

Comparative Study of Crystal Structures and Thermal and Magnetic Properties of a Y_2Cu_8 and a Nd_2Cu_8 Complex

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Two heteronuclear Y-Cu and Nd-Cu metal complexes with the formulas $Y_2Cu_8(\mu_4-O)_2(\mu-PyO)_{12}(\mu-Cl)_2(NO_3)_4(H_2O)_2$ (1) and $Nd_2Cu_8(\mu_4-O)_2(\mu-PyO)_{12}(\mu-Cl)_2(OCH_3)_4(H_2O)_4$ (2) have been synthesized by the reactions of 2-hydroxypyridine (PyOH) and $Cu(OCH_3)_2$ with $Y(NO_3)_3 \cdot 4H_2O$ and $CuCl_2$ or $NdCl_3 \cdot 6H_2O$ in methanol in good yields. The structural features displayed by both compounds are very similar. The central core structures of these two compounds contain a $Y_2Cu_4O_2$ or $Nd_2Cu_4O_2$ unit which resembles that of a $YBa_2Cu_3O_{7-x}$ superconductor. The thermal properties of both compounds were studied by TGA and mass spectrometry. At temperatures below 200 °C, H_2O and methanol ligands were released as the major volatile components. At temperatures above 200 °C, fragmentation of both compounds occurs. Volatile fragments of $Cu(PyO)^+$, $Cu_2(PyO)^+$, and $Cu_2(PyO)_2^+$ along with PyOH were observed. Magnetic susceptibilities of both compounds were measured in the temperature range 5–300 K. Y_2Cu_8 showed characteristic antiferromagnetic interaction of Cu(II) ions, while Nd_2Cu_8 showed typical paramagnetic behavior dominated by the two Nd(III) ions. Crystal data: 1, $C_{60}H_{52}Y_2Cu_8Cl_2O_{23}N_{16}$, 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, $Z = 4$; 2, $C_{64}H_{68}Nd_2Cu_8Cl_2O_{22}N_{12}$, tetragonal, space group $P4_2/mnm$, No. 136, $a = b = 18.136$ (6) Å, $c = 15.670$ (7) Å, $V = 5154$ (5) Å³, $Z = 2$.

Introduction

There is much current interest in the synthesis of molecular species related to high-temperature superconductors.¹ Research in this area has been stimulated by two prospects. First, molecular complexes are possible precursors for the production of high-temperature superconductors by chemical processes such as MOCVD and sol-gel processes which are superior in many aspects, such as quality control and fabrication of the products, to the conventional method. Secondly, molecular complexes might serve as molecular models for the study of chemical and physical properties of superconductors. To date most of the molecular complexes reported related to superconductors are homonuclear species.² Although these homonuclear species might find use in the synthesis of superconductors, they provide little information regarding the chemical process and the properties of superconductors. Some recent studies have suggested that heteronuclear species may be important intermediates of the chemical processes.³ Synthesis and study of such heteronuclear species not only might help us to understand the reactions involved in the chemical process, and thus to design better precursors, but also enable us to synthesize better molecular model complexes of superconductors. We have been interested in heteronuclear complexes

related to the $YBa_2Cu_3O_{7-x}$ superconductor or 1–2–3 superconductor. Several related heteronuclear complexes have been reported recently. Among them are $Ba\{Cu(OCMe(CF_3)_2\}_3\}_2$, the most volatile Ba-Cu complex,^{3b} $(CuO)_3Ba_2Y(OCH_2CH_2OCH_3)_7$, used in the synthesis of the 1–2–3 superconductor,^{3c} and $Ba_2Cu_2(OCH_2CH_2OCH_3)_4(acac)_4(HOCH_2CH_2OCH_3)_2$, isolated from the precursor solutions to $YBa_2Cu_3O_7$ thin films.^{3a} Our research has been focused on the design and synthesis of heteronuclear complexes with structures resembling those of superconductors, particularly those involving yttrium, lanthanide, barium, and copper ions. In a preliminary communication^{3a} we reported the synthesis and some of the structural features of a Y_2Cu_8 compound. This compound was initially obtained from the reaction of $Y(NO_3)_3 \cdot 4H_2O$ and PyOH with $Cu(OCH_3)_2$ contaminated by chlorine impurity. We have found an improved method to synthesize this compound in high purity. Additional structural information has been obtained for this compound. A new Nd_2Cu_8 compound which has structural features similar to those found in Y_2Cu_8 has also been synthesized. A comparative study on the structures and magnetic and thermal properties of these two compounds has been carried out. The details are reported here.

Experimental Section

General Information. All reactions were performed under nitrogen atmosphere using the standard Schlenk line techniques. $Cu(OCH_3)_2$, $Y(NO_3)_3 \cdot 4H_2O$, and $NdCl_3 \cdot 6H_2O$ were purchased from Strem Chemicals, Inc. and Aldrich Chemicals Co. The reagent grade methanol solvent was used without further purification. Elemental analyses were performed at Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada, and Desert Analytics, Tucson, AZ.

Synthesis of $Y_2Cu_8O_2(PyO)_{12}Cl_2(NO_3)_4(H_2O)_2$ (1). A 140-mg (1.12-mmol) sample of $Cu(OCH_3)_2$ was placed in a flask containing 30 mL of methanol. Then 164 mg (1.73 mmol) of 2-hydroxypyridine and 100 mg (0.29 mmol) of $Y(NO_3)_3 \cdot 4H_2O$ were added to the stirred methanol solution. The mixture changed color rapidly from blue to green in a few

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minutes. CuCl_2 (16 mg, 0.12 mmol) was added. The mixture was stirred at 23 °C for 6 h. The insoluble solid was removed by filtration. The volume of the solution was then concentrated to about 10 mL in vacuo. After a few days dark green crystals of **1** formed and were isolated from the solution (70 mg, 0.032 mmol, 22% yield). Anal. Calcd for $\text{C}_{60}\text{H}_{52}\text{Y}_2\text{Cu}_8\text{Cl}_2\text{O}_{28}\text{N}_{16}$: C, 32.72; H, 2.38; N, 10.18. Found: C, 32.98; H, 2.48; N, 9.20.

Synthesis of $\text{Nd}_2\text{Cu}_8\text{O}_2(\text{PyO})_{12}\text{Cl}_2(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ (2**).** A 175-mg (1.40-mmol) sample of $\text{Cu}(\text{OCH}_3)_2$ was placed in a flask containing 30 mL of methanol. Then 100 mg (0.28 mmol) of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and 160 mg (1.68 mmol) of 2-hydroxypyridine were added to the methanol solution. The mixture was stirred for 6 h at 23 °C. A dark green solution was obtained. The insoluble material was removed by filtration. The solution was concentrated to about 10 mL in vacuo. After a few days dark green crystals of **2** were obtained (120 mg, 0.054 mmol, 38% yield). Anal. Calcd for $\text{C}_{64}\text{H}_{68}\text{Nd}_2\text{Cu}_8\text{Cl}_2\text{O}_{22}\text{N}_{12}$: C, 34.55; H, 3.08; N, 7.55. Found: C, 34.12; H, 2.81; N, 7.23.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured on a SQUID device (SHF variable-temperature susceptometer) at Michigan State University. The samples were quenched to 5 K at zero applied field. The field was cycled to minimize the residual field. Samples were loaded in a nitrogen-filled glovebag and run in an Al–Si alloy bucket.

TGA and Mass Spectroscopic Analyses. TGA analysis was performed at E.I. Du Pont de Nemours & Co., Deepwater, NJ. Mass spectra were recorded on a MAT 95Q mass spectrometer at the BFGoodrich Co., Brecksville, OH. The samples were heated in vacuo in the direct probe at a rate of 15 °C/min over the range 20–300 °C. Ionization was by electron impact (70 eV EI-MS) and field ionization (FI-MS). The spectra for both compounds were rather similar. Only small amounts of volatile chemicals were released up to about 220 °C. They include water (18 amu) methanol (32 amu) CO_2 (44 amu), and PyOH (95 amu). A rather sudden eruption of volatile chemicals occurred for both materials in the temperature region about 220–300 °C. PyOH was released along with some $\text{Cu}_m(\text{PyO})_n$ fragments, $\text{Cu}(\text{PyO})^+$ (157 amu), $\text{Cu}_2(\text{PyO})^+$ (222 amu), $\text{Cu}_2(\text{PyO})_2^+$ (314 amu), and $\text{Cu}_2(\text{PyO})_3^+$ (409 amu).

X-ray Crystallographic Analysis. Single crystals of **1** and **2** with rectangular shapes were obtained from the concentrated methanol solutions at 23 °C. Both crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected over the range $3 < 2\theta < 50^\circ$ for both samples at 23 °C on a Rigaku four-circle AFC6-S diffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation operated at 50 kV, 25 mA. The initial orientation matrix for **1** was obtained from 20 reflections ($13^\circ < 2\theta < 16^\circ$) located by the SEARCH routine. Attempted high-angle refinements of this matrix were unsuccessful due to too few available strong reflections at high angles. The initial orientation matrix for **2** was obtained from 20 reflections ($9^\circ < 2\theta < 12^\circ$) located by the SEARCH routine. This matrix was refined by using 18 high-angle reflections ($20^\circ < 2\theta < 26^\circ$). Three standard reflections were measured every 197 reflections. No significant decay was observed. All data processing was performed on a VAX workstation 3520 using the TEXSAN crystallographic package. Data were corrected for Lorentz–polarization effects and absorptions. The intensities of most of the reflections were weak for both crystals despite their considerable sizes and nearly perfect appearances. In addition, our X-ray tube was running at low intensity because of some defect problems. As a result, out of 8038 unique reflections collected for **1** only 1968 reflections were with the intensity greater than 3σ , and out 2644 unique reflections collected for **2** only 860 reflections had intensities greater than 3σ .

The crystal of **1** belongs to the monoclinic crystal system. The systematic absences agree with both of space groups Cc and $C2/c$. $C2/c$ was chosen. The correctness of this choice was confirmed by the successful solution and refinements of the structure. The crystal of **2** belongs to the tetragonal crystal system. The systematic absences agree with two acentric space groups, $P4_2nm$ (No. 102) and $P4n2$ (No. 118), and a centrosymmetric space group $P4_2/mnm$ (No. 136). The centrosymmetric space group $P4_2/mnm$ was chosen. The correctness of this choice was confirmed by the successful solution and refinements of the structure. The molecule of **1** has a inversion center of symmetry. The molecule of **2** possesses three reflection planes of symmetry. The positions of the metal atoms in both structures were determined by the direct method (MITHRIL). All other non-hydrogen atoms were located by subsequent difference Fourier syntheses. The positions of hydrogen atoms on the PyO^- ligand except those on the reflection plane in **2** were calculated using a fixed C–H bond length, 0.95 Å. Their temperature factors were tied to the temperature factor of the carbon atom to which they are bonded (multiplied by 1.10). Their contribution in structural factor calculations was included.

Table I. Crystallographic Data for **1** and **2**

	1	2
formula	$\text{C}_{60}\text{H}_{52}\text{Y}_2\text{Cu}_8\text{Cl}_2\text{O}_{28}\text{N}_{16}$	$\text{C}_{64}\text{H}_{68}\text{Nd}_2\text{Cu}_8\text{Cl}_2\text{O}_{22}\text{N}_{12}$
fw	2201.1	2223.7
space group	$C2/c$	$P4_2/mnm$
<i>a</i> , Å	21.932 (5)	18.136 (6)
<i>b</i> , Å	23.763 (7)	18.136 (6)
<i>c</i> , Å	18.683 (6)	15.670 (7)
β , deg	93.47 (2)	
<i>V</i> , Å ³	9719 (5)	5154 (5)
<i>Z</i>	4	2
<i>d</i> _{calc} , g cm ⁻³	1.53	1.44
μ (Mo $K\alpha$), cm ⁻¹	30.3	27.2
<i>T</i> , °C	22	22
<i>R</i> ^a	0.087	0.088
<i>R</i> _w ^b	0.103	0.098

$$^a R = \sum_{i=1}^n (|F_{o,i}| - |F_{c,i}|) / \sum_{i=1}^n |F_{o,i}|. \quad ^b R_w = (\sum_{i=1}^n w_i |F_{o,i}| - |F_{c,i}|)^2 / \sum_{i=1}^n w_i |F_{o,i}|^2)^{1/2}, \quad W = 1/\sigma^2(F_o).$$

Due to the limited numbers of reflections, only metal atoms, the chlorine atom, and some of the oxygen atoms were refined anisotropically in both structures. The pyridine rings except those on the reflection plane in **2** were refined as rigid bodies. The methoxy ligands bonded to the Nd atom in **2** are disordered over the two crystallographic reflection planes. The positions of the disordered oxygen atoms were determined. One of the possible positions for the methyl groups was located. However, we were unable to model completely this disorder. An ORTEP diagram showing the entire molecule with the partially resolved methoxy ligands is given in the supplementary material. The largest residue in the final difference Fourier map of **1** is $1.114 \text{ e } \text{Å}^{-3}$, not close to any atoms, while the largest residue in the final difference Fourier map of **2** is $1.761 \text{ e } \text{Å}^{-3}$, 0.95 Å from the disordered oxygen atom O(5). The data of crystallographic analysis is given in Table I.

Results and Discussion

Synthesis and Crystal Structures. The synthesis of heteronuclear yttrium, lanthanide, and copper complexes is a challenge to chemists due to the fact that the requirement for ligand environments of yttrium(III) and lanthanide(III) ions are very different from that of the copper(II) ion.⁴ Metal–ligand bonds in yttrium and lanthanide complexes are dominated by electrostatic interactions while metal–ligand bonds in copper complexes are mainly covalent in character. Yttrium and lanthanide ions prefer to coordinate to a hard base such as oxygen and nitrogen atoms. Bifunctional ligands with both neutral and negatively charged coordination sites containing nitrogen or oxygen atoms are therefore ideal for the formation of heteronuclear lanthanide–yttrium–copper complexes. It has been found⁵ that amino alcohols and 2-hydroxypyridine are excellent ligands for binding both lanthanide(yttrium) and copper ions. The reaction of PyOH with $\text{Cu}(\text{OCH}_3)_2$ and $\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ in the presence of CuCl_2 in methanol yielded dark green crystals of the Y_2Cu_8 compound in 22% yield. The reaction of PyOH with $\text{Cu}(\text{OCH}_3)_2$ and $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in methanol yielded the dark green crystals of the Nd_2Cu_8 compound in 38% yield. Both compounds are stable for weeks in the solid state upon exposure to air. Elemental analysis and single-crystal X-ray diffraction analysis established that these two compounds have the formula $\text{Y}_2\text{Cu}_8(\mu_4\text{-O})_2(\mu\text{-PyO})_{12}(\mu\text{-Cl})_2(\text{NO}_3)_4(\text{H}_2\text{O})_2$ (**1**) and $\text{Nd}_2\text{Cu}_8(\mu_4\text{-O})_2(\mu\text{-PyO})_{12}(\mu\text{-Cl})_2(\text{OCH}_3)_4(\text{H}_2\text{O})_4$ (**2**) respectively.

The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. Positional and thermal parameters are given in Table II. Selected bond distances and angles are listed in Table III. The molecule of **1** possesses a crystallographic inversion center, while the molecule of **2** possesses three crystallographic reflection planes. Consequently, **1** has approximate C_{2h} symmetry, while **2** has D_{2h} symmetry. The structural features displayed by these two compounds are quite similar. Each molecule consists of two yttrium atoms or neodymium atoms and eight copper atoms. The eight copper atoms belong to two different groups which are mutually orthogonal. In one group the two copper

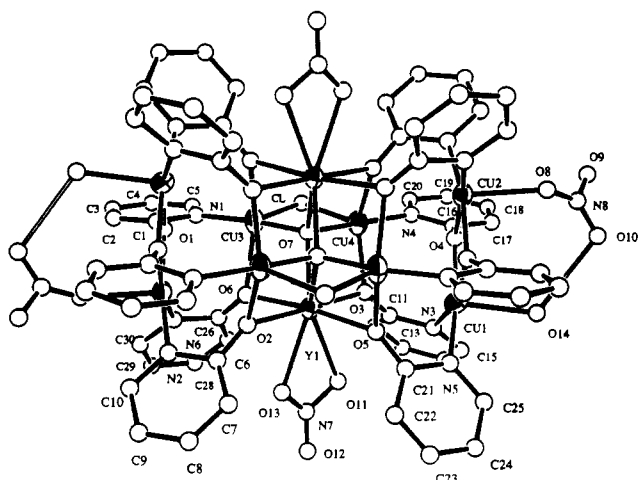


Figure 1. Molecular structure of **1** with the labeling scheme and 50% thermal ellipsoids for metal atoms. All nonmetal atoms are shown with radii fixed at 0.15 Å for clarity.

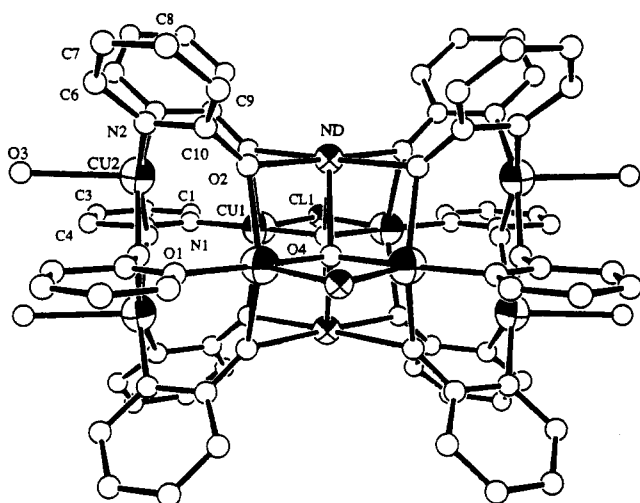


Figure 2. Molecular structure of **2** with the labeling scheme and 50% thermal ellipsoids for metal atoms. All nonmetal atoms are shown with radii fixed at 0.15 Å.

atoms are bridged by two oxygen atoms of the PyO⁻ ligands while in the other group the two copper atoms are bridged by a chlorine and an oxygen atom. The Cu–Cu separations in both compounds are similar, about 3 Å (Table IV), typical for dinuclear copper(II) complexes with single-atom bridges.⁶ These two distinct groups of copper atoms also have different coordination geometries. In the group with PyO⁻ bridging ligands, each copper atom is coordinated by two oxygen and two nitrogen atoms in a square-planar fashion. The fifth position of the copper atom in this group is occupied by an oxygen atom with a long Cu–O bond. In compound **1** this oxygen atom is from either a H₂O ligand (Cu(1)–O(14) = 2.31 (2) Å) or a NO₃⁻ ligand (Cu(2)–O(8) = 2.29 (3) Å), while in the compound **2** this oxygen atom is from the H₂O ligand only (Cu(2)–O(3) = 2.55 (2) Å). As a result, the coordination geometry of copper atoms in this group is square-pyramidal. In the other group each copper atom has a distorted-trigonal-bipyramidal geometry, with the two oxygen atoms from the PyO⁻ ligands and the chlorine atom occupying the equatorial positions, and the nitrogen atom and the oxide ligand occupying the axial positions, as indicated by the corresponding bond angles (see Table III). Such square-pyramidal or trigonal-bipyramidal geometry displayed by the copper atoms in these compounds has

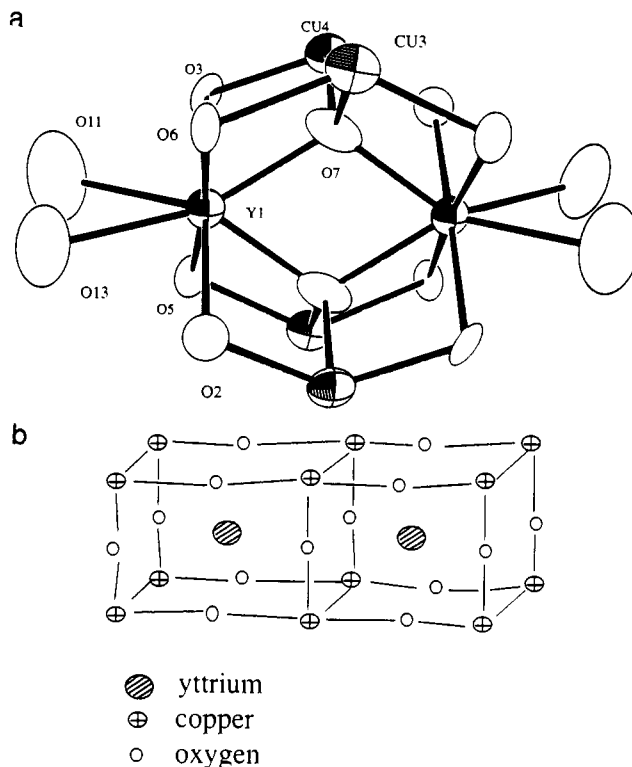


Figure 3. (a) Core structure of **1** with the labeling scheme and 50% thermal ellipsoids. (b) Coordination environment of yttrium ions in the YBa₂Cu₃O₇ superconductor.

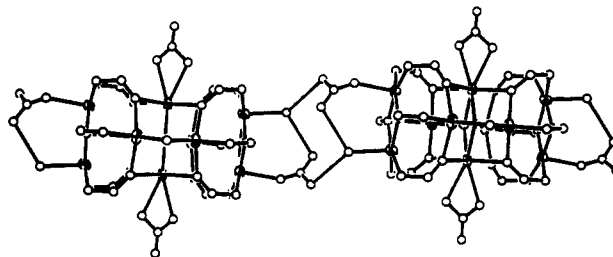


Figure 4. Diagram showing the intra- and intermolecular hydrogen bonding in **1**.

been frequently observed previously.^{7a} The corresponding Cu–O distances in both compounds are comparable (see Table IV).

The most important feature in these two structures is the central core unit M₂Cu₄O₁₀, M = Y, Nd. The core structure of **1** is shown in Figure 3a. The M^{III} ions are bridged to the four copper atoms through eight oxygen atoms of PyO⁻ ligands and two oxide ligands. The two M^{III} ions in each compound are also bridged to each other by the two oxide ligands. In **1** the yttrium atom is also coordinated by two oxygen atoms of a nitrate ligand while in **2** these positions are occupied by two methoxide ligands. These methoxide ligands are disordered over the two crystallographic reflection planes. Our attempt to determine the precise positions of these disordered ligands was unsuccessful. The coordination geometry for each M^{III} ion in these compounds can be described as a distorted square antiprism. Such coordination geometry for yttrium and neodymium has been observed previously.^{7b} The nonbonding distance between the two oxide ligands in **1** and **2** is 2.60 (5) and 2.58 (6) Å, respectively. The M₂O₂ unit, M = Y (Nd), is parallel to the two Cu₂O₂ units. Although there are

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Table II. Positional and Thermal Parameters

atom	x	y	z	$B(\text{eq}),^a \text{Å}^2$	atom	x	y	z	$B(\text{eq}),^a \text{Å}^2$
a. For 1									
Y(1)	0.2754 (2)	0.2197 (2)	0.5905 (2)	2.7 (2)	C(7)	0.466 (1)	0.2046 (7)	0.618 (1)	5 (1)
Cu(1)	0.1621 (2)	0.0864 (2)	0.5397 (3)	3.3 (3)	C(8)	0.524 (1)	0.2128 (9)	0.652 (1)	3.2 (9)
Cu(2)	0.1178 (2)	0.1377 (2)	0.3909 (3)	2.9 (3)	C(9)	0.5415 (8)	0.266 (1)	0.676 (1)	4 (1)
Cu(3)	0.2108 (2)	0.3495 (2)	0.5664 (3)	3.6 (3)	C(10)	0.502 (1)	0.3117 (8)	0.665 (1)	4 (1)
Cu(4)	0.1301 (2)	0.2480 (2)	0.5369 (3)	3.3 (3)	N(2)	0.444 (1)	0.3035 (8)	0.632 (1)	2.7 (7)
Cl	0.1056 (5)	0.3399 (5)	0.5881 (8)	7.5 (8)	C(11)	0.149 (1)	0.1634 (9)	0.653 (1)	2.2 (8)
O(1)	0.321 (1)	0.411 (1)	0.564 (1)	4 (1)	C(12)	0.127 (1)	0.1838 (8)	0.717 (2)	7 (1)
O(2)	0.375 (1)	0.248 (1)	0.573 (1)	3.5 (6)	C(13)	0.095 (1)	0.148 (1)	0.761 (1)	6 (1)
O(3)	0.176 (1)	0.1950 (9)	0.609 (1)	3 (1)	C(14)	0.086 (1)	0.092 (1)	0.742 (1)	6 (1)
O(4)	0.098 (1)	0.1339 (9)	0.491 (1)	3.0 (6)	C(15)	0.108 (1)	0.0713 (7)	0.678 (1)	4 (1)
O(5)	0.282 (1)	0.1305 (9)	0.547 (1)	3 (1)	N(3)	0.1397 (9)	0.107 (1)	0.634 (1)	2.0 (6)
O(6)	0.274 (1)	0.307 (1)	0.645 (1)	3 (1)	C(16)	0.049 (1)	0.155 (1)	0.517 (1)	3 (1)
O(7)	0.207 (1)	0.278 (1)	0.530 (1)	4 (1)	C(17)	-0.006 (1)	0.1250 (7)	0.518 (1)	5 (1)
O(8)	0.062 (2)	0.061 (1)	0.351 (2)	8 (2)	C(18)	-0.058 (1)	0.151 (1)	0.542 (1)	4 (1)
O(9)	-0.027 (2)	0.043 (1)	0.360 (2)	11 (3)	C(19)	-0.056 (1)	0.207 (1)	0.564 (1)	5 (1)
O(10)	0.027 (2)	-0.009 (2)	0.408 (3)	13 (3)	C(20)	-0.002 (1)	0.2372 (7)	0.563 (1)	5 (1)
O(11)	0.273 (2)	0.158 (2)	0.697 (2)	11 (3)	N(4)	0.0507 (9)	0.211 (1)	0.539 (1)	3.0 (7)
O(12)	0.340 (2)	0.144 (1)	0.785 (2)	9 (2)	C(21)	0.288 (1)	0.0804 (7)	0.574 (1)	2.9 (9)
O(13)	0.343 (2)	0.196 (2)	0.698 (2)	10 (3)	C(22)	0.344 (1)	0.058 (1)	0.599 (1)	5 (1)
O(14)	0.106 (1)	0.004 (1)	0.528 (1)	4 (2)	C(23)	0.347 (1)	0.003 (1)	0.626 (1)	6 (1)
N(7)	0.319 (3)	0.169 (2)	0.737 (3)	7 (1)	C(24)	0.294 (1)	-0.0293 (8)	0.627 (1)	6 (1)
N(8)	0.025 (3)	0.031 (2)	0.371 (3)	7 (1)	C(25)	0.238 (1)	-0.007 (1)	0.601 (1)	5 (1)
C(1)	0.286 (1)	0.445 (1)	0.600 (1)	4 (1)	N(5)	0.2350 (9)	0.048 (1)	0.575 (1)	3.0 (7)
C(2)	0.3019 (9)	0.498 (1)	0.628 (1)	4 (1)	C(26)	0.292 (1)	0.3276 (9)	0.703 (1)	3 (1)
C(3)	0.259 (1)	0.5294 (8)	0.664 (1)	5 (1)	C(27)	0.2664 (8)	0.320 (1)	0.769 (2)	4 (1)
C(4)	0.201 (1)	0.508 (1)	0.671 (1)	4 (1)	C(28)	0.293 (1)	0.346 (1)	0.830 (1)	5 (1)
C(5)	0.1845 (8)	0.456 (1)	0.643 (1)	5 (1)	C(29)	0.345 (1)	0.379 (1)	0.826 (1)	4 (1)
N(1)	0.227 (1)	0.4239 (7)	0.608 (1)	3.8 (8)	C(30)	0.3705 (8)	0.3867 (8)	0.760 (1)	3 (1)
C(6)	0.4259 (8)	0.250 (1)	0.608 (1)	2.2 (8)	N(6)	0.344 (1)	0.361 (1)	0.698 (1)	2.9 (7)
b. For 2									
Nd	0.0761 (1)	-0.0760	1/2	3.2 (2)	C(2)	0.175 (2)	0.1748	0.156 (3)	6 (1)
Cu(1)	0.0597 (2)	0.0597	0.3472 (3)	4.8 (1)	C(3)	0.220 (2)	0.2203	0.207 (4)	11 (2)
Cu(2)	0.2254 (3)	0.1043 (3)	1/2	5.7 (3)	C(4)	0.221 (2)	0.2214	0.302 (3)	8 (1)
Cl(1)	0	0	0.224 (1)	8 (2)	C(5)	0.1667	0.1667	0.335 (2)	4.4 (8)
O(1)	0.160 (1)	0.1605	0.4167	5 (3)	C(11)	0.238 (4)	-0.2302	1/2	4 (1)
O(2)	0.1474 (8)	-0.007 (1)	0.398 (1)	5 (1)	N(2)	0.2644 (9)	0.0418 (7)	0.4062 (8)	5.0 (5)
O(3)	0.327 (1)	0.201 (1)	1/2	3 (1)	C(6)	0.3362 (8)	0.0464 (9)	0.375 (1)	6.1 (7)
O(4)	0	0	0.418 (2)	3 (3)	C(7)	0.3576 (8)	0.003 (1)	0.306 (1)	8.7 (9)
O(5)	0.191 (2)	-0.163 (2)	0.548 (2)	9 (1)	C(8)	0.307 (1)	-0.046 (1)	0.268 (1)	10 (1)
N(1)	0.126 (1)	0.1263	0.285 (2)	4.7 (7)	C(9)	0.235 (1)	-0.0502 (8)	0.300 (1)	7.2 (8)
C(1)	0.128 (2)	0.1280	0.197 (3)	8 (1)	C(10)	0.2140 (7)	-0.007 (1)	0.369 (1)	4.4 (6)

$$^a B_{\text{eq}} = (8\pi^2/3) \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i^* a_j^* \bar{a}_i \bar{a}_j.$$

a few recent reports^{5,8} describing bimetallic lanthanide-copper compounds, to our knowledge, compounds **1** and **2** are the first example of bimetallic lanthanide(yttrium)-copper complexes with oxide bridging ligands. The formation of oxides in these complexes is probably due to the reaction of the H₂O molecule with the methoxide ligand. The formation of oxides in the other systems involving yttrium and lanthanides have been reported recently.⁹

The features displayed by the central core units of these two compounds closely resemble those¹⁰ found in the 1-2-3 superconductor (Figure 3b). In the 1-2-3 superconductor each yttrium ion is surrounded by eight oxygen atoms with Y-O separations similar to those in **1**. The 1-2-3 superconductor has a layered structure with the YO₄ unit being sandwiched between two Cu₄O₂ units. The core structures of **1** and **2** might be described as a half-sandwich since only one Cu₄O₂ unit is present. The Y-Y separations in the adjacent units of the orthorhombic YBa₂Cu₃O₇ superconductor are 3.83 Å (*a* axis) and 3.89 Å (*b* axis). These distances are comparable to the Y-Y distance of 3.782 (8) Å in **1**. It has been observed that the substitution of the yttrium ion in the YBa₂Cu₃O₇ superconductor by the neodymium ion changes the unit cell parameters^{10b} such that the Nd-Nd distances become

3.88 Å (*a* axis) and 3.96 Å (*b* axis), longer than the corresponding Y-Y separations. This is consistent with our results. In **2** the Nd-Nd separation is 3.904 (3) Å, considerably longer than the Y-Y separation in **1**. Besides the difference of the distance between the M(III) ions in **1** and **2**, there is also considerable variation in the M-Cu and M-O distances. The Y-Cu and Y-O distances in **1** are much shorter than those of Nd-Cu and Nd-O in **2**. A similar trend was also observed in superconductors. For the purpose of comparison, the related bond distances are tabulated in Table IV.

Another important feature of the structure of **1** is that the Y₂Cu₃ units are linked together through intermolecular hydrogen bonds to form an extended one-dimensional structure, as shown in Figure 4. The hydrogen atoms of the H₂O ligand coordinated to Cu(1) form an intramolecular hydrogen bond with the O(10) atom and an intermolecular hydrogen bond with the O(9) atom of the nitrate ligand coordinated to Cu(2), as evidenced¹¹ by the angles of O(14)-O(10)-N(8), 112 (4)°, and O(14)-O(9)-N(8)', 112 (3)°, and the distances of O(14)-O(10), 2.76 Å, and O(14)-O(9)', 3.01 (5) Å. Hydrogen bonds have been used to direct the

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Table III. Selected Bond Distances (Å) and Angles (deg) (Estimated Standard Deviations in the Least Significant Figure Given in Parentheses)

a. Bond Distances for 1					
Y(1)–O(2)	2.32 (2)	Cu(2)–O(4)	1.95 (2)	Cu(4)–N(4)	1.95 (2)
Y(1)–O(3)	2.31 (2)	Cu(2)–O(8)	2.29 (3)	O(1)–C(1)	1.32 (3)
Y(1)–O(5)	2.27 (2)	Cu(2)–N(2)	1.97 (2)	O(2)–C(6)	1.27 (3)
Y(1)–O(6)	2.31 (2)	Cu(2)–N(6)	1.91 (2)	O(3)–C(11)	1.29 (3)
Y(1)–O(7)	2.29 (2)	Cu(3)–Cl	2.38 (1)	O(4)–C(16)	1.31 (3)
Y(1)–O(7')	2.30 (3)	Cu(3)–O(5)	2.19 (2)	O(5)–C(21)	1.29 (3)
Y(1)–O(11)	2.47 (4)	Cu(3)–O(6)	2.20 (2)	O(6)–C(26)	1.23 (3)
Y(1)–O(13)	2.49 (4)	Cu(3)–O(7)	1.83 (2)	O(8)–N(8)	1.16 (7)
Cu(1)–O(1)	2.00 (2)	Cu(3)–N(1)	1.95 (2)	O(9)–N(8)	1.19 (7)
Cu(1)–O(4)	1.99 (2)	Cu(4)–Cl	2.46 (1)	O(10)–N(8)	1.17 (7)
Cu(1)–O(14)	2.31 (2)	Cu(4)–O(2)	2.05 (2)	O(11)–N(7)	1.25 (7)
Cu(1)–N(3)	1.92 (2)	Cu(4)–O(3)	2.06 (2)	O(12)–N(7)	1.15 (6)
Cu(1)–N(5)	1.92 (2)	Cu(4)–O(7)	1.85 (2)	O(13)–N(7)	1.14 (7)
Cu(2)–O(1)	1.93 (2)				
Bond Angles for 1					
O(2)–Y(1)–O(3)	177.8 (8)	O(4)–Cu(2)–O(8)	97 (1)	Y(1)–O(7)–Cu(3)	111 (1)
O(2)–Y(1)–O(5)	97.9 (8)	O(4)–Cu(2)–O(8)	97 (1)	Y(1)–O(7)–Cu(4)	108 (1)
O(2)–Y(1)–O(6)	81.0 (8)	O(4)–Cu(2)–N(6)	166.9 (9)	Y(1)–O(7')–Cu(3)	110 (1)
O(2)–Y(1)–O(7)	110.0 (8)	O(8)–Cu(2)–N(2)	98 (1)	Y(1)–O(7')–Cu(4)	107 (1)
O(2)–Y(1)–O(7')	69.2 (8)	O(8)–Cu(2)–N(6)	89 (1)	Cu(3)–O(7)–Cu(4)	110 (1)
O(2)–Y(1)–O(11)	111 (1)	N(2)–Cu(2)–N(6)	97.6 (9)	Cu(2)–O(8)–N(8)	139 (4)
O(2)–Y(1)–O(13)	70 (1)	Cl–Cu(3)–O(5)	108.0 (7)	Y(1)–O(11)–N(7)	108 (3)
O(3)–Y(1)–O(5)	84.3 (8)	Cl–Cu(3)–O(6)	114.6 (7)	Y(1)–O(13)–N(7)	111 (4)
O(3)–Y(1)–O(6)	96.9 (8)	Cl–Cu(3)–O(7)	87.5 (8)	O(11)–N(7)–O(12)	130 (5)
O(3)–Y(1)–O(7)	68.5 (8)	Cl–Cu(3)–N(1)	100.1 (8)	O(11)–N(7)–O(13)	97 (5)
O(3)–Y(1)–O(7')	111.3 (8)	O(5)–Cu(3)–O(6)	132.3 (8)	O(12)–N(7)–O(13)	128 (6)
O(3)–Y(1)–O(11)	70 (1)	O(5)–Cu(3)–O(7)	81 (1)	O(8)–N(8)–O(9)	118 (5)
O(3)–Y(1)–O(13)	110 (1)	O(5)–Cu(3)–N(1)	99.4 (9)	O(8)–N(8)–O(10)	134 (6)
O(5)–Y(1)–O(6)	173.9 (8)	O(6)–Cu(3)–O(7)	80.5 (9)	O(9)–N(8)–O(10)	107 (5)
O(5)–Y(1)–O(7)	116.4 (8)	Cl–Cu(4)–O(7)	84.8 (8)	O(1)–C(1)–C(2)	126 (2)
O(5)–Y(1)–O(7')	70.1 (8)	Cl–Cu(4)–N(4)	99.9 (7)	O(1)–C(1)–N(1)	113 (2)
O(5)–Y(1)–O(11)	75 (1)	O(2)–Cu(4)–O(3)	132.3 (9)	O(6)–Cu(3)–N(1)	93.5 (9)
O(5)–Y(1)–O(13)	92 (1)	O(2)–Cu(4)–O(7)	84 (1)	O(7)–Cu(3)–N(1)	172 (1)
O(6)–Y(1)–O(7)	69.5 (8)	O(2)–Cu(4)–N(4)	92.8 (9)	Cl–Cu(4)–O(2)	110.5 (8)
O(6)–Y(1)–O(7')	114.8 (8)	O(3)–Cu(4)–O(7)	83 (1)	Cl–Cu(4)–O(3)	113.6 (7)
O(6)–Y(1)–O(11)	100 (1)	O(3)–Cu(4)–N(4)	96.6 (9)	Cu(1)–N(5)–C(21)	114 (2)
O(6)–Y(1)–O(13)	82 (1)	O(7)–Cu(4)–N(4)	175 (1)	Cu(3)–N(1)–C(1)	116 (2)
O(7)–Y(1)–O(7')	68.9 (9)	Cu(3)–Cl–Cu(4)	77.4 (4)	Cu(3)–N(1)–C(5)	124 (2)
O(7)–Y(1)–O(11)	135 (1)	Cu(1)–O(1)–Cu(2)	106 (1)	Cu(2)–N(2)–C(6)	114 (1)
O(7)–Y(1)–O(13)	151 (1)	Cu(1)–O(1)–C(1)	129 (2)	Cu(2)–N(6)–C(26)	118 (1)
O(7')–Y(1)–O(11)	145 (1)	Cu(2)–O(1)–C(1)	124 (2)	Cu(2)–N(6)–C(30)	121 (2)
O(7')–Y(1)–O(13)	132 (1)	Y(1)–O(2)–Cu(4)	99.4 (9)	Cu(2)–N(2)–C(10)	126 (1)
O(11)–Y(1)–O(13)	42 (1)	Y(1)–O(2)–C(6)	139 (2)	O(3)–C(11)–C(12)	123 (2)
O(1)–Cu(1)–O(4)	73.1 (9)	Cu(4)–O(2)–C(6)	120 (2)	O(3)–C(11)–N(3)	117 (2)
O(1)–Cu(1)–O(14)	93.5 (9)	Y(1)–O(3)–Cu(4)	100.1 (9)	Cu(1)–N(5)–C(25)	126 (2)
O(1)–Cu(1)–N(3)	162.9 (9)	Y(1)–O(3)–C(11)	136 (2)	O(6)–C(26)–C(27)	127 (2)
O(1)–Cu(1)–N(5)	98.2 (9)	Cu(4)–O(3)–C(11)	123 (2)	O(6)–C(26)–N(6)	113 (2)
O(4)–Cu(1)–O(14)	94.2 (9)	Cu(1)–O(4)–Cu(2)	106 (1)	Cu(1)–N(3)–C(11)	116 (2)
O(4)–Cu(1)–N(3)	93.5 (9)	Cu(1)–O(4)–C(16)	129 (2)	Cu(1)–N(3)–C(15)	123 (2)
O(4)–Cu(1)–N(5)	169 (1)	Cu(2)–O(4)–C(16)	125 (2)	O(2)–C(6)–C(7)	125 (2)
O(14)–Cu(1)–N(3)	98.0 (9)	Y(1)–O(5)–Cu(3)	98.7 (8)	O(2)–C(6)–N(2)	115 (2)
O(14)–Cu(1)–N(5)	93.6 (9)	Y(1)–O(5)–C(21)	137 (2)	Cu(4)–N(4)–C(16)	116 (1)
N(3)–Cu(1)–N(5)	93.6 (9)	Cu(3)–O(5)–C(21)	124 (2)	Cu(4)–N(4)–C(20)	124 (2)
O(1)–Cu(2)–O(4)	75 (1)	Y(1)–O(6)–Cu(3)	98.2 (8)	O(5)–C(21)–C(22)	123 (2)
O(1)–Cu(2)–O(8)	91 (1)	Y(1)–O(6)–C(26)	137 (2)	O(5)–C(21)–N(5)	117 (2)
O(1)–Cu(2)–N(2)	166 (1)	Cu(3)–O(6)–C(26)	124 (2)	O(4)–C(16)–C(17)	122 (2)
O(1)–Cu(2)–N(6)	93 (1)	Y(1)–O(7)–Y(1)	111.1 (9)	O(4)–C(16)–N(4)	118 (2)
b. Bond Distances for 2					
Nd–O(2)	2.40 (2)	Cu(2)–O(3)	2.55 (2)	N(1)–C(1)	1.38 (5)
Nd–O(4)	2.34 (2)	Cu(2)–N(2)	1.99 (1)	N(1)–C(5)	1.30 (3)
Nd–O(5)	2.71 (4)	Cu(2)–N(2)	1.99 (1)	C(1)–C(2)	1.36 (4)
Cu(1)–O(4)	1.89 (2)	O(1)–C(5)	1.29 (4)	C(2)–C(3)	1.41 (5)
Cu(1)–N(1)	1.96 (2)	O(2)–C(10)	1.29 (2)	C(3)–C(4)	1.49 (7)
Cu(1)–Cl(1)	2.46 (1)	O(5)–C(11)	1.68 (5)	C(4)–C(5)	1.50 (3)
Cu(1)–O(2)	2.15 (2)	O(5)–C(11')	1.72 (7)		
Bond Angles for 2					
O(2)–Nd–O(2)	96.8 (8)	O(1)–Cu(2)–O(3)	94.1 (5)	Cu(1)–N(1)–C(5)	113 (2)
O(2)–Nd–O(4)	83.2 (8)	O(1)–Cu(2)–N(2)	91.0 (4)	C(1)–N(1)–C(5)	125 (2)
O(2)–Nd–O(5)	178.5 (8)	O(1)–Cu(2)–N(2)	165.5 (7)	N(1)–C(1)–C(2)	120 (3)
O(4)–Nd–O(4)	69.2 (5)	O(1)–Cu(2)–O(3)	94.1 (5)	C(1)–C(2)–C(3)	118 (4)
O(2)–Nd–O(4)	112.2 (5)	O(1)–Cu(2)–N(2)	165.5 (7)	C(2)–C(3)–C(4)	125 (3)
O(2)–Nd–O(5)	84.4 (8)	O(1)–Cu(2)–N(2)	91.0 (4)	C(3)–C(4)–C(5)	109 (3)
O(2)–Nd–O(5)	72.8 (8)	O(3)–Cu(2)–N(2)	97.8 (5)	C(2)–C(5)–N(1)	120 (2)
O(2)–Nd–O(5)	105.7 (8)	Cu(1)–O(4)–Cu(1)	108 (2)	O(1)–C(5)–N(1)	120 (2)

Table III (Continued)

a. Bond Angles for 2					
O(2)-Nd-O(5)	94.1 (8)	Nd-O(5)-C(11)	134 (2)	N(1)-C(5)-C(4)	123 (3)
O(4)-Nd-O(4)	67 (1)	Nd-O(5)-C(11)	131 (2)	Cu(2)-N(2)-C(6)	124 (1)
O(4)-Nd-O(5)	161.2 (9)	Nd-O(2)-Cu(1)	98.2 (6)	Cu(2)-N(2)-C(10)	116 (1)
O(4)-Nd-O(5)	129.8 (9)	Nd-O(2)-C(10)	138 (1)	C(6)-N(2)-C(10)	116 (1)
Cl(1)-Cu(1)-O(2)	111.5 (5)	Cu(1)-O(2)-C(10)	123 (1)	N(2)-C(6)-C(7)	120 (1)
Cl(1)-Cu(1)-O(4)	87.3 (8)	Nd-O(4)-Nd	113 (1)	C(6)-C(7)-C(8)	120 (1)
Cl(1)-Cu(1)-N(1)	98.9 (8)	Nd-O(4)-Cu(1)	108.8 (1)	C(7)-C(8)-C(9)	120 (2)
O(2)-Cu(1)-O(2)	134.0 (9)	N(2)-Cu(2)-N(2)	95.5 (8)	C(8)-C(9)-C(10)	120 (2)
O(2)-Cu(1)-O(4)	83.3 (5)	Cu(1)-Cl(1)-Cu(1)	77.0 (4)	O(2)-C(10)-N(2)	118 (1)
O(2)-Cu(1)-N(1)	94.4 (7)	Cu(2)-O(1)-Cu(2)	99.7 (2)	O(2)-C(10)-C(9)	122 (2)
O(4)-Cu(1)-N(1)	174 (1)	Cu(2)-O(1)-C(5)	129 (1)	N(2)-C(10)-C(9)	120 (1)
O(1)-Cu(2)-O(1)	80.0 (5)	Cu(1)-N(1)-C(1)	121 (1)		

Table IV

compd	1	2	YBa ₂ Cu ₃ O ₇	NdBa ₂ Cu ₃ O ₇
M-M (M = Y, Nd)	3.782 (8)	3.904 (3)	3.82, 3.87	3.88, 3.96
M-Cu	3.373 (av)	3.448 (1)	3.21	
Cu-Cu	Cu(1)-Cu(2) = 3.135 (7) Cu(3)-Cu(4) = 3.022 (7)	Cu(2)-Cu(2') = 3.11 (1) Cu(1)-Cu(1') = 3.064 (5)		
M-O	2.30 (av)	2.34 (2)	2.40 (av)	
PyO	2.30 (av)	2.40 (2)		
OCH ₃		2.71 (4)		
NO ₃	2.48 (av)			
Cu-O	1.84 (av)	1.89 (2)	1.91 (av)	2.35 (axial)
PyO	2.05 (av)	2.09 (av)		
H ₂ O	2.31 (2)	2.55 (2)		
NO ₃	2.29 (3)			

Table V. Radii (Å)

radius (Å)	Y	La	Nd
M ³⁺	1.06	1.22	1.04
atomic	1.81	1.88	1.82
covalent	1.62	1.69	1.64

assembly of supramolecules.¹² We have reported recently that hydrogen bonds can also be used to assemble polynuclear metal complexes in one-dimensional arrays.¹³ It has been known that hydrogen bonds play important roles in the sol-gel process.¹⁴ The intermolecular hydrogen bond linkage in **1** suggests that it is possible to preorient molecular metal precursor compounds in a certain direction through the formation of hydrogen bonds. Using such preoriented metal complexes as precursors could facilitate the fabrication of superconductors into useful forms such as films and wires. Compound **2** does not have such an extended structure in the solid.

The selective binding of the coordinating atoms of the PyO⁻ ligand to metal centers in **1** and **2** is obvious. All nitrogen atoms are bonded to the copper ions while the yttrium and neodymium ions are surrounded by negatively charged oxygen atoms only. Such selective binding by the 2-hydroxypyridine ligand has also been observed in other bimetallic complexes.⁵ We have also attempted to synthesize the analogous compound of lanthanum by the same approach since this element is an important component in superconductors. However, the attempt was unsuccessful. Both yttrium and neodymium ions have very similar ionic, atomic, and covalent radii,¹⁵ as shown in Table V. In contrast the corresponding radii of lanthanum are considerably larger than those of Y and Nd. Since metal-ligand interactions in the complexes of these ions are mainly electrostatic, and the effective nuclear charges of these ions are similar, the ionic radii of these ions may be the dominating factor in the formation of the complexes of **1** and **2**.

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Magnetic Properties. It has been observed that substitutions of yttrium ions in the YBa₂Cu₃O₇ superconductor by most paramagnetic lanthanides ions did not destroy the superconductivity, although they did effect the critical temperature *T_c* and resistivity.^{10b} On the other hand, the partial substitution of copper ions in the superconductor by nonmagnetic metal ions with ionic radii similar to Cu(II) and Cu(III) could destroy the superconductivity completely. This appears to imply that magnetic interactions of the copper ions play an important role in the superconductivity of copper oxide superconductors. In fact it has been suggested by theorists that the superconductivity is magnetic in origin.¹⁶ Polynuclear molecular complexes with structures resembling those of superconductors could serve as molecular models to study magnetic interactions in this system. For these reasons we have studied the magnetic properties of compounds **1** and **2**. The molar magnetic susceptibilities of compounds **1** and **2** were measured at three different magnetic field strengths, 0.5, 3, and 7 kG over the temperature range 5–300 K. No field-dependent behavior was observed for both compounds. **1** and **2** are complex magnetic systems due to the presence of polynuclear paramagnetic Cu(II) ions (²D) and Nd(III) ions (⁴I_{9/2}). The theoretical fitting for the data has not been achieved. However, certain information regarding the magnetic behavior of these metal ions can be obtained from the apparent features in the data. The susceptibility of compound **1** has a maximum at about 30 K. At temperatures above 30 K, it decreases smoothly. At temperatures below 30 K, it decreases and reaches a minimum at about 7.5 K. Above 7.5 K, the susceptibility rises again slightly, apparently caused by the presence of a small percentage of paramagnetic impurity. The susceptibility data of **1** suggest that antiferromagnetic exchange is dominant in this system.¹⁷ This can be seen more clearly from the plot of reciprocal χ and magnetic

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 (17) (a) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. (b) Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Co.: Philadelphia, 1977.

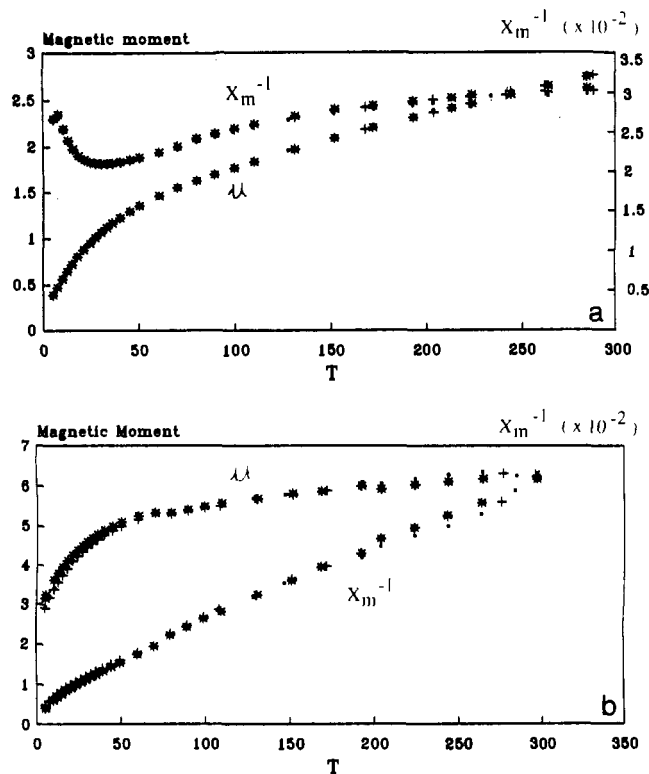


Figure 5. (a) Reciprocal susceptibility and magnetic moment vs T of 1. (b) Reciprocal susceptibility and magnetic moment vs T of 2. Key: (●) at 0.5 kG; (+) at 3 kG; (*) at 7 kG.

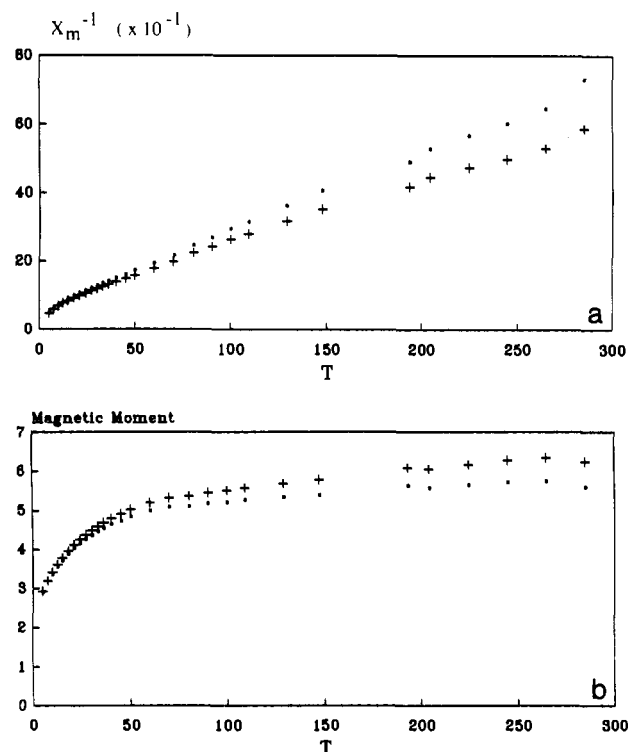


Figure 6. (a) Reciprocal susceptibility of 2 vs T at 0.5 kG (+) and χ_{Nd}^{-1} vs T at 0.5 kG (●). (b) Magnetic moments of 2 vs T at 0.5 kG (+) and μ_{Nd} vs T at 0.5 kG (●).

moment (Figure 5a). At 285 K, the magnetic moment for 1 is 2.77 μ_B , 0.35 μ_B /copper atom, much smaller than the spin-only value of 1.73 μ_B for a Cu(II) ion. In the YBa₂Cu₃O₇ superconductor mixed-valence copper ions (Cu(II), Cu(III)) appear to be present. This superconductor behaves as a diamagnet. Antiferromagnetic coupling was observed in the reduced YBa₂Cu₃O₆ material where Cu(II) ion is the only paramagnetic source.^{10b}

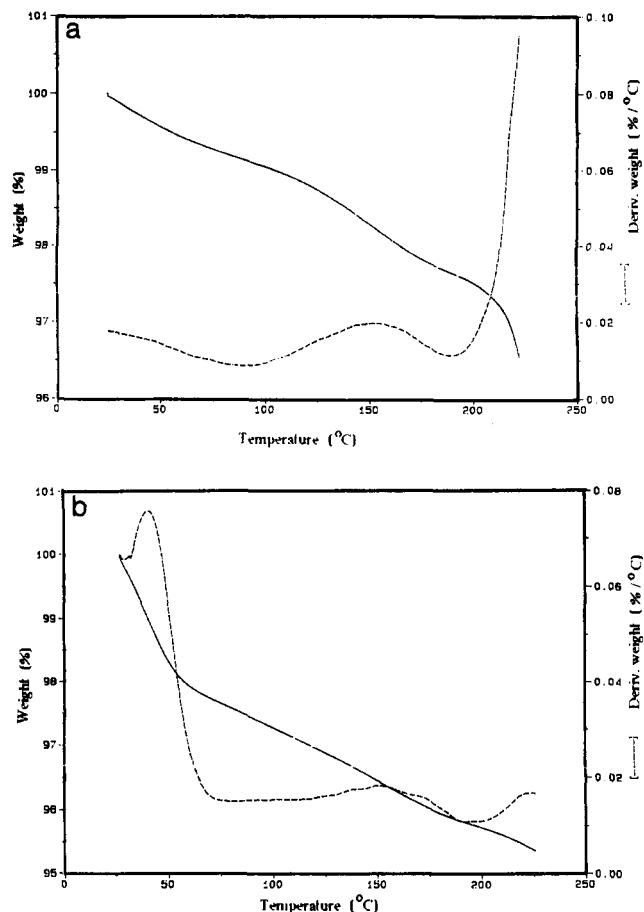


Figure 7. (a) TGA diagram of 1. (b) TGA diagram of 2.

The substitution of yttrium ions in 1 by the paramagnetic neodymium ions resulted the dramatic change of magnetic susceptibility, as shown in Figure 5b. The plot of χ^{-1} vs T is almost a straight line, following the Curie-Weiss law,¹⁷ an indication of paramagnetism. However, the magnetic moment of 2 is not a constant in the temperature range 5–300 K, as shown in Figure 5b. This suggests the presence of a certain degree of spin-exchange interactions. The negative intercept of the χ^{-1} plot at the temperature axis indicates that the exchange is antiferromagnetic in nature. The magnetic moment at 285 K for 2 is 6.22 μ_B . If the contribution from copper ions is ignored, the magnetic moment for each neodymium(III) ion is 3.11 μ_B . From the data of 1 it is clear that the eight copper(II) ions have a substantial amount of magnetic susceptibility over the entire temperature range. Since magnetic susceptibility is an additive quantity and the structures of 1 and 2 are very similar, the contribution from copper(II) ions to the total susceptibility in 2 can be removed by subtracting the molar susceptibility χ_1 of 1 from that of 2, χ_2 . The resulting susceptibility χ_{Nd} can be considered as the contribution from the two neodymium ions only. This approximation is valid because it is known that copper-lanthanide magnetic exchange is very small and negligible compared with the Nd-Nd interaction.^{17,18} The plots of χ_{Nd}^{-1} and χ_2^{-1} at 0.5 kG are shown in Figure 6a. The plots of μ_{Nd} and μ_2 are shown in Figure 6b. These plots show that the contribution of copper ions is significant at high temperature, but negligible at low temperature. After the correction for the copper contribution, the magnetic moment at 285 K for 2 is about 5.62 μ_B , 2.81 μ_B /Nd atom. This value is smaller than the calculated μ_{eff} for the Nd(III) ion, 3.62 μ_B , and the experimentally¹⁷ observed μ_{eff} for a mononuclear Nd(III) compound, 3.5 μ_B , a result of

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antiferromagnetic exchange. The small intercept of χ_{Nd}^{-1} at the T axis (about 20 K) suggests that the magnetic exchange between the two Nd(III) ions is weak. This is in agreement with the known fact that magnetic exchange of lanthanide ions is generally very small.^{17,18} The magnetic behavior observed in compound **2** is very similar to that of a neodymium-substituted 1–2–3 superconductor. In fact paramagnetism and antiferromagnetic coupling have been observed in most of magnetic lanthanide-substituted 1–2–3 superconductors.^{10b}

Thermal Properties. Thermal properties are important for the application of molecular compounds as precursors for high- T_c superconductors, since they affect the processing conditions and the composition of the final products.¹ The thermal properties of compounds **1** and **2** attracted our attention mainly due to the unusual color changes of these compounds upon heating. When the crystalline samples of **1** and **2** were heated under air, their colors gradually darkened and changed from grass green to brown-green. When the temperature is below 200 °C, the color change appeared reversible; i.e. when the heating was stopped below 200 °C for **1** and 150 °C for **2** and when the samples were allowed to cool to room temperature, the color of the samples changed back to their original grass-green color. This process was reproducible. In order to understand these phenomena, TGA measurements were carried out for both samples. The results are shown in Figure 7a,b. The TGA diagram shows that **1** lost about 2% of the total weight at the temperature below 150 °C. This weight loss was probably caused by the release of water molecules since **1** contains about 1.6% water. Additional weight loss occurred in the temperature range 150–200 °C. At about 200 °C, a sudden weight loss was observed which probably was caused by the irreversible pyrolysis of **1**. It appeared that compound **2** went through two stages of weight loss in the temperature range 30–160 °C. The first stage occurred at about 30–75 °C, which probably was caused by the loss of methanol ligand. The second stage occurred at 75–160 °C, which might be attributed to the loss of water molecules. The weight loss of **2** continued above 160 °C, although no sudden weight loss such as that of **1** was observed in the temperature range measured. To

further understand these processes, the compounds were heated up at the controlled temperature range under vacuum and mass spectrometry was used to identify the escaped fragments. The mass analysis confirmed that below 220 °C the major volatile components were H₂O and CH₃OH. Small amount of PyOH, its derivative pyrrole, and CO were also detected at this temperature range for both compounds. In the temperature range 220–300 °C PyOH was detected as the major component. Interestingly, species such as Cu(PyO), Cu₂(PyO), Cu₂(PyO)₂, and Cu₂(PyO)₃ were also observed. This suggests that the two dinuclear units Cu₂(PyO)₄ in the structures of **1** and **2** were eliminated at this temperature. The residue probably still contains the M₂Cu₄ core component. The precise composition of the residue was not determined. The color change of the crystals of **1** and **2** at the low-temperature range was probably caused by the loss of water and methanol molecules.

Conclusion. Heteronuclear yttrium, lanthanide, and copper complexes can be synthesized by using bifunctional ligands such as 2-hydroxypyridine. The structures of **1** and **2** resemble those of 1–2–3 superconductors. The magnetic properties displayed by these compounds are comparable to those of 1–2–3 high-temperature superconductors. These compounds can be used as molecular models for superconductors. Future study will be focused on the generation of mixed-valence states of copper ions in these compounds and new molecular model compounds. Magnetic properties of these compounds and their roles in superconductivity will be examined further.

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Supplementary Material Available: Tables of positional and thermal parameters of hydrogen atoms and anisotropic thermal parameters and an ORTEP diagram for the entire molecule of **2** (4 pages). Ordering information is given on any current masthead page.