

Heterometallic Yttrium-Copper Complexes.
Synthesis and Crystal Structure of
 $Y_2Cu_8(\mu-PyO)_2(\mu-Cl)_2(\mu_4-O)_2(NO_3)_4(H_2O)_2 \cdot 2H_2O$
 (PyO⁻ = Deprotonated 2-Hydroxypyridine)

There is a growing interest in the production of high-temperature superconductors by chemical processes such as the sol-gel process using soluble covalent molecular precursors. Compared with the conventional method, the chemical method allows for more precise control of the composition and the homogeneous phase of the product.¹ Recent studies have also shown that it is possible to fabricate the high T_c superconductors into useful forms such as films, wires, and fibers by chemical sol-gel processes.^{1c} However, the application of this method is limited by the availability of precursor compounds and the lack of understanding of the solution chemistry in the process. Some recent studies have suggested that heterometallic species may be important intermediates in the chemical sol-gel processes. A tetranuclear Cu_2Ba_2 compound has been isolated² recently from a precursor solution of the 1-2-3 ($YBa_2Cu_3O_{7-x}$) superconductor. We are particularly interested in heterometallic complexes containing yttrium, lanthanides, and copper atoms since these compounds not only may model the intermediate species for high T_c superconductors but also may find direct use as precursors for the preparation of superconductors. We report here the synthesis and structural determination of a novel Y_2Cu_8 compound.

The reaction of $Y(NO_3)_3 \cdot 4H_2O$ (40 mg), $Cu(OCH_3)_2$ (58 mg) and 2-hydroxypyridine (70 mg) in a ratio of 1:4:6 ratio in the solvent (15 mL) of CH_2Cl_2 or THF at 22 °C yielded a clear green solution. After a few hours a microcrystalline green solid formed and precipitated from the solution as a major product, **2** (about 50% yield). This solid is insoluble in common organic solvents, such as CH_2Cl_2 , THF, and ethanol. The recrystallization of this material was, therefore, unsuccessful. After the separation of this solid from the solution dark green crystals with rectangular shape were obtained as a minor product, **1** (about 30% yield). The result was reproducible if the same starting materials were used.³ **1** is insoluble in CH_2Cl_2 , THF, and ethanol. The molecular structure of this minor product was determined by a single-crystal X-ray diffraction analysis.⁴

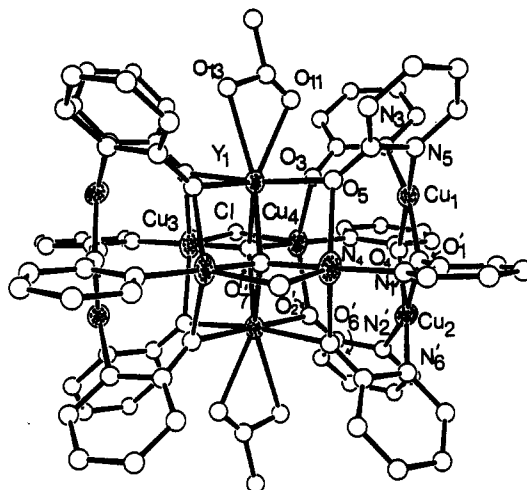


Figure 1. ORTEP diagram of **1** with labeling scheme. Carbon atoms and nitrate nitrogen atoms are not labeled. The H_2O and NO_3^- ligands coordinated to copper atoms are omitted for clarity. Selected bond distances and angles: Y(1)-O(2) = 2.30 (2), Y(1)-O(3) = 2.29 (2), Y(1)-O(5) = 2.28 (2), Y(1)-O(6) = 2.29 (2), Y(1)-O(7) = 2.30 (2), Y(1)-O(7') = 2.26 (3), Y(1)-O(11) = 2.49 (4), Y(1)-O(13) = 2.44 (4), Cu(1)-O(1) = 1.98 (2), Cu(1)-O(4) = 1.97 (2), Cu(1)-O(14) = 2.33 (2), Cu(1)-N(3) = 1.91 (2), Cu(1)-N(5) = 1.94 (2), Cu(2)-O(1) = 1.96 (2), Cu(2)-O(4) = 1.95 (2), Cu(2)-O(8) = 2.35 (3), Cu(2)-N(2) = 1.94 (2), Cu(2)-N(6) = 1.91 (2), Cu(3)-Cl = 2.37 (1), Cu(4)-Cl = 2.47 (1), Cu(3)-O(5) = 2.17 (2), Cu(3)-O(6) = 2.23 (2), Cu(3)-O(5') = 2.17 (2), Cu(3)-O(6') = 2.23 (2), Cu(3)-O(7) = 1.85 (2), Cu(3)-N(1) = 1.92 (2), Cu(4)-N(4) = 1.95 (2), Cu(4)-O(2) = 2.08 (2), Cu(4)-O(3) = 2.08 (2), Cu(4)-O(7) = 1.87 (2) Å; O(2)-Y(1)-O(3) = 178.0 (8), O(5)-Y(1)-O(6) = 174.1 (8), O(7)-Y(1)-O(7') = 68 (1), Y(1)-O(7)-Y(1') = 112 (1), O(11)-Y(1)-O(13) = 45 (1), O(7)-Cu(3)-N(1) = 171 (1), O(7)-Cu(4)-N(4) = 174 (1), N(3)-Cu(1)-O(1) = 164 (1), N(6)-Cu(2)-O(4) = 167.1 (9), Y(1)-O(3)-Cu(4) = 100.0 (9), Y(1)-O(6)-Cu(3) = 98.3 (8), Cu(3)-Cl-Cu(4) = 77.5 (4), Cu(3)-O(7)-Cu(4) = 109 (1), Cu(1)-O(1)-Cu(2) = 105 (1), Cu(1)-O(4)-Cu(2) = 106 (1), Cl-Cu(3)-N(1) = 100.2 (8), Cl-Cu(4)-N(4) = 100.1 (7), Y(1)-O(2)-Cu(4) = 99.0 (9), Y(1)-O(5)-Cu(3) = 99.3 (8)°.

Compound **1** was found to have the composition $Y_2Cu_8(\mu-PyO)_2(\mu_4-O)_2(\mu-Cl)_2(NO_3)_4(H_2O)_2 \cdot 2H_2O$ (PyO⁻ = deprotonated 2-hydroxypyridine). The crystal structure and selected bond distances and angles are given in Figure 1. The molecule has an approximate C_{2h} symmetry. Half of the molecule is related to the other half by an operation of a center of symmetry. There are two distinct groups of dicopper units. One group consists of Cu(1), Cu(2), Cu(1'), and Cu(2'). In this group, Cu(1) and Cu(2) or Cu(1') and Cu(2') are bridged by two oxygen atoms on the PyO⁻ ligand. Each copper atom is also coordinated by two nitrogen atoms on the pyridine ring. In addition, Cu(1) and Cu(2) (or Cu(1') and Cu(2')) are weakly bonded by one water molecule, Cu(1)-O(14) = 2.33 (2) Å, and an oxygen atom on the nitrate ligand, Cu(2)-O(8) = 2.35 (3) Å, respectively. As a result, the copper atoms in this group have a square-pyramidal geometry. The separation of copper atoms in the dimeric unit, Cu(1)-Cu(2) = 3.138 (7) Å, is similar to those in other known dimeric copper compounds bridged by oxygen atoms.^{5a-c} The other dimeric copper group consists of Cu(3), Cu(4), Cu(3'), and Cu(4'). In this group, Cu(3) and Cu(4) or Cu(3') and Cu(4') are bridged by an oxide ligand and a chloride ion with a Cu(3)-Cu(4) separation of 3.029 (7) Å. The unexpected chloride was found to come from the starting material $Cu(OCH_3)_2$ containing chloride impurity.³ In this unit, each copper atom is also coordinated by two oxygen atoms and a nitrogen atom of the PyO⁻ ligand. The geometry around the copper atom is a distorted trigonal bipyramid. This coordination geometry is similar to those in the class of

- (1) (a) *Ceramic Superconductors*; Yan, M. F., Ed., American Ceramic Society: Westerville, OH, 1988. (b) *Chemistry of High Temperature Superconductors*; Nelson, D. L., Whittingham, N. S., and George, T. F., Eds., ACS Symposium Series 351; American Chemical Society: Washington, DC, 1987. (c) Ulrich, D. R. *Chem. Eng. News* January 1, 1990, (Jan 1) 28.
- (2) Sauer, N. N.; Garcia, E.; Salazar, K. V.; Ryan, R. R.; Martin, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 1524.
- (3) The $Cu(OCH_3)_2$ compound was purchased from the Strem Chemical Co. Elemental analysis indicated it contains 3.36% chlorine. We were told that due to technical problems it is difficult to keep the chlorine content in this compound below 1%. The amount of chlorine content in this particular material is sufficient to produce **1** in more than 35% yield. Elemental analysis for **1** was unsuccessful due to the contamination of the sample by the cocrystallized microcrystalline compound **2**.
- (4) Crystal data: $C_{60}H_{56}Y_2Cu_8Cl_2O_{30}N_{16}$, $M_r = 2239.3$, monoclinic, space group $C2/c$, $a = 21.932$ (5) Å, $b = 23.763$ (7) Å, $c = 18.683$ (6) Å, $\beta = 93.47$ (2)°, $V = 9719$ (5) Å³, $Z = 4$, $D_{\text{calc}} = 1.53$ g cm⁻³. Data were collected on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Although the crystal of **1** had a nearly perfect appearance and reasonable size, the intensities of most of the reflections were weak. In addition, due to defect problems, the X-ray tube was operating at low intensity (50 kV, 25 mA). As a result, out of 8038 unique reflections collected, only 1971 reflections are with the intensity greater than 3σ . The structure solution and refinements were carried out by using the TEXSAN software program package on a VAX workstation, Model 3520. The structure was solved by direct methods (MITHRIL). Metal and chlorine atoms were refined anisotropically. Convergence to final R values of $R = 0.087$ and $R_w = 0.103$ was achieved by using 1971 reflections [$F^2 \geq 3\sigma(F^2)$] and 255 parameters. The crystals of **1** appeared to contain solvent molecules, possibly CH_3OH , as evidenced by the rapid collapse of the crystals upon isolation from the solution. However, due to the limited numbers of reflections we were unable to confirm it by the X-ray diffraction analysis. This could also account for the high R factors. Bond distances, angles, final positional and thermal parameters, observed and calculated structure factors, and crystallographic experimental details can be found in the supplementary material.

- (5) (a) Andrew, J. E.; Blake, A. B. *J. Chem. Soc., Dalton Trans.* **1973**, 1102. (b) Estes, E. D.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 334. (c) Hasse, W. *Chem. Ber.* **1973**, *106*, 3132. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988.

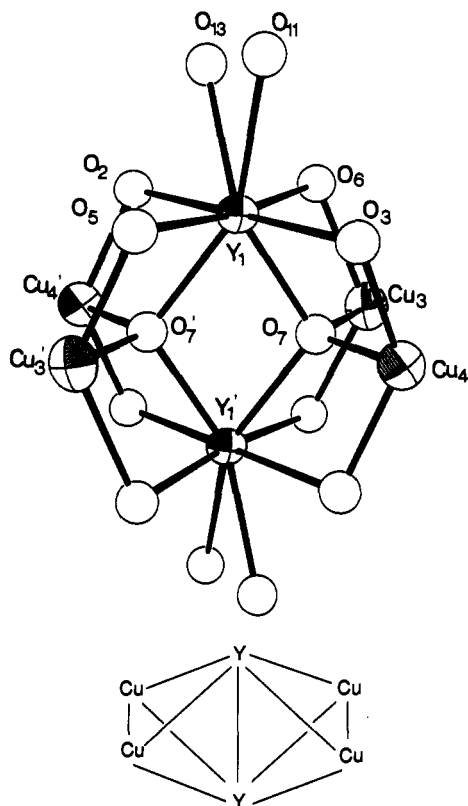


Figure 2. (a) Top: ORTEP diagram of the central core structure of Y_2Cu_4 . (b) Bottom: Diagram showing the arrangement of metal atoms in the central core.

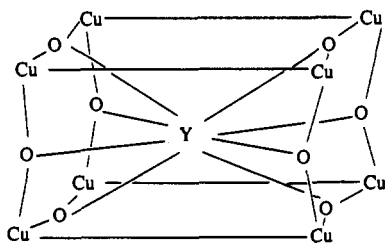
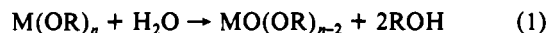


Figure 3. Diagram showing the bonding environment of Y and Cu atoms in the 1-2-3 superconductor.

$Cu_4OCl_6L_4$ ($L = OPEt_3, Py, NH_3$) molecules.^{5d} This dicopper unit is perpendicular to the other dicopper unit.

The most important feature in this molecule is the central core unit of Y_2Cu_4 . In this unit, there are two oxide ligands, each of which bridges two yttrium atoms and two copper atoms. The $Y(1)-Y(1')$ separation is 3.785 (8) Å. The separations of yttrium atoms bridged by oxygen atoms in previous reported homonuclear yttrium compounds span a considerable range, 3.3–4.0 Å.^{6,11} The yttrium atoms are also bridged to the copper atoms through the oxygen atoms on the PyO^- ligands. In addition, a nitrate ligand is coordinated to the yttrium atom. As a result, the yttrium atom is surrounded by eight oxygen atoms. If the nitrate coordinated to the yttrium atom was replaced by another unit of Cu_4O_2 , the

environment of the yttrium and the copper atoms in the central core of this molecule would remarkably resemble that found in the oxygen-deficient perovskite structure⁷ of the $YBa_2Cu_3O_{7-x}$ superconductor as shown in Figures 2 and 3. As found in the structure of the 1-2-3 superconductor, the four copper atoms and the two oxide ligands are approximately in the same plane with the maximum deviation (± 0.010 (5) Å) of $Cu(3)$ and $Cu(3')$ from the plane. The $Cu(3)-O(7)-Cu(4)$ angle, 109 (1)°, is, however, much smaller than that in $YBa_2Cu_3O_{7-x}$ (about 165°), apparently caused by the additional chloride ligand. The four oxygen atoms $O(2)$, $O(3)$, $O(5)$, and $O(6)$ are approximately in the same plane with the $Y(1)$ atom and coordinate to $Y(1)$ in a square-planar fashion: $O(2)-Y(1)-O(3) = 178.0$ (8)°; $O(5)-Y(1)-O(6) = 174.1$ (8)°. Within the Y_2Cu_4 unit the $Y-Cu$ separations are $Y(1)-Cu(3) = 3.422$ (6) Å, $Y(1)-Cu(3') = 3.392$ (7) Å, $Y(1)-Cu(4) = 3.353$ (6) Å, and $Y(1)-Cu(4') = 3.334$ (7) Å. The distance $Cu(3)-Cu(4')$ is very long, 4.74 Å. Therefore, the geometry of this Y_2Cu_4 unit could be best described as two tetrahedra sharing the common edge $Y(1)-Y(1')$ (Figure 2b). Although there are a few recent reports describing bimetallic Ln-Cu compounds in which the Ln and Cu atoms are bridged either by a hydroxy ligand^{8a} or a PyO^- ligand,^{8b} to our knowledge, bimetallic Ln-Cu or Y-Cu compounds with oxide bridges are previously unknown. In fact, the Y_2Cu_8 compound described here is the first example of bimetallic Y-Cu compounds. The formation of oxide ligands in this molecule is not unexpected. There have been several reports describing the formation of oxide ligands in the yttrium-alkoxide system.⁹ It has been suggested¹⁰ by Caulton and Hubert-Pfalzgraf that a hydrolysis process (eq 1) might account for the formation of the O^{2-} ligand.



Although the major product **2** has not been fully characterized, it appears to have the composition¹¹ of $Y_2Cu_8(PyO)_4(O)_2(NO_3)_4(H_2O)_4$, based on the result of elemental analysis. Both compounds **1** and **2** dissolve readily in water and yield green solutions, which undergo rapid hydrolysis and produce a light blue powder, presumably a mixture of metal oxides and hydroxides. The further characterization of compound **2** and the hydrolysis process is underway. The syntheses of bimetallic complexes with different ratios of yttrium and copper atoms and trimetallic compounds containing barium, yttrium (lanthanides), and copper atoms are in progress. Efforts have also been taken to study the magnetic interactions of multiple paramagnetic copper(II) centers in this system.

Acknowledgment. I thank the University of Windsor for supporting this research.

Supplementary Material Available: Details of the X-ray diffraction analysis, listings of atomic coordinates, crystallographic data, thermal parameters, bond lengths, and bond angles, and an ORTEP diagram for the entire molecule (16 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

Department of Chemistry and Biochemistry
University of Windsor
Windsor, Ontario, N9B 3P4 Canada

Suning Wang

Received December 4, 1990

- (6) (a) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Inorg. Chem.* **1990**, *29*, 2883. (b) Poncelet, O.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1990**, *9*, 1305.
- (7) (a) Garbaskas, M. F.; Arendt, R. H.; Kasper, J. S. *Inorg. Chem.* **1987**, *26*, 3191. (b) Hazen, R. M. *The Breakthrough—The Race for the Superconductor*; Summit Book: New York, 1988.
- (8) (a) Benelli, C.; Caneschi, A.; Gatteschi, D.; Guillou, O.; Pardi, L. *Inorg. Chem.* **1990**, *29*, 1750. (b) Goodgame, D. M. L.; Williams, D. J.; Winpenny, R. E. P. *Polyhedron* **1989**, *8*, 1531.
- (9) (a) Evans, W. J.; Sollberger, M. S. *Inorg. Chem.* **1988**, *27*, 4417. (b) Poncelet, O. P.; Sartain, W. J.; Hubert-Pfalzgraf, L. G.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 263.
- (10) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969–995.
- (11) Calcd for **2**: $C_{70}H_{24}Y_2Cu_8O_{28} \cdot 4H_2O$: C, 35.69; H, 2.71; N, 10.71. Found: C, 36.47; H, 3.29; N, 10.44.

Synthesis and Structural Characterization of Spontaneously Resolved $[M(aet)_3M'_4O]^{6+}$ ($M = Rh(III), Ir(III)$; $M'_4 = Zn^{II}_{4-x}Co^{II}_x$; $aet = 2$ -Aminoethanethiolate): Conversion of a Linear- to a Cage-Type S-Bridged Polynuclear Structure

There has been considerable research interest in stereochemistry of the S-bridged polynuclear metal complexes with multidentate sulfur-containing ligands such as 2-aminoethanethiolate (*aet*) and L-cysteinate (*L-cys*).¹⁻⁷ In particular, *fac(S)*- $[M(aet)_3]$ and