(2-pyridyl)amine](trifluoromethanesulfonato)copper(I) has been characterized by a low-temperature X-ray diffraction analysis and found to be a cubane-like tetramer of formula $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2[\text{N}(\text{C}_5\text{H}_4\text{N})_3]_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$, with cupric ions and hydroxyl oxygen atoms at alternating vertices of a cube. Each cupric ion is essentially octahedrally coordinated, being bound to three OH bridges, two pyridine N atoms, and one triflate O atom. The cube is of approximate D_{2d} symmetry, the elongation along one axis possibly arising as a consequence of Jahn-Teller distortion. In this complex the tris(2-pyridyl)amine acts as a *bidentate* rather than a tridentate ligand and each triflate ligand spans two vertices of the cluster. Magnetic susceptibility measurements reveal that the cupric ions in the cube are antiferromagnetically coupled, and this observation is readily rationalized on the basis of the structural data. Isotopic tracer experiments demonstrate that the hydroxyl oxygen atoms in the product originate largely in the molecular oxygen used in the reaction and that the hydrogen atoms originate largely in other tris(pyridyl)amine molecules. The material crystallizes with four formula units in space group $C_{2h}^2-P2_1/n$ of the monoclinic system in a cell of dimensions $a = 18.848$ (7) Å, $b = 13.804$ (5) Å, $c = 29.491$ (10) Å, and $\beta = 99.29$ (3)°. The structure has been refined isotropically to an R index of 0.098 on the basis of 337 variable parameters and 8904 unique observations obtained at -150°C .

The importance of copper ions as catalysts in both enzymic² and nonenzymic^{3,4} chemical systems is well-known. Many of the copper proteins activate molecular oxygen, and the functions of these proteins are varied; they serve as oxygen carriers (hemocyanin)⁵ or, more often, as catalysts in oxygenation (oxygenases)^{2,6} or oxidation (oxidases) reactions.^{2,6} The high catalytic activity of both enzymic and nonenzymic copper ions has been attributed to, among other factors, the ease with which Cu(I) is oxidized by O_2 to Cu(II). It has been difficult in the past to study this oxidation reaction in model systems because of both the very rapid oxygenation of Cu(I) in aqueous solution ($k > 10^5 \text{ M}^{-1} \text{ s}^{-1}$)⁷ and the paucity of Cu(I) salts soluble in aprotic media. Early work was carried out with CuCl in dilute acidic solution,^{8,9} followed by experiments in glacial acetic acid,¹⁰ where CuCl is less soluble and hence

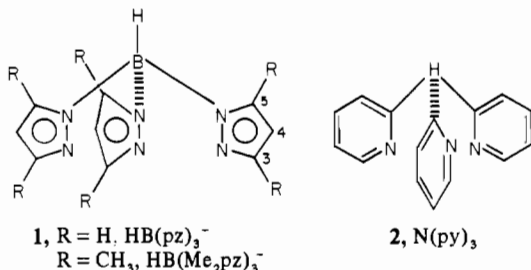
oxidized less rapidly. In the aqueous solutions the rate of Cu(I) oxidation was found to be dependent on $[\text{H}^+]$ and first order with respect to both molecular oxygen and Cu(I) concentrations. In glacial acetic acid the oxidation reaction showed first-order dependency on O_2 and second-order dependency on Cu(I). More recently the oxidation of $[\text{Cu}(\text{imidazole})_2]^+$ and $[\text{Cu}(\text{NH}_3)_2]^+$ has also been studied.¹¹ The oxidation of a cuprous 2,2',2''-terpyridine complex in aqueous acetonitrile¹² and the reaction of O_2 with $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{ClO}_4]$ in perchloric acid-acetonitrile solutions¹³ were also examined, as was the oxidation of $\text{Cu}(\text{bpy})_2^+$ in buffered aqueous solution.¹⁴ All of these reactions were found to be first order in $[\text{Cu}^+]$ and $[\text{O}_2]$. These latter studies with aromatic nitrogenous ligands may be more relevant to the biological systems because in many of the copper proteins histidine (imidazole) has been implicated as a ligand.¹⁵⁻¹⁷ Also noteworthy are the series of kinetic studies^{7,18,19} performed with $\text{Cu}(\text{l},10\text{-phen})_2^+$ in the aprotic solvent nitromethane; not only is phenanthroline a heterocyclic nitrogenous base, as is imidazole, but the aprotic

- (1) Camille and Henry Dreyfus Teacher-Scholar.
- (2) (a) Vanneste, W. H.; Zuberbühler, A. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; pp 371-404. (b) Malkin, R. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; pp 689-709. (c) Malkin, R.; Malmstrom, B. G. *Adv. Enzymol.* **1970**, *33*, 177-244. (d) Beinert, H. *Coord. Chem. Rev.* **1980**, *33*, 55-85 and references therein.
- (3) Khan, M. M.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1974; Vol. 1, pp 114-174.
- (4) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; Chapter 6.
- (5) (a) Lontie, R.; Vanquickenborne, L. *Met. Ions Biol. Syst.* **1974**, *3*, 183-200. (b) Bannister, J. V., Ed. "Structure and Function of Hemocyanin"; Springer-Verlag: Berlin, 1977. (c) Lontie, R.; Witter, R. In "Inorganic Biochemistry"; Eichhorn, G. L., Ed.; Elsevier: New York, 1973; pp 344-358.
- (6) Peisach, J.; Aisen, P.; Blumberg, W. E., Eds. *Biochem. Copper, Proc. Symp.* **1966**, Part 5.
- (7) Arce, J. A.; Spodine, E.; Zamudio, W. *J. Inorg. Nucl. Chem.* **1975**, *37*, 1304-1305.
- (8) Wieland, H.; Franke, W. *Liebigs Ann. Chem.* **1929**, *473*, 289-300.
- (9) Nord, H. *Acta Chem. Scand.* **1955**, *9*, 430-437.

- (10) Henry, P. M. *Inorg. Chem.* **1966**, *58* 688-689.
- (11) Zuberbühler, A. *Helv. Chim. Acta* **1967**, *50*, 466-474.
- (12) Crumbliss, A. L.; Poulos, A. T. *Inorg. Chem.* **1975**, *14*, 1529-1534.
- (13) Gray, R. D. *J. Am. Chem. Soc.* **1969**, *91*, 56-62.
- (14) Pecht, I.; Anbar, M. *J. Chem. Soc. A* **1968**, 1902-1904.
- (15) (a) Salvato, B.; Zatta, P.; Ghirelli-Magaldi, A.; Ghirelli, F. *FEBS Lett.* **1973**, *32*, 35-36. (b) Wood, E. J.; Bannister, W. H. *Biochim. Biophys. Acta* **1968**, *154*, 10-16. (c) Van Holde, K. E. *Biochemistry* **1967**, *6*, 93-99.
- (16) (a) Solomon, E. I.; Hare, J. W.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 1389-1393. (b) Siiman, O.; Young, N. M.; Carey, P. R. *J. Am. Chem. Soc.* **1976**, *98*, 744-748.
- (17) Bereman, R. D.; Kosman, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 7322-7325.
- (18) Zagal, J.; Spodine, E.; Zamudio, W. *J. Chem. Soc., Dalton Trans.* **1974**, 85-87.
- (19) Arce, J. A.; Spodine, E.; Zamudio, W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 2029-2031.

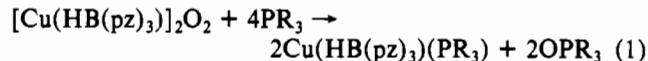
solvent more closely approximates the hydrophobic environment believed to exist at the active sites of the copper proteins.⁵ Unfortunately, none of the kinetic investigations have provided very much information on the nature of the oxygen-copper intermediate. Recent studies of the oxygenation of a bis(pyridyl)(isoindolino)copper(I) carbonyl^{20a} have shown that carbonate, μ -hydroxo, and ligand hydroxylated products can be obtained. Related hydroxylations have also been reported.^{20b,c} In addition to these investigations of irreversible oxidation, recent studies indicate that, with appropriate, imidazole-like ligation, mono- and dinuclear Cu(I) complexes can bind molecular oxygen in a manner that is at least partially reversible.²¹

In this laboratory we have attempted to simulate multiimidazole binding environments in copper proteins with multi-dentate ligands composed of arrays of imidazole-like heterocyclic bases. Examples are the hydrotris(pyrazolyl)borate ligand (1)^{22,23} and the tris(2-pyridyl)amine (N(py)₃) ligand (2).²⁴ One attractive feature of these rather rigid ligands is



the possibility of forcing copper to adopt unusual coordination geometries. There is considerable evidence^{16,17,18,25} that the cupric ions in some metalloproteins exist in coordination geometries unlike the tetragonal (4 + 2) or square-pyramidal (4 + 1) geometries usually found in complexes of Cu(II).²⁶

Initial experiments with Cu(I) bound to HB(pz)₃⁻ produced interesting results.²² The complex Cu(HB(pz)₃)₂, which is dimeric in solution and which reacts with CO to form a carbonyl complex having a value of ν_{CO} nearly as low as that in carboxyhemocyanin,^{22,27} was found to react irreversibly with molecular oxygen in aprotic solvents.²² The green, diamagnetic product was formulated as [Cu(HB(pz)₃)₂]₂O₂ (elemental analysis, mass spectrum, cryoscopic molecular weight in benzene). Solutions of this compound reacted with P(C₆H₅)₂(C₆H₅)₂ according to eq 1,²² which is chemically consistent



with the presence of a copper-oxygen complex.²⁸ However, the failure to detect $\nu_{16\text{O}-16\text{O}}$ or $\nu_{18\text{O}-18\text{O}}$ transitions in the vibrational spectra (infrared and Raman) of "[Cu(HB(pz)₃)₂]₂O₂"²⁹ ($\nu_{\text{Cu}-16\text{O}}$ and $\nu_{\text{Cu}-18\text{O}}$ were detected²²) and the failure to obtain crystals of sufficient quality for diffraction studies hindered the secure identification of this compound as a complex of intact (O₂) molecular oxygen.

In this contribution, we report observations on the oxygenation chemistry of Cu(I) bound to a different, potentially more imidazole-like ligand, N(py)₃. The pK_a of the conjugate acid (BH⁺) of pyridine (5.25) is more comparable with the pK_a of imidazole (6.95) than is the pK_a of pyrazole (2.48),³⁰ and the basicities of the nitrogen donor ligands have been found to influence the rate of Cu(I) oxidation.¹⁹ In addition, N(py)₃ lacks the B-H functionality that may complicate the oxygenation chemistry of HB(pz)₃ complexes. We report here that oxygenation of Cu(N(py)₃)(SO₃CF₃) ultimately yields, by way of a dark green solution similar in properties to that of "[Cu(HB(pz)₃)₂]₂O₂", a blue, paramagnetic material. This material has been characterized by single-crystal X-ray diffraction and other physicochemical techniques; it is seen to contain a cubane-like Cu₄(OH)₄ cluster with bidentate N(py)₃ ligands and coordinated triflate anions bridging vertices of the cluster. Isotopic labeling studies provide information on the source of the OH moieties.

Experimental Section

Analytical and Physical Measurements. Elemental analyses were performed by Ms. H. Beck of the Northwestern University Analytical Services Laboratory or by Dornis and Kolbe Analytical Laboratory, Mulheim, a.d. Ruhr, West Germany. Electronic spectra were recorded on a Cary 17D spectrophotometer. Spectra of solid samples were obtained from Nujol mulls between quartz plates. Infrared spectra were recorded with Perkin-Elmer 267 and 283 spectrophotometers. Mulls of air-sensitive species were prepared in a glovebox with dry, degassed Nujol or Fluorolube. Proton nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R20B (60 MHz, CW) instrument.

The magnetic susceptibility of [Cu₄(OH)₄(SO₃CF₃)₂(N(py)₃)₄][SO₃CF₃]₂·C₂H₆O was determined between 77 and 293 K by the Faraday method using HgCo(CNS)₄ as a calibrant. Diamagnetic corrections were made with published values.³¹

Raman spectra were recorded on a 0.85-m Spex 1401 double monochromator with photon-counting detection. A light-stabilized Spectra Physics 164 Ar⁺ laser was employed; the 514.5-nm excitation was used in all cases. Polycrystalline samples were studied in spinning Pyrex tubes.

Reagents and Syntheses. All operations involving air-sensitive materials were carried out under dinitrogen in Schlenk ware or in a glovebox. Solvents were distilled under dinitrogen from an appropriate drying agent immediately prior to use. Acetone and other ketones were predried over Drierite or molecular sieves and then distilled under nitrogen from Drierite. Acetonitrile and dichloromethane were distilled under nitrogen from P₂O₅.

Trifluoromethanesulfonic acid anhydride was purchased from Aldrich Chemical Co. The ligand tris(2-pyridyl)amine was prepared by a literature procedure³² and was recrystallized from hot water or

- (20) (a) Gagne, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem.* **1979**, *18*, 771-781. (b) Karlin, K. D.; Dahlstrom, P. L.; Cozzette, S. N.; Scensny, P. M.; Zubieta, J. J. *Chem. Soc., Chem. Commun.* **1981**, 881-882. (c) Urbach, F. L.; Knopp, U.; Zuberbühler, A. D. *Helv. Chim. Acta*, **1978**, *61*, 1097-1106.
- (21) (a) Simmons, M. G.; Merrill, C. L.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1827-1837. (b) Bulkowski, J. E.; Burk, P. L.; Ludmann, M.-T.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498-499.
- (22) (a) Arcus, C. S.; Wilkinson, J. L.; Mealli, C.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 7564-7565. (b) Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *Ibid.* **1976**, *98*, 711-718. (c) Arcus, C. S.; Wilkinson, J. L.; Marks, T. J., unpublished results.
- (23) (a) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 3114-3118. (b) Marks, T. J. *Fundam. Res. Homogeneous Catal.* **1978**, *2*, 285-300. (c) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180-4192. (d) Thompson, J. S.; Sorrell, T.; Marks, T. J.; Ibers, J. A. *Ibid.* **1979**, *101*, 4193-4200. (e) For results with a closely related N₂S ligand, see: Thompson, J. S.; Zitzmann, J. L.; Marks, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1980**, *46*, L101-L105.
- (24) Dedert, P. L.; Thompson, J. S.; Ibers, J. A.; Marks, T. J. *Inorg. Chem.* **1982**, *21*, 969-977.
- (25) Miskowski, V.; Targ, S. P. W.; Spiro, T. G.; Shapiro, E.; Moss, T. H. *Biochemistry* **1975**, *4*, 1244-1250.
- (26) Cotton, F. A.; Wilkinson, G. W. "Advanced Inorganic Chemistry", 4th ed.; Interscience: New York, 1972, pp 811-814.
- (27) (a) Bruce, M. I.; Ostaszewski, A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433-2436. (b) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209-226.

- (28) (a) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235-245. (b) Choy, V. J.; O'Connor, C. J. *Coord. Chem. Rev.* **1972**, *9*, 145-170. (c) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139-179. (d) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295-383.
- (29) A similar situation obtains in the copper oxygen carrier derived from the 2,6-bis[1-(2-(imidazol-4-yl)ethylimino)ethyl]pyridine ligand.^{21a}
- (30) Cullingworth, A. R.; Pidcock, A.; Smith, J. D. *Chem. Commun.* **1966**, 89-90.
- (31) (a) Selwood, P. W. "Magnetochemistry", 2nd ed.; Interscience: New York, 1956; p 78. (b) Jolly, W. "Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 371.
- (32) Wibaut, J. P.; La Bastide, G. L. C. *Recl. Trav. Chim. Pays-Bas* **1933**, *52*, 493-498.

acetone and dried under high vacuum until satisfactory analysis, melting point, and infrared spectrum were obtained. The $^{18}\text{O}_2$ was purchased from Bio-Rad Laboratories, Richmond, CA.

Cuprous triflate was prepared in two forms, as the uncomplexed salt and as the benzene complex, $[\text{Cu}(\text{SO}_3\text{CF}_3)_2(\text{C}_6\text{H}_6)]$, according to the method of Dines.³³ Purer products were obtained with the benzene complex as starting material. The starting material in the preparation of the cuprous triflate, cuprous oxide, was prepared by a literature procedure.³⁴

$\text{Cu}^{\text{I}}(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$ (3). In a typical preparation, 0.65 g (1.3 mmol) of the white, extremely air-sensitive starting material, $[\text{Cu}(\text{SO}_3\text{CF}_3)_2(\text{C}_6\text{H}_6)]$, was transferred in a glovebox to a three-necked flask. The ligand $\text{N}(\text{py})_3$ (0.64 g, 2.6 mmol) was added to the flask, and then ca. 30 mL of freshly distilled benzene was added to the flask by syringe. Immediately upon addition of the benzene, a yellow mixture resulted, with some precipitation of a black material. After overnight stirring, the black precipitate was no longer visible, and the reaction mixture was a light yellow-green. The solid was allowed to settle, and the solvent was withdrawn by syringe. After the product was washed with hexane, the very light yellow-green solid was dried in vacuo. The yield was ca. 80% on the basis of copper.

Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{CuF}_3\text{N}_4\text{O}_3\text{S}$: C, 41.63; H, 2.62; N, 12.16. Found: C, 41.89; H, 3.16; N, 11.99.

Complete infrared data (Nujol and Fluorolube mulls): 3080 vw, br, 1670 vs, 1600 sh, 1587 s, 1566 s, 1473 vs, 1465 sh, 1447 vs, 1440 sh, 1337 s, 1316 m, 1307 m, 1290 m, 1275 m, 1265 m, 1241 m, 1227 m, 1220 sh, 1171 s, 1160 s, 1150 sh, 1108 w, 1103 w, 1068 w, 1060 w, 1051 m, 1032 vs, 1025 sh, 997 w, 995 w, 950 w, 939 vw, 900 w, 890 w, 798 m, 778 vs, 774 sh, 760 sh, 756 sh, 750 m, 747 m, 659 s, 646 m, 637 vs, 618 m, 575 s, 548 vw, 518 vs, 509 sh, 495 w, 477 w, 429 m, 425 m, 407 m, 354 cm^{-1} .

Major Raman bands: 249 w, br, 283 w, 350 w, 435 w, 546 m, 636 m, 649 m, br, 747 s, 763 m, 781 w, 792 w, 943 m, br, 953 m, br, 996 s, 1025 vs, 1035 vs, 1055 m, 1110 w, 1162 w, 1233 s, 1249 w, 1289 m, vbr, 1340 m, br, 1444 m, br, 1479 w, br, 1568 s, 1606 s, br cm^{-1} .

$[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$ (4-Me₂CO). In a typical experiment $\text{Cu}^{\text{I}}(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$ (60 mg, 0.13 mmol) was dissolved in distilled, degassed acetone, with rigorous exclusion of air, to yield a very pale yellow-green solution. A serum cap was wired onto the Schlenk tube and 1.5 mL of O_2 (ca. 6.5 mmol at 296 K) was injected by gastight syringe through the serum cap into the N_2 atmosphere above the acetone solution. (The oxygen was first passed through two -78°C traps, one of silica gel and one of molecular sieves, to remove moisture.) The Schlenk tube was clamped to a stable rack at room temperature. After diffusion of the oxygen the solution was much darker green. Within 3 days blue crystals began to precipitate from the green solution. After the crystals had grown undisturbed for $3\frac{1}{2}$ weeks, the supernatant solution (still green) was removed by syringe. The blue crystals were washed with acetone and dried in a stream of nitrogen; they were of sufficient quality for X-ray analysis (vide infra). The yield was 0.014 g or ca. 20% on the basis of Cu.

Anal. Calcd for $\text{C}_{67}\text{H}_{58}\text{Cu}_4\text{F}_{12}\text{N}_{16}\text{O}_{17}\text{S}_4$: C, 40.85; H, 2.97; N, 11.38. Found: C, 40.59; H, 3.16; N, 11.20.

Complete infrared data (Nujol and Fluorolube mulls): 3470 m, vbr, 1714 m, 1608 m, 1598 m, 1594 sh, 1577 m, 1569 w, 1493 m, 1469 vs, 1439 vs, 1335 m, 1367 s, vbr, 1243 sh, 1226 m, 1157 s, 1125 w, 1100 w, 1030 vs, 1003 m, 939 w, 797 m, 783 s, 759 m, 756 m, 748 m, 739 w, 665 w, 649 sh, 636 vs, 573 m, 539 w, 517 m, 479 m, br, 428 m, 358 w, br cm^{-1} .

Major Raman bands: 207 m, 238 m, 269 m, 309 s, 330 m, 357 s, 433 w, 537 w, 544 sh, 574 m, 626 m, 650 m, 743 s, 756 s, 783 w, br, 897 s, 939 m, 952 m, 1001 s, 1008 sh, 1020 w, 1035 vs, 1052 m, br, 1065 m, 1123 w, 1155 w, 1202 m, 1222 s, 1255 m, 1272 s, 1286 sh, 1302 w, 1324 w, 1336 w, 1438 m, 1473 w, 1567 s, 1578 m, 1589 w cm^{-1} .

Partial evaporation of the green supernatant from some preparations produced a pale blue powder, of the same composition as the blue crystals, without the acetone of solvation (vide infra).

$[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2$ (4). This complex can be obtained from several solvents—acetone, 2-butanone, dichloromethane, and acetonitrile—by bubbling dry oxygen through solutions

Table I. Crystal Data for $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{C}_5\text{H}_4\text{N})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$

mol formula	$\text{C}_{67}\text{H}_{58}\text{Cu}_4\text{F}_{12}\text{N}_{16}\text{O}_{17}\text{S}_4$
mol wt	1969.8
<i>a</i>	18.848 (7) Å
<i>b</i>	13.804 (5) Å
<i>c</i>	29.491 (10) Å
β	99.29 (3) $^\circ$
<i>V</i>	7572 Å ³
<i>Z</i>	4
ρ_{calcd}	1.727 g/cm^3 (-150°C)
temp	-150°C^a
space group	$C_{2h}^2-P2_1/n$
crystal faces	{110}, {101}, {001}; $V = 0.114 \text{ mm}^3$
radiation	monochromatized Mo $\text{K}\alpha_1$ ($\lambda(\text{Mo } \text{K}\alpha_1) = 0.70930 \text{ Å}$)
scan speed	$2^\circ/\text{min}$ in 2θ
scan range	0.65° below $\text{K}\alpha_1$ to 0.65° above $\text{K}\alpha_2$
2θ limits	$2.5^\circ < 2\theta < 46.5^\circ$
receiving aperture	4.4 mm high by 4.3 mm wide, 32 cm from crystal
takeoff angle	2.3°
bkgd counting time	10 s with rescan option ^b
abs coeff	13.15 cm^{-1}
transmission factors	0.572–0.627
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	8904
<i>p</i>	0.04
no. of variables	337
<i>R</i>	0.098
R_w	0.126
error in observn of unit wt	3.85 electrons

^a The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. ^b The diffractometer was operated under the disk-oriented Vanderbilt system: Lenhart, P. G. *J. Appl. Crystallogr.* 1975, 8, 568–570.

of $\text{Cu}^{\text{I}}(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$. A fine blue powder precipitates from the green solution within minutes of beginning the bubbling process. The infrared spectra of these powders are nearly identical with that of the acetone solvate, with the exception of the missing C=O stretch of acetone.

Anal. Calcd for $\text{C}_{64}\text{H}_{52}\text{Cu}_4\text{F}_{12}\text{N}_{16}\text{O}_{16}\text{S}_4$: C, 40.20; H, 2.74; N, 11.72. Found: C, 39.88; H, 3.26; N, 11.50.

Solid-State Reaction of $\text{Cu}^{\text{I}}(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$ with O_2 . The starting material was placed in a flask fitted with two gas inlets. After the flask was evacuated, one inlet was connected to an oxygen tank and the other to a mineral oil bubbler. The flask was placed in an oil bath, and the temperature was raised to ca. 90°C . Oxygen was passed over the warm sample for $3\frac{1}{2}$ weeks. Any change in the appearance of the sample occurred so gradually as to be imperceptible. At the end of the reaction period, however, the color of the sample was compared with that of the unreacted starting material, and it was obvious that the product was a much darker green than the original material. Despite the fact that this product is not blue, its elemental analysis is very close to that expected for the product $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2$. However, the analysis is equally good for a product formulated as $\text{Cu}^{\text{I}}(\text{SO}_3\text{CF}_3)(\text{N}(\text{py})_3)(\text{H}_2\text{O})$. Extensive pumping on the product did not reverse the reaction.

Anal. Calcd for the latter formulation, $\text{C}_{16}\text{H}_{14}\text{CuF}_3\text{N}_4\text{O}_4\text{S}$: C, 40.13; H, 2.95; N, 11.70. Found: C, 40.03; H, 2.56; N, 11.62.

Complete infrared data (Nujol mull): 3600 sh, 3480 m, vbr, 1606 m, 1598 m, 1586 sh, 1574 sh, 1567 m, 1490 m, 1470 vs, 1440 vs, 1335 m, 1307 m, 1287 sh, 1271 s, 1261 s, 1258 sh, 1249 sh, 1242 sh, 1227 m, 1160 s, 1126 w, 1101 w, 1061 w, 1030 vs, 1002 m, 991 vw, 977 w, 939 w, 797 sh, 781 m, 777 sh, 759 m, 751 w, 741 w, 667 w, 660 w, 638 vs, 619 sh cm^{-1} .

Solution of the Crystal Structure of $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$ (4-Me₂CO). The crystal chosen for X-ray analysis was grown from an acetone solution of $\text{Cu}^{\text{I}}(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$ and molecular oxygen at room temperature. A series of Weissenberg and precession photographs determined that the compound crystallizes in space group $P2_1/n$ of the monoclinic system. Crystal data and related details of data collection and refinement are given in Table I. In general, the procedures usual for this laboratory were followed

(33) Dines, M. B. *Sep. Sci.* 1973, 8, 661–672.

(34) Schlessinger, G. G. "Inorganic Laboratory Preparations"; Chemical Publishing Co.: New York, 1962; p 11.

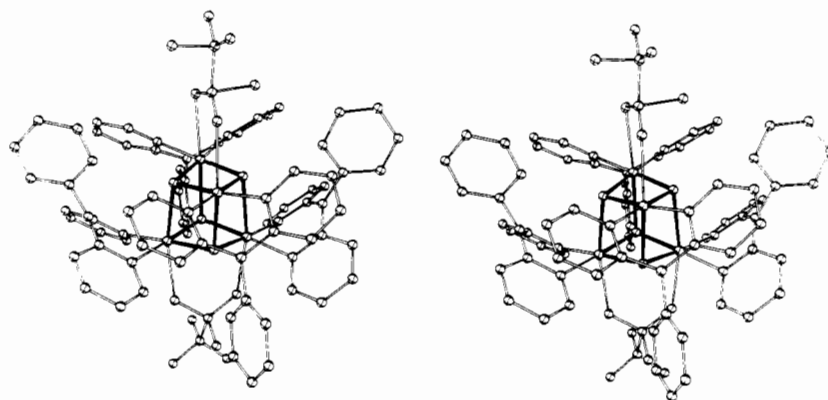
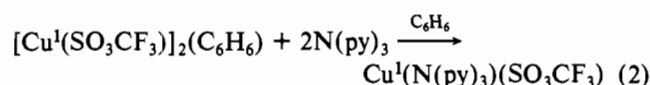


Figure 1. Stereoscopic view of the cation $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4]^{2+}$. The thermal ellipsoids are of arbitrary size. Hydrogen atoms are omitted.

in the collection of the data and in the solution and refinement of the structure.³⁵ The structure was solved by direct methods (MULTAN) and refined by isotropic least-squares methods, with the pyridine rings constrained to rigid groups.³⁶ As established from the X-ray analysis, the material is $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$. Of the two coordinated triflate ions, triflate 2³⁷ is disordered, as judged by the high thermal parameters of some of its component atoms (greater than 10 \AA^2 for data collected at $-150 \text{ }^\circ\text{C}$). All efforts to resolve this disorder failed. The presence of disorder, the absence of bound molecular oxygen, and the expense and doubtful efficacy of an anisotropic refinement of these low-temperature data, which would involve potentially over 1000 variable parameters, led us to terminate the refinement at convergence of this isotropic model. Table II lists the positional and thermal parameters of the atoms of the complex. Table III³⁸ tabulates $10|F_o|$ vs. $10|F_c|$ in electrons for those reflections used in the refinement.

Results and Discussion

Syntheses and Properties. The cuprous complex $\text{Cu}^I(\text{N}(\text{py})_3)(\text{SO}_3\text{CF}_3)$ (**3**) can be synthesized in good yield via the route of eq 2. Although the elemental analysis of the product



of eq 2 is consistent with the formulation given, the product samples are invariably contaminated with traces of a copper(II) species, as evidenced by the pale green color, by the broadening of the ¹H NMR signal of solutions of this complex, and by the appearance of an EPR signal from powdered samples. Despite many preparations involving rigorous attempts to exclude air, a sample completely devoid of Cu^{II} was never obtained. The solid is stable in dry air at room temperature.

The cuprous complex **3** is soluble in a number of polar solvents, including acetone, 2-butanone, dichloromethane, acetonitrile, dimethylformamide (DMF), nitromethane, and pyridine. The solutions are a pale yellow-green and are rel-

atively stable at room temperature as long as they remain oxygen free. In the presence of oxygen, acetone, butanone, and dichloromethane, solutions of **3** are readily oxidized to form a dark green solution and a blue precipitate, **4**. Solutions of the cuprous complex in CH₃CN and pyridine are much less rapidly oxidized by molecular oxygen. Neither pyridine nor DMF solutions of **3** ever yield **4** upon oxygenation. Addition of an organic phosphine, e.g., P(*n*-C₄H₉)₃ to the dark green, oxygenated solution of **3** immediately turns the solution colorless, similar to the results achieved when phosphines are added to an oxygenated solution of Cu^I(HB(pz)₃).²² Under the aforementioned oxygenation conditions, complex **4**, which will be seen to be the Cu(II) tetramer $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2$ (vide infra), forms reproducibly in approximately 20% yield. When oxygenation is carried out in acetone, deep blue crystals of the acetone solvate are obtained. These crystals are of two habits, prisms and flat plates. X-ray studies established that the unit cells for the two crystal types are identical. The crystals with the flat-plate habit were found to be far superior for X-ray study; these may be produced from acetone solutions at room temperature. One such crystal grown at room temperature was used for the X-ray determination. Below room temperature, the oxidation of **3** in acetone chiefly produces crystals of the prism type. Compound **4** is indefinitely stable in air at room temperature. It is insoluble in all solvents tried except DMF and nitromethane, in which it decomposes. Solution spectroscopic studies were therefore impossible, as was recrystallization of the product. Interestingly, **4** could not be prepared via reaction of appropriate quantities of Cu(SO₃CF₃)₂, N(py)₃, and aqueous NaOH, an approach analogous to procedures for other μ -hydroxo cupric complexes.³⁹ Instead, only Cu(N(py)₃)₂(SO₃CF₃)₂, which we have described previously,²⁴ was isolated. Compound **4** did not result from the solid-state oxygenation^{21b} of **3** at a variety of temperatures.

Description of the Crystal Structure of the Acetone Solvate of 4. $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$ (**4**·Me₂CO) has a cubane-like core with Cu²⁺ ions and hydroxide oxygen atoms at alternating corners of a distorted cube. The distortions of the cube are those of the point group *D*_{2d}-42*m*. The asymmetric unit, shown in Figure 1, contains one Cu₄(OH)₄ core, two discrete triflate anions, and one acetone of solvation. There is no evidence that the H atoms on the OH groups enter into hydrogen bonding: there are no cation-anion non-hydrogen atom interactions less than 3.2 Å in length. The principal dimensions of the core and the atom labeling scheme are shown in Figure 2, while Tables IV and

(35) See, for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(36) La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511–519. The following bond distances and angles were used, starting at N, around the ring: 1.35, 1.39, 1.38, 1.37, 1.39, 1.34 Å; 119, 122, 118, 121, 118, 122°.

(37) For the N(py)₃ ligand atoms, the first number of the label corresponds to the copper atom to which the ligand is bonded and varies from 1 to 4. The second number corresponds to the individual rings of each N(Py)₃ group and varies from 1 to 3. The third number corresponds to the position of the atom within the ring and so will vary from 1–6. Hence, the three pyridine nitrogens in the N(py)₃ ligand coordinated to Cu(2) are labeled N(211), N(221), and N(231), respectively. The first number in each label corresponding to an atom of a triflate anion represents the particular triflate group and hence varies from 1–4. Thus the oxygens labeled O(21) and O(22) are both part of the same triflate anion.

(38) Supplementary material.

(39) (a) Harris, C. M.; Sinn, E.; Walker, W. R.; Woollams, P. R., *Aust. J. Chem.* **1968**, *21*, 631–640. (b) Hoskins, B. F.; Whillans, F. D. *J. Chem. Soc., Dalton Trans.* **1975**, 1267–1272.

Table II. Positional and Thermal Parameters of the Atoms of $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$

ATOM	X ^A	Y	Z	B ₁₁ ^{A2}	ATOM	X	Y	Z	B ₁₁ ^{A2}
Cu(1)	-0.083068(65)	0.168987(88)	0.309740(42)	1.06(3)	O(1)	0.03318(36)	-0.04273(48)	0.31592(23)	1.20(13)
Cu(2)	0.011515(64)	0.003636(88)	0.375370(42)	1.06(3)	O(11)	-0.00210(40)	-0.16926(54)	0.39958(26)	1.98(15)
Cu(3)	0.052913(65)	0.107891(88)	0.279640(42)	1.10(3)	O(12)	-0.07314(37)	-0.21937(51)	0.32749(24)	1.72(13)
Cu(4)	-0.065463(64)	-0.064091(88)	0.284923(42)	1.09(3)	O(13)	-0.12410(47)	-0.22388(65)	0.39763(30)	3.16(18)
S(1)	-0.06103(14)	-0.22684(20)	0.376895(92)	1.51(5)	O(21)	-0.05470(51)	0.32879(70)	0.27129(33)	3.40(20)
S(2)	0.00402(22)	0.34437(29)	0.25255(14)	4.16(8)	O(22)	0.04924(46)	0.28009(64)	0.23722(30)	2.74(18)
S(3)	0.24169(16)	0.18462(22)	0.02636(11)	2.18(6)	O(23)	0.05733(90)	0.3844(13)	0.29737(59)	10.12(47)
S(4)	-0.10360(17)	0.24691(23)	-0.03731(11)	2.63(6)	O(31)	0.25273(44)	0.10612(61)	-0.00344(29)	3.09(17)
F(11)	-0.01549(40)	-0.37089(55)	0.43047(26)	3.68(16)	O(32)	0.19942(50)	0.26299(70)	0.00528(33)	3.98(20)
F(12)	-0.07743(42)	-0.41364(58)	0.36569(27)	4.23(17)	O(33)	0.30397(48)	0.21224(66)	0.05717(31)	3.49(19)
F(13)	0.02970(43)	-0.36466(60)	0.36887(28)	4.54(18)	O(41)	-0.15836(65)	0.17817(89)	-0.05138(47)	6.09(28)
F(21)	-0.04205(73)	0.4394(10)	0.18587(48)	11.12(36)	O(42)	-0.08097(57)	0.29894(78)	-0.07343(37)	5.21(24)
F(22)	0.06061(46)	0.48444(63)	0.21141(30)	4.83(19)	O(43)	-0.11441(42)	0.30361(58)	0.00075(28)	2.58(16)
F(23)	-0.02914(42)	0.52638(59)	0.24325(28)	4.48(17)	N(100)	-0.21305(49)	0.16266(67)	0.35957(37)	1.94(18)
F(31)	0.22247(36)	0.06372(50)	0.09162(23)	3.12(14)	N(200)	0.08392(48)	0.15529(66)	0.44372(31)	1.93(17)
F(32)	0.12873(41)	0.08491(55)	0.04077(26)	3.95(16)	N(300)	0.17741(47)	-0.02791(64)	0.26978(30)	1.95(17)
F(33)	0.16125(45)	0.19544(63)	0.09054(29)	4.58(19)	N(400)	-0.12844(49)	-0.06203(68)	0.18175(32)	2.17(18)
F(41)	-0.03319(43)	0.12012(59)	0.01925(28)	4.24(17)	C(1)	0.06307(71)	0.39622(96)	0.09440(46)	2.92(26)
F(42)	0.03202(48)	0.22807(67)	-0.00545(31)	5.09(20)	C(2)	0.01928(73)	0.31440(89)	0.10779(47)	3.32(28)
F(43)	-0.01098(46)	0.11261(63)	-0.04968(30)	4.92(19)	C(3)	0.0471(10)	0.4375(14)	0.04588(65)	6.01(43)
O(4)	0.01992(36)	0.15875(49)	0.33450(23)	1.32(13)	C(11)	-0.02844(64)	-0.34895(88)	0.38588(47)	2.38(23)
O(2)	-0.05131(36)	0.09718(48)	0.25885(23)	1.32(13)	C(21)	0.01154(91)	0.4571(12)	0.23228(50)	5.19(36)
O(3)	-0.08582(35)	0.00889(48)	0.33952(23)	1.14(12)	C(31)	0.18651(68)	0.12951(94)	0.06348(44)	2.51(25)
O(5)	0.11580(62)	0.42552(84)	0.12036(40)	5.27(26)	C(41)	-0.02632(74)	0.1736(10)	-0.01732(48)	3.46(28)
N(111)	-0.18777(21)	0.17435(45)	0.28364(18)	1.10(15)	N(311)	0.08512(32)	0.05671(41)	0.22196(17)	1.18(16)
C(112)	-0.20924(26)	0.18226(48)	0.23797(17)	1.09(18)	C(312)	0.04909(31)	0.07915(41)	0.18069(20)	1.48(20)
C(113)	-0.28114(30)	0.17911(52)	0.21881(14)	1.32(19)	C(313)	0.05937(36)	0.03216(50)	0.14097(16)	1.73(21)
C(114)	-0.33157(22)	0.16755(52)	0.24753(20)	1.50(19)	C(314)	0.11070(37)	-0.04266(47)	0.14540(18)	1.85(20)
C(115)	-0.30972(26)	0.15947(52)	0.29413(19)	1.28(19)	C(315)	0.14897(33)	-0.06674(43)	0.18892(22)	1.68(21)
C(116)	-0.23703(29)	0.16316(48)	0.31120(14)	1.22(18)	C(316)	0.13362(32)	-0.01415(45)	0.22592(16)	1.22(19)
N(121)	-0.10909(32)	0.25393(42)	0.36035(18)	1.29(16)	N(321)	0.15772(24)	0.12543(41)	0.30267(20)	1.11(15)
C(122)	-0.06358(29)	0.32527(47)	0.37715(21)	1.82(21)	C(322)	0.18139(29)	0.20288(36)	0.32747(22)	1.35(19)
C(123)	-0.07267(33)	0.37651(44)	0.41607(23)	1.61(21)	C(323)	0.25102(33)	0.21163(40)	0.35026(23)	1.83(21)
C(124)	-0.12994(37)	0.35331(48)	0.43790(19)	1.88(22)	C(324)	0.29793(25)	0.13387(48)	0.34646(24)	1.92(21)
C(125)	-0.17639(31)	0.28054(49)	0.42078(21)	1.47(20)	C(325)	0.27326(29)	0.05180(41)	0.32030(25)	1.72(21)
C(126)	-0.16443(30)	0.23196(40)	0.38174(21)	1.24(18)	C(326)	0.20238(31)	0.05210(36)	0.29921(21)	1.14(19)
N(131)	-0.22965(31)	0.00322(43)	0.38214(21)	1.56(17)	N(411)	-0.16759(23)	-0.07550(47)	0.25342(18)	1.27(16)
C(132)	-0.26030(38)	-0.06579(34)	0.40482(25)	2.16(21)	C(412)	-0.22055(30)	-0.08217(51)	0.27893(14)	1.63(19)
C(133)	-0.31281(40)	-0.04361(46)	0.43089(26)	2.81(27)	C(413)	-0.29214(26)	-0.07706(53)	0.25922(19)	1.50(19)
C(134)	-0.33385(37)	0.05178(53)	0.43346(26)	2.88(25)	C(414)	-0.30902(23)	-0.06483(53)	0.21224(20)	1.72(20)
C(135)	-0.30262(39)	0.12224(38)	0.41033(26)	2.02(22)	C(415)	-0.25503(31)	-0.05803(54)	0.18618(15)	1.69(20)
C(136)	-0.25039(35)	0.09547(38)	0.38482(23)	1.49(20)	C(416)	-0.18447(27)	-0.06366(49)	0.20793(18)	1.02(17)
N(211)	0.11134(23)	0.00643(42)	0.41045(21)	1.22(16)	N(421)	-0.04182(32)	-0.14715(42)	0.23262(17)	1.23(16)
C(212)	0.15826(31)	-0.06443(35)	0.40484(22)	1.62(19)	C(422)	0.00941(34)	-0.21556(48)	0.24189(17)	1.94(22)
C(213)	0.23090(28)	-0.05512(41)	0.42119(25)	1.86(21)	C(423)	0.03470(35)	-0.26570(47)	0.20720(24)	2.07(22)
C(214)	0.25523(23)	0.02914(48)	0.44371(24)	1.94(21)	C(424)	0.00635(39)	-0.24448(50)	0.14216(20)	2.42(24)
C(215)	0.20741(32)	0.10148(38)	0.44945(24)	1.77(21)	C(425)	-0.04592(38)	-0.17470(52)	0.15268(15)	2.06(21)
C(216)	0.13542(29)	0.08783(37)	0.43233(23)	1.35(20)	C(426)	-0.06898(30)	-0.12708(42)	0.18887(20)	1.26(19)
N(221)	-0.01714(29)	0.05120(39)	0.43417(18)	1.12(15)	N(431)	-0.12461(35)	0.09819(44)	0.15759(17)	1.53(18)
C(222)	-0.07917(30)	0.01957(37)	0.44609(21)	1.39(19)	C(432)	-0.13386(40)	0.16927(34)	0.12590(23)	2.25(23)
C(223)	-0.11058(27)	0.06624(46)	0.47926(23)	1.55(19)	C(433)	-0.15517(44)	0.14941(45)	0.07978(21)	2.64(24)
C(224)	-0.07706(33)	0.14708(44)	0.50042(20)	1.39(19)	C(434)	-0.16706(43)	0.05420(53)	0.06633(17)	2.63(25)
C(225)	-0.01378(32)	0.17941(39)	0.48829(21)	1.59(19)	C(435)	-0.15764(43)	-0.01837(38)	0.09862(23)	2.49(24)
C(226)	0.01495(26)	0.12961(42)	0.45486(21)	0.97(18)	C(436)	-0.13627(38)	0.00614(38)	0.14422(20)	1.37(19)
N(231)	0.10082(35)	0.30086(43)	0.40756(17)	1.67(17)	N(331)	0.16189(27)	-0.17492(44)	0.30559(22)	1.61(17)
C(232)	0.11990(40)	0.39485(43)	0.40731(19)	2.18(21)	C(332)	0.20360(33)	-0.12119(36)	0.28232(23)	1.33(19)
C(233)	0.14526(44)	0.44389(37)	0.44752(25)	2.95(27)	C(333)	0.26783(32)	-0.15627(46)	0.27205(24)	1.78(20)
C(234)	0.15092(43)	0.39455(50)	0.48868(19)	2.82(25)	C(334)	0.28911(30)	-0.24864(48)	0.28617(26)	2.20(22)
C(235)	0.13148(42)	0.29866(50)	0.48897(17)	2.15(23)	C(335)	0.24660(37)	-0.30352(38)	0.30992(27)	2.44(23)
C(236)	0.10650(38)	0.25364(36)	0.44761(22)	1.58(21)	C(336)	0.18296(34)	-0.26437(43)	0.31914(24)	2.48(23)

^A ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES.

V give relevant bond distances and angles for the core and the triflate anions.³⁷ The copper coordination sphere is a distorted, tetragonally elongated octahedron. Two pyridine nitrogen atoms from the bidentate ligand $\text{N}(\text{py})_3$ and two hydroxide oxygen atoms act as equatorial ligands. One axial site on each copper ion is occupied by a triflate oxygen atom and the other by a hydroxide oxygen atom. Jahn–Teller distortion of the copper coordination sphere may be responsible for the resulting

elongation of the $\text{Cu}_4(\text{OH})_4$ cube seen in Figure 2.

The distortion of each copper coordination sphere is evidenced by the following observations: (a) the equatorial ligands are not strictly coplanar, which can be seen in the deviations from the best weighted least-squares planes for the equatorial ligands (Table VI); (b) the axial hydroxide oxygen atom is not bonded perpendicularly to the equatorial plane (mean $\text{O}(\text{H})_{\text{ax}}-\text{Cu}-\text{N} = 97.9^\circ$, mean $\text{O}(\text{H})_{\text{ax}}-\text{Cu}-\text{O}(\text{H})_{\text{eq}} =$

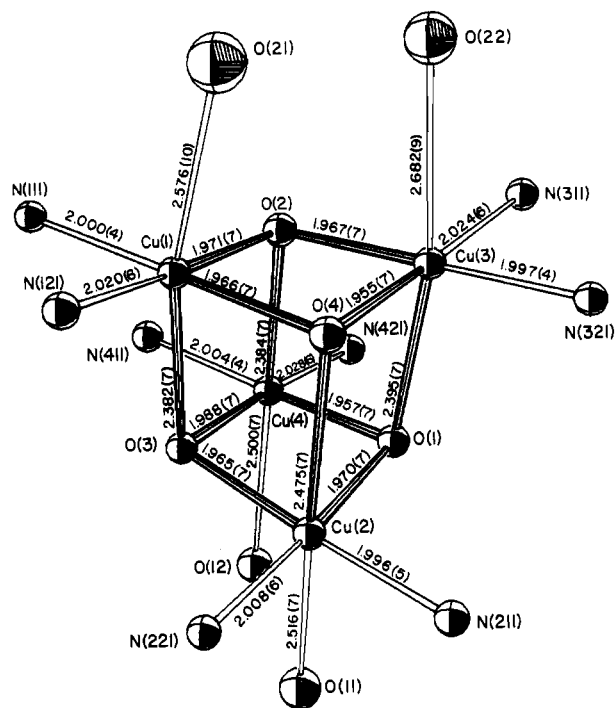


Figure 2. A portion of the $\text{Cu}_4(\text{OH})_4$ core, showing 50% probability spheres.

81.1°); (c) the angle between the axial ligands is significantly less than 180° (mean $\text{O}(\text{H})\text{-Cu-O}(\text{SO}) = 168.3^\circ$); and (d) the axial bond to a triflate oxygen atom is longer than a bond to an axial hydroxide oxygen atom.

The mean value for the O-Cu-O angles is 81.1°, while the average value for the Cu-O-Cu angles is 98.3°. Each face of the polyhedron is therefore a rhomb, but these rhombs are distinctly nonplanar, as shown by the weighted least-squares planes in Table VII. The diagonal planes defined by $\text{Cu}(n)$, $\text{Cu}(m)$, $\text{O}(n)$, $\text{O}(m)$ ($1 \leq n \leq 3$, and $n < m \leq 4$) are more nearly perfect, but only one of these six planes, that defined by $\text{Cu}(2)$, $\text{Cu}(3)$, $\text{O}(2)$, $\text{O}(3)$, is perfect within experimental error.

The D_{2d} symmetry of the core divides each group of angles and distances into two sets in the following manner: Cu-Cu (2 + 4), Cu-O (4 + 8); Cu-Cu-Cu , O-Cu-O , Cu-O-Cu (all 4 + 8). The expected subgrouping is resolvable except for the angles O-Cu-O and Cu-O-Cu (Tables IV and V). The two short Cu-Cu distances (mean value 2.970 Å) are found in the dimer planes (the horizontal faces in Figure 2). The four long Cu-Cu distances (mean value 3.337 Å) occur in the vertical faces, parallel to the $\bar{4}$ axis, and correspond to the interdimer copper-copper distances.

Within the tris(2-pyridyl)amine ligands, the mean value for the dihedral angle between the two coordinated pyridine rings is 47°. The coordination around the bridgehead nitrogen atom in each ligand is nearly planar, as can be readily seen in Figure 1. The bridging nitrogen atoms are each less than 0.07 Å out of the least-squares plane defined by the atoms $\text{C}(n16)$, $\text{C}(n26)$, $\text{C}(n36)$ ($1 \leq n \leq 4$), the carbon atoms of each ring bonded to the amine nitrogen atom (Table VIII). As a result of this planar coordination about the amine nitrogen atom, the third pyridine ring on each $\text{N}(\text{py})_3$ ligand is not in a position suitable for coordination to the Cu^{2+} ion (Figure 1). The conformation of the $\text{N}(\text{py})_3$ ligand is very similar to that observed in the complex $[\text{Cu}(\text{N}(\text{py})_3)_2(\text{CH}_3\text{CN})_2](\text{SO}_3\text{CF}_3)_2$.²⁴

Two triflate ions in each asymmetric unit are not connected with the cubane core. In these two anions the mean S-O distance of 1.417 Å appears to be smaller than the mean S-O distances of 1.430 (8) and 1.437 (21) Å observed in two other

Table IV. Selected Bond Distances (Å) in $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}$

Cation			
Cu...Cu			
Cu(1)-Cu(3)	2.967 (2)	mean	2.970
Cu(2)-Cu(4)	2.974 (2)		
Cu(1)-Cu(2)	3.320 (2)	Cu(3)-Cu(4)	3.279 (2)
Cu(1)-Cu(4)	3.328 (2)	mean	3.32 (4) ^a
Cu(2)-Cu(3)	3.371 (2)		
Cu-N			
Cu(1)-N(111)	2.000 (4)	Cu(3)-N(321)	1.997 (4)
Cu(1)-N(121)	2.020 (6)	Cu(4)-N(411)	2.004 (4)
Cu(2)-N(211)	1.996 (5)	Cu(4)-N(421)	2.028 (6)
Cu(2)-N(221)	2.008 (6)	mean	2.010 (6)
Cu(3)-N(311)	2.024 (6)		
Cu-O* ^b			
Cu(1)-O(21)	2.576 (10)	Cu(4)-O(12)	2.500 (7)
Cu(2)-O(11)	2.516 (7)	mean	2.57 (4)
Cu(3)-O(22)	2.682 (9)		
Cu-O			
Cu(1)-O(2)	1.971 (7)	Cu(2)-O(3)	1.965 (7)
Cu(1)-O(4)	1.966 (7)	Cu(4)-O(1)	1.957 (7)
Cu(3)-O(2)	1.967 (7)	Cu(4)-O(3)	1.988 (7)
Cu(3)-O(4)	1.955 (7)	mean	1.967 (7)
Cu(2)-O(1)	1.970 (7)		
Cu(1)-O(3)	2.382 (7)	Cu(4)-O(2)	2.384 (7)
Cu(2)-O(4)	2.475 (7)	mean	2.41 (2)
Cu(3)-O(1)	2.395 (7)		
Anions (Uncoordinated)			
S-O*			
S(3)-O(31)	1.431 (9)	S(4)-O(42)	1.407 (12)
S(3)-O(32)	1.425 (10)	S(4)-O(43)	1.410 (9)
S(3)-O(33)	1.416 (9)	mean	1.417 (10)
S(4)-O(41)	1.414 (12)		
S-C			
S(3)-C(31)	1.796 (14)	S(4)-C(41)	1.795 (14)
C-F			
C(31)-F(31)	1.338 (14)	C(41)-F(42)	1.333 (16)
C(31)-F(32)	1.333 (14)	C(41)-F(43)	1.337 (17)
C(31)-F(33)	1.347 (16)	mean	1.336 (15)
C(41)-F(41)	1.329 (17)		
Anions (Coordinated)			
S-O*			
S(1)-O(11)	1.440 (8)	S(1)-O(13)	1.422 (10)
S(1)-O(12)	1.442 (8)	mean	1.435 (11)
S(2)-O(21)	1.332 (11)	S(2)-O(23)	1.623 (16)
S(2)-O(22)	1.357 (10)	mean	1.437
S-C			
S(1)-C(11)	1.80 (1)	S(2)-C(21)	1.68 (2)
C-F			
C(11)-F(11)	1.33 (1)	C(11)-F(13)	1.30 (2)
C(11)-F(12)	1.35 (1)	mean	1.33 (3)
C(21)-F(21)	1.58 (2)	C(21)-F(23)	1.30 (2)
C(21)-F(22)	1.25 (2)	mean	1.38

^a If given, the value in parentheses is the standard deviation of a single observation, based on the larger of that estimated from the agreement among the averaged values or that estimated from the average standard deviation of a single observation from the inverse matrix. ^b Oxygen atoms from SO_3CF_3^- anions are denoted O*.

well-characterized triflate structures.^{24,40} The other distances and angles of these uncoordinated triflates agree well with the published values. As in the other triflates,^{24,40} the O-S-O and F-C-S angles are greater than 109°, while the F-C-F and

Table V. Selected Bond Angles (Deg) in $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4][\text{SO}_3\text{CF}_3]_2 \cdot \text{C}_3\text{H}_6\text{O}^a$

		Cation			
		Cu-O-Cu			
Cu(2)-O(1)-Cu(3)	100.7 (3)	Cu(1)-O(3)-Cu(4)	98.8 (3)	Cu(1)-O(2)-Cu(3)	97.8 (3)
Cu(3)-O(1)-Cu(4)	97.3 (3)	Cu(2)-O(4)-Cu(3)	98.4 (3)	Cu(2)-O(3)-Cu(4)	97.6 (3)
Cu(1)-O(2)-Cu(4)	99.2 (3)	Cu(1)-O(4)-Cu(2)	96.1 (3)	Cu(1)-O(4)-Cu(3)	98.4 (3)
Cu(3)-O(2)-Cu(4)	97.3 (3)	Cu(2)-O(1)-Cu(4)	98.4 (3)	mean	98.2
		O*-Cu-O			
O(21)-Cu(1)-O(3)	167.3 (3)	O(22)-Cu(3)-O(1)	169.7 (2)	mean	168.3
O(11)-Cu(2)-O(4)	167.5 (2)	O(12)-Cu(4)-O(2)	168.8 (2)		
O(21)-Cu(1)-O(2)	89.2 (3)	O(11)-Cu(2)-O(3)	93.4 (3)	O(12)-Cu(4)-O(1)	91.3 (2)
O(21)-Cu(1)-O(4)	87.8 (3)	O(22)-Cu(3)-O(2)	88.4 (3)	O(12)-Cu(4)-O(3)	89.6 (3)
O(11)-Cu(2)-O(1)	89.4 (3)	O(22)-Cu(3)-O(4)	94.6 (3)	mean	90.5
		O-Cu-O			
O(2)-Cu(1)-O(4)	81.0 (3)	O(3)-Cu(2)-O(4)	80.4 (2)	O(1)-Cu(4)-O(2)	82.1 (2)
O(2)-Cu(1)-O(3)	80.9 (2)	O(1)-Cu(3)-O(2)	81.6 (2)	O(1)-Cu(4)-O(3)	80.7 (3)
O(3)-Cu(1)-O(4)	82.8 (2)	O(1)-Cu(3)-O(4)	81.3 (2)	O(2)-Cu(4)-O(3)	80.5 (2)
O(1)-Cu(2)-O(3)	81.0 (3)	O(2)-Cu(3)-O(4)	81.4 (3)	mean	81.1
O(1)-Cu(2)-O(4)	79.0 (2)				
		N-Cu-N			
N(111)-Cu(1)-N(121)	85.4 (2)	N(311)-Cu(3)-N(321)	85.0 (2)	mean	85.1
N(211)-Cu(2)-N(221)	84.8 (2)	N(411)-Cu(4)-N(421)	85.2 (2)		
		Cu-Cu-Cu			
Cu(2)-Cu(1)-Cu(4)	53.15 (4)	Cu(2)-Cu(3)-Cu(4)	53.11 (4)	mean	53.06
Cu(1)-Cu(2)-Cu(3)	52.64 (4)	Cu(1)-Cu(4)-Cu(3)	53.36 (4)		
Cu(2)-Cu(1)-Cu(3)	64.56 (4)	Cu(3)-Cu(2)-Cu(4)	61.86 (4)	Cu(1)-Cu(4)-Cu(2)	63.28 (4)
Cu(3)-Cu(1)-Cu(4)	62.47 (4)	Cu(1)-Cu(3)-Cu(2)	62.79 (4)	Cu(2)-Cu(4)-Cu(3)	65.03 (4)
Cu(1)-Cu(2)-Cu(4)	63.57 (4)	Cu(1)-Cu(3)-Cu(4)	64.17 (4)	mean	63.47
		O*-Cu-N			
O(21)-Cu(1)-N(111)	93.5 (3)	O(11)-Cu(2)-N(221)	90.6 (2)	O(12)-Cu(4)-N(411)	92.1 (2)
O(21)-Cu(1)-N(121)	85.4 (3)	O(22)-Cu(3)-N(311)	84.6 (2)	O(12)-Cu(4)-N(421)	86.3 (2)
O(11)-Cu(2)-N(211)	90.1 (2)	O(22)-Cu(3)-N(321)	90.0 (2)	mean	89.1
		O-Cu-N			
O(3)-Cu(1)-N(121)	104.1 (2)	O(4)-Cu(2)-N(211)	100.7 (2)	O(2)-Cu(4)-N(411)	94.2 (2)
O(3)-Cu(1)-N(111)	95.6 (2)	O(1)-Cu(3)-N(311)	99.3 (2)	O(2)-Cu(4)-N(421)	103.5 (2)
O(4)-Cu(2)-N(221)	96.1 (2)	O(1)-Cu(3)-N(321)	90.0 (2)	mean	97.9
		Anions (Uncoordinated)			
		O-S-O			
O(31)-S(3)-O(32)	115.7 (5)	O(41)-S(4)-O(42)	114.6 (7)	O(42)-S(4)-O(43)	114.8 (6)
O(31)-S(3)-O(33)	114.2 (5)	O(41)-S(4)-O(43)	114.4 (7)	mean	114.8
O(32)-S(3)-O(33)	115.0 (6)				
		O-S-C			
O(31)-S(3)-C(31)	102.1 (6)	O(41)-S(4)-C(41)	103.4 (7)	O(43)-S(4)-C(41)	105.4 (6)
O(32)-S(3)-C(31)	104.4 (6)	O(42)-S(4)-C(41)	102.0 (7)	mean	103.4
O(33)-S(3)-C(31)	103.0 (6)				
		F-C-F			
F(31)-C(31)-F(32)	106.8 (10)	F(41)-C(41)-F(42)	106.5 (10)	F(42)-C(41)-F(43)	106.2 (12)
F(31)-C(31)-F(33)	106.5 (10)	F(41)-C(41)-F(43)	107.0 (11)	mean	106.4
F(32)-C(31)-F(33)	105.7 (10)				
		F-C-S			
F(31)-C(31)-S(3)	112.3 (9)	F(41)-C(41)-S(4)	113.5 (10)	F(43)-C(41)-S(4)	112.2 (9)
F(32)-C(31)-S(3)	113.3 (9)	F(42)-C(41)-S(4)	110.9 (10)	mean	112.3
F(33)-C(31)-S(3)	111.7 (9)				
		Anions (Coordinated)			
		O-S-O			
O(11)-S(1)-O(12)	114.5 (5)	O(12)-S(1)-O(13)	115.2 (5)	mean	114.8
O(11)-S(1)-O(13)	114.8 (5)				
		O-S-C			
O(11)-S(1)-C(11)	103.3 (5)	O(13)-S(1)-C(11)	104.6 (6)	mean	103.4
O(12)-S(1)-C(11)	102.2 (5)				
		F-C-F			
F(11)-C(11)-F(12)	106.7 (10)	F(12)-C(11)-F(13)	106.2 (10)	mean	107.1
F(11)-C(11)-F(13)	108.3 (9)				
		F-C-S			
F(11)-C(11)-S(1)	111.2 (8)	F(13)-C(11)-S(1)	112.9 (9)	mean	111.8
F(12)-C(11)-S(1)	111.2 (8)				

Table V (Continued)

		Anions (Coordinated) ^a			
		O-S-O			
O(21)-S(2)-O(22)	129.9 (6)	O(22)-S(2)-O(23)	98.9 (7)	mean	109.4
O(21)-S(2)-O(23)	99.4 (8)				
		O-S-C			
O(21)-S(2)-C(21)	114.8 (8)	O(23)-S(2)-C(21)	84.1 (8)	mean	104.0
O(22)-S(2)-C(21)	113.2 (8)				
		F-C-F			
F(21)-C(21)-F(22)	92.3 (12)	F(22)-C(21)-F(23)	114.5 (14)	mean	99.1
F(21)-C(21)-F(23)	90.5 (11)				
		F-C-S			
F(21)-C(21)-S(2)	94.9 (10)	F(23)-C(21)-S(2)	120.4 (13)	mean	113.3
F(22)-C(21)-S(2)	124.5 (13)				

^a This SO₃CF₃⁻ is nonrepresentative, as some of its component atoms show isotropic thermal parameters in excess of 10 Å² at -150 °C.

Table VI. Best Weighted Least-Squares Planes for the Equatorial Ligand Atoms around Copper

$Ax + By + Cz = D$ (monoclinic coordinates)									
plane no.	A	B	C	D	plane no.	A	B	C	D
1	4.602	11.529	-15.505	-3.232	3	-0.578	-12.761	11.206	1.723
2	3.294	13.037	-8.935	-3.265	4	3.126	11.581	-15.874	-5.471
deviations from planes, Å									
plane no.	Cu(<i>n</i>) ^a	O(1)	O(2)	O(3)	O(4)	N(<i>n</i> 11) ^a	N(<i>n</i> 21) ^a		
1	-0.005 (1)		0.103 (7)		-0.033 (7)	-0.020 (6)	-0.070 (6)		
2	-0.004 (1)	-0.006 (7)		0.064 (7)		0.048 (6)	-0.004 (6)		
3	0.003 (1)		-0.033 (7)		-0.012 (7)	-0.009 (6)	-0.023 (6)		
4	0.001 (1)	0.065 (7)		-0.084 (7)		0.050 (6)	-0.056 (6)		

^a *n* = plane number.

Table VII. Best Weighted Least-Squares Planes for Cu₄O₄ Core

$Ax + By + Cz = D$ (monoclinic coordinates)					$Ax + By + Cz = D$ (monoclinic coordinates)				
plane no.	A	B	C	D	plane no.	A	B	C	D
1	2.753	2.404	-12.739	-2.083	7	7.170	4.454	23.413	7.408
2	7.265	-5.980	-25.547	-9.523	8	15.148	8.131	-1.372	-0.310
3	17.130	0.466	7.771	1.066	9	7.436	3.490	-27.590	-8.573
4	3.102	12.531	-12.012	-4.422	10	17.437	-3.794	-12.027	-4.326
5	17.108	0.417	7.857	3.144	11	3.707	-12.478	-11.988	-4.502
6	7.451	-5.909	-25.536	-7.390	12	11.459	-7.460	14.031	3.725
deviations from plane, Å									
atom	1	2	3	4	5	6			
Cu(1)	0.005 (1)	-0.004 (1)	-0.004 (1)						
Cu(2)		-0.005 (1)		-0.005 (1)	0.004 (1)				
Cu(3)	0.005 (1)				0.003 (1)	0.006 (1)			
Cu(4)			-0.003 (1)	-0.006 (1)		0.005 (1)			
O(1)				0.195 (7)	-0.112 (7)	-0.178 (7)			
O(2)	-0.150 (7)		0.112 (7)			-0.177 (7)			
O(3)		0.172 (6)	0.106 (7)	0.189 (7)					
O(4)	-0.154 (7)	0.173 (7)			-0.109 (7)				
deviations from plane, Å									
	7	8	9	10	11	12			
Cu(1)	0.009 (1)	0.001 (1)	-0.001 (1)						
Cu(2)		-0.001 (1)		-0.001 (1)	0.000 (1)				
Cu(3)	-0.001 (1)				0.000 (1)	0.000 (1)			
Cu(4)			0.001 (1)	0.001 (1)		0.000 (1)			
O(1)	-0.367 (7)	0.032 (7)	-0.046 (7)						
O(2)		-0.032 (7)		-0.050 (7)	-0.003 (7)				
O(3)	-0.035 (7)				0.003 (7)	-0.011 (7)			
O(4)			0.046 (7)	0.048 (7)		0.012 (7)			

O-S-C angles are less than 109°.

Two triflate anions are coordinated as bidentate ligands to each cubane core. One of the coordinated triflates is clearly nonrepresentative; the thermal parameters observed for the atoms of this group are much larger than those expected to arise from data collected at -150 °C. Hence, this particular

triflate must be partially disordered. Within the ordered coordinated triflate, the two S-O bonds involving the oxygen atoms coordinated to the copper ions appear to be longer than the S-O bond involving the noncoordinated oxygen atom (1.441 (8) Å vs. 1.422 (10) Å). Also, the mean S-O distance appears to be longer than that observed for the uncoordinated

Table VIII. Best Weighted Least-Squares Planes for Atoms Coordinated to Amine Nitrogen Atoms

plane no.	$Ax + By + Cz = D$			
	A	B	C	D
1	14.165	-9.048	-5.752	-6.616
2	4.450	-1.709	26.926	12.088
3	16.670	1.793	-17.256	-1.703
4	7.732	9.270	16.003	1.314
deviations from plane, Å				
atom	1	2	3	4
N(n00) ^a	0.058 (9)	-0.032 (9)	-0.045 (10)	0.026 (9)
C(n16)	-0.008 (6)	0.006 (6)	0.006 (6)	-0.004 (6)
C(n26)	-0.008 (6)	0.005 (6)	0.007 (6)	-0.003 (6)
C(n36)	-0.008 (6)	0.005 (6)		-0.003 (6)
C(332) ^b			0.008 (7)	

^a In every case, n = plane no. ^b N(300) is bonded to C(332) rather than C(336).

anions. The C-F distances and the mean values for the angles remain largely unaffected by coordination to the metal, as judged by comparison with the free anions. As for coordinated and uncoordinated perchlorates, the mean bond distances and angles of the coordinated triflate are not outside the range of angles and distances also found in the uncoordinated triflates; the effects of coordination can only be seen in the significant inequality of S-O or Cl-O bond lengths within the same coordinated anion.

Triflate was originally chosen for this study because it is generally assumed to be a very weakly coordinating ligand. The bridging, bidentate coordination in the present case is completely unexpected and is the only such example known to us. Triflate coordination to a cupric ion has been previously proposed, on the basis of IR evidence, for $\text{Cu}(\text{N}(\text{py})_3)_2(\text{SO}_3\text{CF}_3)_2$.²⁴ In another structure, in which two cupric ions are coordinated to the ligand formed by the condensation of 1,2,4,6-tetrakis(aminomethyl)benzene with 4 mol of pyridine-2-carboxaldehyde,⁴¹ unidentate triflate ions are coordinated in the axial sites of each copper ion. A preliminary communication⁴² of the crystal structure of the complex $\text{Cu}(\text{SO}_3\text{CF}_3) \cdot \frac{1}{2}\text{C}_6\text{H}_6$ showed the triflate ions to be tridentate, each coordinated to three cuprous ions.

Comparison with Other M_4Y_4 Structures. The structure of the inner Cu_4O_4 core of **4** can be easily recognized as a member of the series $\text{X}_n\text{M}_4\text{Y}_4$ ($n > 4$), in which the tetranuclear cluster forms a cubane-like core of metal atoms bridged by ligands Y at alternate vertices of the cube. Many of the members of this series, with various metals, have been analyzed by X-ray diffraction methods. Some of these structural studies have been summarized in ref 43 and have been further analyzed to determine the symmetry of the M_4Y_4 core. The symmetries of the cubane-type cores are found to vary from T_d to lower than D_{2d} . Table IX lists the previously reported⁴³ results of symmetry analyses for two other M_4Y_4 cores as well as the results of the symmetry analysis of the Cu_4O_4 core of $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{N}(\text{py})_3)_4](\text{SO}_3\text{CF}_3)_2 \cdot \text{C}_3\text{H}_6\text{O}$ (**4**· Me_2CO).

Of particular interest in the present case are X-ray structure determinations of other Cu_4O_4 complexes.⁴⁴⁻⁴⁶ All of these

structures contain bridging alkoxide oxygen atoms and of ten^{46c,d,f,h,j,l-n,p} have bidentate coordination of (dialkylamino)ethanol to the copper atoms. The structure reported here is the only Cu_4O_4 example known to us in which hydroxide oxygen atoms act as the bridging ligands and is also unique in that aromatic, nitrogenous ligands are present in the cubane-like cluster. One Cu_6O_6 structure containing two triply bridging hydroxide ions has been reported previously.⁴⁷

Clusters of the Cu_4O_4 type have been classified into groups depending upon the arrangement of long and short Cu-O bonds.^{46j} Clusters of type I have four long Cu-O bonds "parallel" to each other, while in type II clusters two of the longest Cu-O bonds are "perpendicular" to the other two longest Cu-O bonds. In addition, type I clusters contain two short (mean 2.92 Å) and four long (mean 3.44 Å) intramolecular Cu-Cu separations, while type II clusters exhibit two long (mean 3.45 Å) and four intermediate (mean 3.18 Å) Cu-Cu distances. Clusters of an intermediate type also exist, in which Cu-Cu separations tend to become equal. In most Cu_4O_4 clusters of type I, the O-Cu-O and Cu-O-Cu angles are readily resolvable into two subgroups (4 + 8) in accord with D_{2d} symmetry, and the subgroups correspond to "in-plane" ("intradimer") and "out-of-plane" ("interdimer") angles. In the intermediate clusters where two subgroups (4 + 8) of O-Cu-O and Cu-O-Cu angles are found, the subgroups do not correspond to inter- and intradimer angles. In the intermediate clusters containing three subgroups of O-Cu-O and Cu-O-Cu angles, the four in-plane angles are intermediate in size between two groups of out-of-plane extremes, just as occurs in the type II clusters.

Table X compares bond distances and angles in Cu_4O_4 cores of type I and intermediate type clusters. The compound **4**· Me_2CO is clearly a type I cluster, with the four longest Cu-O bonds parallel between the dimers and with two short (mean 2.970 Å) and four long (mean 3.32(4) Å) Cu-Cu bonds. The O-Cu-O and Cu-O-Cu angles cannot be meaningfully divided into subsets, however, as can those in other Cu_4O_4 clusters of less than T_d symmetry. Even in $\text{Cu}_4(\text{CH}_3\text{O})_4(\text{C}_6\text{H}_4\text{Cl}_3\text{O})_4(\text{CH}_3\text{OH})_4$,^{46a} another example of a Cu_4O_4 complex in which the bridging oxygen atoms are not part of a chelate ring, subdivisions of these angles are resolvable. Thus, the present $\text{Cu}_4(\text{OH})_4$ structure is unique in that the two in-plane (intradimer) copper atoms are triply bridged because of the presence of the bidentate triflate anions. None of the anions in other Cu_4O_4 compounds has been found to form additional bridges between copper atoms in the core.

Although **4**· Me_2CO is the only reported Cu_4O_4 structure with bridging hydroxide ions rather than bridging alkoxide oxygen atoms, the distances and angles shown in Table X demonstrate that it is very similar to the other known Cu_4O_4

(41) Jason, M.; Sorrell, T.; Ibers, J. A.; Marks, T. J., manuscript in preparation.

(42) Dines, M. B.; Bird, P. H. *J. Chem. Soc., Chem. Commun.* **1973**, 12.

(43) Averill, B. A.; Herskovitz, T.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 3523-3534.

(44) Bertrand, J. A.; Kelley, J. A. *Inorg. Chim. Acta* **1970**, *4*, 203-209.

(45) (a) Mergehenn, R.; Merz, L.; Haase, W.; Allmann, R. *Acta Crystallogr., Sect. B* **1976**, *B32*, 505-510. (b) Haase, W. *Chem. Ber.* **1973**, *106*, 3132-3148. (c) Estes, E. D.; Hodgson, D. L. *Inorg. Chem.* **1975**, *14*, 334-338. (d) Mergehenn, R.; Haase, W.; Allmann, R. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1847-1853. (e) Matsumoto, N.; Ueda, I.; Nishida, Y.; Kida, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1308-1312.

(46) (a) Ablov, A. V.; Simonov, Y. S.; Matuzenko, G. S.; Dvorkin, A. A.; Yampol'skaya, M. A.; Malinovskii, T. I. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 1335-1338. (b) Nieminen, K. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 693-699. (c) Smolander, K.; Turpeinen, U.; Ahlgren, M. *Finn. Chem. Lett.* **1978**, 195-198. (d) Merz, L.; Haase, W. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2128-2133. (e) Nieminen, K.; Pajunen, A. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 493-499. (f) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1978**, 1594-1598. (g) Nieminen, K. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 375-381. (h) Ahlgren, M.; Hämäläinen, R.; Turpeinen, U. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2870-2874. (i) Mergehenn, R.; Haase, W. *Ibid.* **1977**, *B33*, 2734-2739. (j) Mergehenn, R.; Haase, W. *Ibid.* **1977**, *B33*, 1877-1882. (k) Pajunen, A.; Nieminen, K. *Finn. Chem. Lett.* **1975**, 67-70. (l) Mergehenn, R.; Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 1703-1709. (m) Turpeinen, U.; Hämäläinen, R.; Ahlgren, M.; Smolander, K. *Finn. Chem. Lett.* **1979**, 108-111. (n) Turpeinen, U.; Ahlgren, M.; Hämäläinen, R. *Acta Chem. Scand., Ser. A* **1979**, *A33*, 593-596. (o) Pajunen, A. *Acta Crystallogr., Sect. B* **1980**, *B35*, 1691-1693. (p) Turpeinen, U.; Hämäläinen, R.; Ahlgren, M. *Ibid.* **1979**, *B36*, 927-930.

(47) Ahlgren, M.; Turpeinen, U.; Smolander, K. *Acta Crystallogr., Sect. B* **1980**, *B36*, 1091-1095.

Table IX. Comparison of Core Structures of X₄M₄Y₄ Complexes^a

complex	M ₄ Y ₄ core	space group	Z ^b	imposed symmetry ^c	Q, ^d Å	σ ² , ^d	probable symmetry
[Cu ₄ (OH) ₄ (SO ₃ CF ₃) ₂ (N(py) ₃) ₄] ²⁺ e	Cu ₄ O ₄	P2 ₁ /c	4	none	0.021	7.06, 144, 220	D _{2d}
Cu ₄ (EIA) ₄ ^f	Cu ₄ O ₄	P4 ₂ /c	2	2	0.0062	0.1, 280, 280	D _{2d}
Me ₁₂ Pt ₄ (OH) ₄ ^g	Pt ₄ O ₄	I43m	2	43m	0	0, 0, 0	T _d (required)

^a Comparison of core structures of Cu₄(EIA)₄ and Me₁₂Pt₄(OH)₄ first given in ref 43. ^b Number of formula units in the cell. ^c Symmetry imposed by crystallographic symmetry elements. ^d Q and σ² fully defined in Appendix to ref 43. The three values of σ² refer to the variance in an observation of unit weight for each of the three possible orientations of the M₄Y₄ core. ^e This work. ^f EIA = MeC(O)CHC(Me)NCH₂-CH₂O; ref 44. ^g Reference 46m.

Table X. Comparison of Selected Mean Distances (Å) and Angles (Deg) in Cu₄O₄ Tetramers of Type I or of Intermediate Type^a

complex	Cu-Cu ^b	Cu-O	O-Cu-O	Cu-O-Cu
[Cu ₄ (OH) ₄ (SO ₃ CF ₃) ₂ (N(py) ₃) ₄] ²⁺ c	2.970, 3.32 (4)	1.967 (2), 2.41 (2) ^d	81.1	98.2
Cu ₄ [(CH ₃) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^e	2.916, 3.443	1.96, 2.47 ^d	78.3, 81.3 ^f	96.1, 100.4 ^g
Cu ₄ [(C ₂ H ₅) ₂ NC ₂ H ₄ O] ₄ Cl ₄ ^h	2.935, 3.434	1.965, 2.471 ^d	78.2, 81.0 ^f	96.6, 100.8 ^g
Cu ₄ (CH ₃) ₄ (C ₂ H ₅ Cl ₃ O) ₄ (CH ₃ OH) ₄ ⁱ	2.970, 3.170	1.95, 2.41 ^d	80.8, 86.8 ^g	92.6, 99.1 ^f
Cu ₄ [(n-C ₄ H ₉) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^j	3.052, 3.254	2.02, 2.24 ^d	78.5, 81.9 ^h	97.2, 101.7 ⁱ
Cu ₄ (EIA) ₄ ^m	3.006, 3.259	1.99, 2.32 ^d	81.5	97.9
Cu ₄ [(n-C ₃ H ₇) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ⁿ	3.168, 3.202	1.922, 2.154, 2.229 ^o	77.2, 80.1, 84.0 ^p	93.8, 99.2, 103.4 ^p
Cu ₄ [(C ₂ H ₅) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^q	3.193	1.936, 2.113, 2.243 ^o	76.5, 79.8, 83.5 ^p	94.2, 99.4, 104.0 ^p

^a Type I Cu₄O₄ complexes have four longest Cu-O bonds parallel. ^b Two short (in-plane), four long (out-of-plane). ^c This work. ^d Eight short (in-plane), four long (out-of-plane). ^e Reference 46j. ^f Eight small (out-of-plane), four large (in-plane). ^g Four small (in-plane), eight large (out-of-plane). ^h Reference 45b,c. ⁱ Reference 46a. ^j Reference 46i. ^k Four small, eight large; no correlation with in-plane or out-of-plane O-Cu-O angles. ^l Eight small, four large; no correlation with in-plane or out-of-plane Cu-O-Cu angles. ^m Reference 44; EIA = CH₃C(O)CHC(CH₃)NC₂H₄O. ⁿ Reference 46d. ^o Four out-of-plane bond lengths intermediate between two sets of four in-plane extremes. ^p Four in-plane angles intermediate between two sets of four out-of-plane extremes. ^q Reference 46f.

cubanes. As in the other complexes, the Cu-Cu distances in [Cu₄(OH)₄(SO₃CF₃)₂(N(py)₃)₄][SO₃CF₃]₂-C₃H₆O are greater than the range of 2.63–2.65 Å found in complexes⁴⁸ in which direct Cu-Cu bonding interactions have been postulated. The overall mean Cu-O bond length of 2.11 Å is within but at the low end of the 2.10–2.17 Å range found in most other known cubane-type Cu-O complexes.

Spectroscopic Properties of [Cu₄(OH)₄(SO₃CF₃)₂(N(py)₃)₄][SO₃CF₃]₂. As noted earlier, the low solubility of **4** prevented solution spectroscopic studies. It was, however, possible to obtain significant data from solid samples. In the electronic spectrum of **4** (Nujol mull) a broad shoulder is observed at ca. 600 nm and a strong band is observed at 318 nm. The absorption at 600 nm is consistent with a tetragonally distorted octahedral Cu(II) complex,⁴⁹ while the higher energy transition is likely py(π) → Cu(II) charge transfer in origin.^{24,50}

Infrared spectral data for **4** are given in the Experimental Section. The O-H stretching vibration occurs at 3470 cm⁻¹, and the displacement of this mode when **4** is prepared with ¹⁸O₂ (vide infra) will be seen to be of mechanistic significance. Copper-oxygen vibrations in dimeric hydroxyl-bridged Cu(II) complexes have usually been found between 480 and 515 cm⁻¹.³⁹ No shifts larger than 2 cm⁻¹ are observed for the absorptions in the 500-cm⁻¹ region of the infrared spectrum of **4** when ¹⁸O is substituted for ¹⁶O. However, a lower energy transition is observed to shift from 358 to 347 cm⁻¹ when the spectra of Cu₄(¹⁶OH)₄ and Cu₄(¹⁸OH)₄ are compared. If this band is indeed the Cu-O stretch, the lower frequency may be readily rationalized since the Cu-O bonds in **4** are significantly longer than the Cu-O bonds in most bis(μ-hydroxo)dicopper(II) complexes.³⁹

As in the case of the cupric complex Cu(N(py)₃)₂(SO₃CF₃)₂,²⁴ the appearance of at least eight bands in the

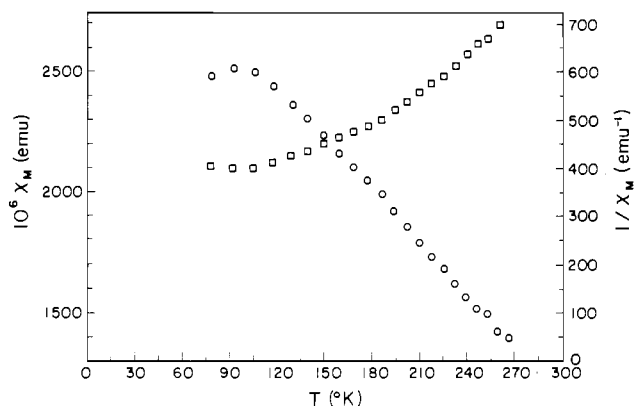


Figure 3. Plot of χ_M (molar magnetic susceptibility per copper ion) vs. T (circles) and $1/\chi_M$ vs. T (squares) for the complex [Cu₄(OH)₄(SO₃CF₃)₂(N(py)₃)₄][SO₃CF₃]₂-C₃H₆O.

1400–1610-cm⁻¹ region of the infrared spectrum of **4** indicates nonequivalence of the three pyridine rings of N(py)₃, consistent with the bidentate coordination of the ligand. The infrared spectrum of the cuprous complex **3** (see Experimental Section for data) indicates that N(py)₃ is acting as a bidentate ligand in that complex as well.

The spectrum of **4** in the 1000–1300-cm⁻¹ region has been previously reported by us and has been interpreted in terms of both coordinated and uncoordinated triflate anions.²⁴ The infrared spectrum of **3** definitely indicates coordination of the triflate anion since the asymmetric S-O stretch has split upon coordination to the metal, one component appearing below 1250 cm⁻¹, at 1241 cm⁻¹.

Magnetic Properties of [Cu₄(OH)₄(SO₃CF₃)₂(N(py)₃)₄][SO₃CF₃]₂-C₃H₆O. Static magnetic susceptibility data for **4**-Me₂CO down to 77 K are shown in Figure 3. It can be seen that the susceptibility is antiferromagnetic ($S = 0$ ground state), as has been observed for a number of other (but not all) Cu₄O₄ clusters.^{45f,51–53} However, it is noteworthy that

(48) (a) Hanic, F.; Stempelova, D.; Hanicova, K. *Acta Crystallogr.* **1964**, *17*, 633–639. (b) Van Niekerk, J. N.; Schoening, F. R. L. *Ibid.* **1953**, *6*, 227–232. (c) Barclay, G. A.; Kennard, C. H. L. *J. Chem. Soc.* **1961**, 5244–5251.

(49) Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196–1199.

(50) Hecht, H. G.; Kerns, R. C. *J. Inorg. Nucl. Chem.* **1969**, *31*, 1983–1992.

(51) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 875–879 and references therein.

Table XI. Comparison of Magnetic Data for Cu₄O₄ Complexes of Cubane-like Structure

complex	type ^a	μ_{eff} , μ_B	comments
[Cu ₄ (OH) ₄ (SO ₃ CF ₃) ₂ (N(py) ₃) ₄][SO ₃ CF ₃] ₂ ·C ₃ H ₆ O ^b	I	1.81	antiferromagnetic
Cu ₄ [(C ₂ H ₅) ₂ NC ₂ H ₄ O] ₄ Cl ₄ ^c	I	1.66	antiferromagnetic
α -Cu ₄ (EIA) ₄ ^d	intermed	1.87	antiferromagnetic
β -Cu ₄ (EIA) ₄ ·2C ₆ H ₆ ^e	II	1.87	ferromagnetic
Cu ₄ [(<i>n</i> -C ₄ H ₉) ₂ NC ₂ H ₄ O] ₄ Cl ₄ ^f	II	1.95	ferromagnetic
γ -Cu ₄ [(<i>n</i> -C ₄ H ₉) ₂ NC ₂ H ₄ O] ₄ Br ₄ ^f	II	1.90	ferromagnetic
β -Cu ₄ (EIA) ₄ ^g		1.85	ferromagnetic; structure unknown
Cu ₄ [(<i>n</i> -C ₃ H ₇) ₂ NC ₂ H ₄ O] ₄ Cl ₄ ^h	intermed	1.85	low-temp magnetic data not reported
Cu ₄ (CH ₃ O) ₄ (C ₆ H ₅ ClO) ₄ (CH ₃ OH) ₄ ⁱ	I	1.46	antiferromagnetic
Cu ₄ [(<i>n</i> -C ₃ H ₇) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^j	intermed	1.89	antiferromagnetic
Cu ₄ [(C ₂ H ₅) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^k	intermed	1.90	antiferromagnetic
Cu ₄ [(CH ₃) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^l	I	1.8	antiferromagnetic
Cu ₄ [(<i>n</i> -C ₄ H ₉) ₂ NC ₂ H ₄ O] ₄ (NCO) ₄ ^m	intermed	1.8	antiferromagnetic
Cu ₄ [(<i>n</i> -C ₄ H ₉) ₂ NC ₂ H ₄ O] ₄ (NCS) ₄ ^m	intermed	1.8	antiferromagnetic
Cu ₄ [(C ₂ H ₅) ₂ NC ₂ H ₄ O] ₄ Br ₄ ·4CCl ₄ ⁿ	II	2.1	ferromagnetic

^a Structural classification based on disposition of long and short Cu–O bonds; type I has four long Cu–O bonds parallel; type II has two of the longest Cu–O bonds perpendicular to the two other longest Cu–O bonds. ^b This work. ^c Structure described in ref 45b,c; magnetic data from ref 53. ^d Structure described in ref 44; magnetic data from ref 53. ^e Structure described in ref 45a; magnetic data from ref 53. ^f Structure described in ref 45d; magnetic data from ref 52. ^g Structure unknown; magnetic data from ref 53. ^h Reference 45e. ⁱ Structure and magnetic data described in ref 46a. ^j Structure and magnetic data described in ref 46d. ^k Structure and magnetic data described in ref 46f. ^l Structure described in ref 46j. ^m Structure described in ref 51. ⁿ Structure described in ref 46i. Magnetic data from ref 51. ⁿ Structure and magnetic data discussed in ref 46l.

T_N (the temperature at which a maximum in χ_M occurs) for 4·Me₂CO is at the extreme high end of the range found for such types of compounds. In the most general case, the description of the magnetic behavior of a cubane-like Cu₄O₄ cluster requires six exchange coupling constants (J_{12} , J_{23} , J_{34} , J_{13} , J_{14} , J_{24}). From the metrical data for 4·Me₂CO and the observation in bis(μ -hydroxo)copper(II) dimers that there is a linear correlation between J and Cu–Cu distances,⁵⁴ it is probable that $J_{13} \approx J_{24} \neq J_{12} \approx J_{14} \neq J_{23} \approx J_{34}$ in the present case. Although a detailed analysis⁵¹ of the magnetic data was not carried out for 4, a qualitative understanding of the behavior follows readily from the structural information.

It has been observed experimentally^{54–56} that there is a linear correlation between the Cu–O–Cu bridge angle and the value of J in bis(μ -hydroxo)copper(II) dimers. When the Cu–O–Cu angles are greater than 97.6°, J is negative (antiferromagnetic interaction); for angles less than 97.6°, J is positive (ferromagnetic interaction); when the bridge angle is exactly 97.6°, J is expected to be zero. In 4·Me₂CO every Cu–O–Cu angle is greater than 97° and all but two are greater than or equal to 97.6°. Thus, J_{13} , J_{14} , J_{23} , and J_{24} are expected to be negative (antiferromagnetic), J_{12} is expected to be approximately zero (on the basis of the mean Cu–O–Cu angle for the Cu(1), Cu(2) face), and J_{34} is expected to be positive (ferromagnetic). The overall result is expected to be antiferromagnetic behavior for the cluster, as observed. Empirical correlations have also been observed between the value of Cu–O–Cu bridge angles and the type of magnetic interaction in alkoxide-bridged Cu₄O₄ complexes of the cubane type.^{46l} In these cases the transition angle is found to be 95.7°. On the basis of a transition angle of 95.7°, 4·Me₂CO is again expected to be antiferromagnetic because all Cu–O–Cu angles are greater than 97°. In each of the two examples where a bis(μ -hydroxo)copper(II) dimer is also bridged by bidentate perchlorate anions,⁵⁴ the sign of the exchange parameter is as predicted from the Cu–O–Cu angle, but the magnitude is considerably larger. If a similar effect is operative in the present case, then J_{13} and J_{24} would be larger (more negative) than normal. This may well explain the high T_N temperature observed for 4·Me₂CO.

In Table XI are compiled magnetic data for a number of cubane-like Cu₄O₄ complexes. It can be seen that each of the tetramers exhibits a room-temperature magnetic moment that is nearly normal for a mononuclear Cu(II) complex. Moreover, as far as the data extend, complexes of pure type I are antiferromagnetic, while complexes of pure type II are ferromagnetic. Examination of the structural data for these compounds shows that each of the pure type II complexes exhibits a very large difference (7–15°) between the mean of the four small Cu–O–Cu angles and the mean of the eight large Cu–O–Cu angles. For example, the type II complexes Cu₄[(*n*-C₄H₉)₂N(CH₂)₂O]₄Cl₄ and Cu₄[(*n*-C₄H₉)₂N(CH₂)₂O]₄Br₄ have four small Cu–O–Cu angles with mean values of 90.8 and 90.1°, respectively; the eight large Cu–O–Cu angles have mean values of 104.0 and 105.0°. In pure type I complexes, these differences are far smaller (Table XI) and, considering the sensitivity of J to such factors, this is reflected in the magnetic behavior. In the alkoxide-bridged Cu₄O₄ systems, it has also been observed that the in-plane (intradimer) exchange interactions are always antiferromagnetic, while the out-of-plane interactions are always ferromagnetic.^{46,f,l} The magnetic behavior of type I systems, including 4·Me₂CO, is thus understandable because the long out-of-plane Cu–O distances ensure that antiferromagnetic coupling predominates.

Mechanisms for the Formation of [Cu(OH)₄(SO₃CF₃)₂(N(py)₃)₄](SO₃CF₃)₂. Perhaps the most interesting question in Cu(N(py)₃)(SO₃CF₃) (3) oxygenation chemistry is the source of the hydroxyl functionalities that are incorporated into the Cu₄O₄ cluster of compound 4. Two isotopic labeling experiments were conducted to investigate this aspect of the reaction mechanism. Oxygenation of 3 with ¹⁸O₂ was carried out in several solvents. In each case, the ν_{OH} transition in the infrared spectrum was observed to shift (entirely) from 3470 to 3452 cm⁻¹. From analysis of the infrared intensities, we estimate that $\geq 90\%$ of the oxygen atoms in the OH groups are derived from the added O₂. In a second experiment to investigate the source of the hydroxyl protons, compound 3 was oxygenated in dry CD₂Cl₂. In this case, the intensity of ν_{OH} relative to the other infrared transitions in 4 was unaltered. There was also no evidence for a ν_{OD} transition, calculated to lie in the ca. 2470-cm⁻¹ region. From these observations we conclude that the predominant source of hydroxyl protons is not the solvent but rather an N(py)₃ ligand. Such a process has precedent in the oxygenation chemistry of the copper(I) carbonyl of 1,3-bis((4-methyl-2-pyridyl)imino)isoindoline

(52) Merz, L.; Haase, W.; Keller, G. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 305–311.

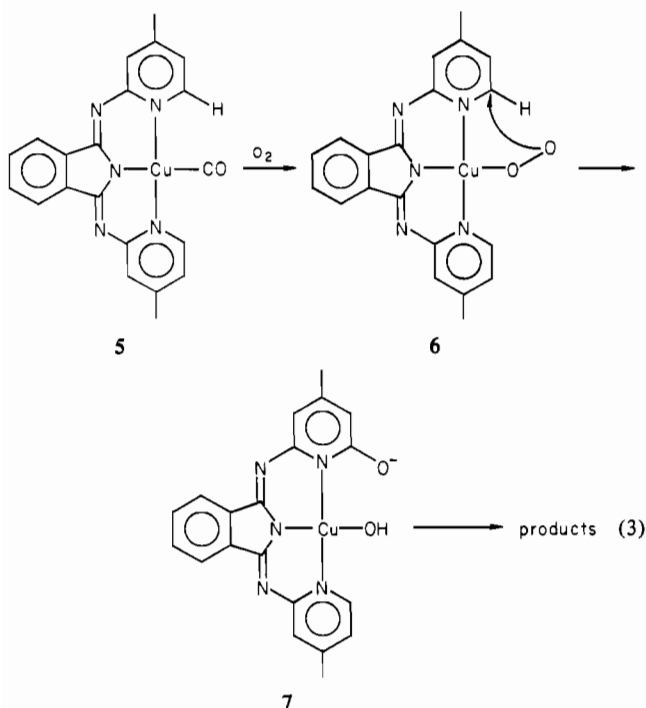
(53) Merz, L.; Haase, W. *Z. Naturforsch., A* **1976**, *31A*, 177–182.

(54) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107–2110.

(55) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173–241.

(56) Hodgson, D. J. *Inorg. Chem.* **1976**, *15*, 3174–3175.

(5).^{20a} In benzene solution, oxygenation results, via a presumed oxygen complex 6, in a pyridyl-hydroxylated, cupric hydroxo complex 7 (eq 3). That the yield of 4 is always considerably



less than quantitative in the oxygenation of 3 is in accord with this mechanism. Presumably hydroxylated N(py)₃ species are among the other noncrystalline oxygenation products of 3. Whether the hydrogen atom abstraction⁷ by the intermediate copper-oxygen complex is intra- or intermolecular has not been determined in the present case.

Conclusions

This investigation sheds new light both upon the oxygenation chemistry of copper(I)-nitrogen heterocyclic complexes in aprotic media and upon the unexpected binding characteristics of ligands that were thought to be reasonably well understood. Thus, oxygenation of mononuclear cuprous complexes can result, via the hydroxylation of aromatic heterocyclic ligands, in the assembly of rather complex, cubane-like tetranuclear μ_3 -hydroxo Cu(II) clusters. Although tris(2-pyridyl)amine has been generally assumed to be a tridentate ligand,²⁴ this study represents the second ([Cu(N(py)₃)₂(CH₃CN)₂]-[SO₃CF₃]₂) is the first²⁴) unambiguous demonstration that it can function as a bidentate ligand (in this case to a metal atom cluster). The trifluoromethanesulfonate anion has generally been assumed to be a noncoordinating anion. The present results further demonstrate²⁴ not only that it can coordinate to a relatively saturated Cu(II) ion (in preference to the third pyridyl ligand of N(py)₃) but also that it can bridge the face of an M₄O₄ cluster in a bidentate fashion.

Acknowledgments. We thank the National Institutes of Health (J.A.I., Grant HL 13157), the National Science Foundation (T.J.M., Grant CHE8009060), and the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR 79-23573) for generous support of this research. P.L.D. thanks the American Association of University Women for a Susan B. Anthony Dissertation Year Fellowship. We thank Mr. J. Anderson for assistance with the magnetic susceptibility measurements.

Registry No. 3, 79991-91-6; 4, 82112-73-0; 4-Me₂CO, 82094-66-4; [Cu(SO₃CF₃)]₂(C₆H₆), 42152-46-5; Cu(SO₃CF₃)(N(py)₃)(H₂O), 82094-67-5; O₂, 7782-44-7.

Supplementary Material Available: Structure amplitude table (Table III) for [Cu₄(OH)₄(SO₃CF₃)₂[N(py)₃]₄][SO₃CF₃]₂·C₃H₆O (30 pages). Ordering information is given on any current masthead page.