

**Figure 1.** ORTEP view of the  $\text{Co}_2(\text{triazaz})_4$  molecule in  $\text{Co}_2(\text{triazaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ . The tolyl carbon atoms have been drawn with arbitrary radii, and hydrogen atoms have been omitted for the sake of clarity. Relevant structural parameters are as follows:  $\text{Co1-Co2}$ , 2.265 (2) Å;  $\text{N1-Co1-Co2-N3}$ , 17.7 (4)°;  $\text{N2-Co1-Co2-N4}$ , 16.2 (4)°.

from concentrated toluene solutions afforded X-ray-quality crystals of  $\text{Co}_2(\text{triazaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ .<sup>6</sup>

The dinuclear molecule has imposed  $C_2$  symmetry, with the two cobalt atoms lying on the crystallographic twofold axis. The geometry is that typical of the quadruply bridged  $\text{M}_2^{4+}$  dimers as represented in I. Because of the steric crowding caused by the tolyl groups around the axial positions, no axial ligation is observed. A view of the molecule is shown in Figure 1. The crystal structure is completed by interstitial toluene molecules that occupy general positions. The separation between the two  $d^7$  cobalt ions is 2.265 (2) Å and is consistent with full pairing of the electrons in a  $\sigma^2\pi^4\delta^2\delta^*\pi^*\pi^*$  MO scheme, as expected on a qualitative basis.<sup>1</sup> A carboxylato compound,  $\text{Co}_2(\text{O}_2\text{CPh})_4(\text{NC}_9\text{H}_9)$ , containing axial quinoline ligands, is the only other structurally characterized compound of cobalt with a structure of type I, and it has a metal-metal separation of 2.832 (2) Å.<sup>7</sup> This and other related carboxylato compounds show magnetic properties consistent with through-the-bridge antiferromagnetic exchange.<sup>8,9</sup> Another ion that can be considered as having a metal-metal interaction between  $\text{Co(II)}$  centers, although of a different structure, is  $[\text{Co}_2(\text{CN})_{10}]^{6-}$ , with a metal-metal separation reported as 2.798 (2)<sup>10</sup> and 2.794 (2) Å<sup>11</sup> in the salt  $\text{Ba}_3[\text{Co}_2(\text{CN})_{10}] \cdot 13\text{H}_2\text{O}$ .

A recent theoretical analysis of  $\text{M}_2(\text{form})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ; form =  $(p\text{-CH}_3\text{C}_6\text{H}_4)\text{NCHN}(p\text{-C}_6\text{H}_4\text{CH}_3)$ ) suggests<sup>4</sup> that the ligand-based orbitals interact extensively with the metal  $d$  orbitals that are involved in the metal-metal interaction and this may result for the cobalt compound in a pattern different from the expected  $\sigma^2\pi^4\delta^2\delta^*\pi^*\pi^*$  relative ordering. A theoretical investigation of the  $\text{Co}_2(\text{triazaz})_4$  compound with the  $X\alpha$ -SCF MO treatment is now in progress and will be reported later.

The molecule of  $\text{Co}_2(\text{triazaz})_4$  is twisted away from the eclipsed conformation by (average) 17.0°. The cobalt atoms are displaced from the least-squares planes determined by the nitrogen atoms of the corresponding coordination spheres by (average) 0.07 Å

- (6) Crystal data for  $\text{Co}_2(\text{triazaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ : orthorhombic, space group  $P2_12_12$ ,  $a = 14.977$  (5) Å,  $b = 17.392$  (6) Å,  $c = 11.999$  (2) Å,  $V = 3125$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $d_{\text{calcd}} = 1.274$  g·cm<sup>-3</sup>,  $R = 0.0605$ ,  $R_w = 0.0792$  for 1554 data with  $F_o^2 > 3\sigma(F_o^2)$ .
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in the outward direction. These features are common to other compounds of structure I, e.g.  $\text{M}_2(\text{form})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ,<sup>4</sup>  $\text{Rh}$ ,<sup>12</sup>  $\text{Ir}^3$ ) and  $\text{M}_2(\text{triazaz})_4$  ( $\text{M} = \text{Ni}, \text{Pd}$ ).<sup>13</sup>

In conclusion, we wish to observe that  $\text{Co}_2(\text{triazaz})_4$ , because of the lack of axial ligands, exhibits a coordination geometry previously unknown to cobalt(II).

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**Supplementary Material Available:** For the compound  $\text{Co}_2(\text{triazaz})_4 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ , an outline of data collection, structure solution, and refinement and tables of crystal data, atomic fractional coordinates, bond distances and angles, and temperature factors (9 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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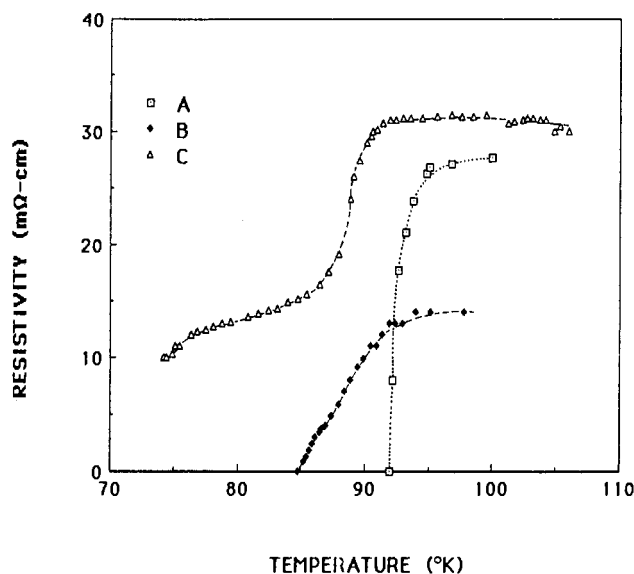
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## Characterization of $\text{YBa}_2(\text{Cu}, \text{Ag})_3\text{O}_7$ Superconductors

Sir:

The recently discovered Y-Ba-Cu-O superconductor,<sup>1</sup> identified as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $x < 0.5$ ),<sup>2</sup> has a structure with two distinct types of Cu, formally  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$ . The Cu is found in  $\text{CuO}_5$  pyramids, with Cu slightly displaced from the basal plane ( $\text{Cu}^{2+}$ ), and in  $\text{CuO}_4$  squares ( $\text{Cu}^{3+}$ ). The former give rise to Cu-O planes and the latter to Cu-O chains.<sup>3</sup> The idea that this arrangement of planes and chains is crucial for superconducting (SC) behavior finds some support in measurements of electrical anisotropy on single crystals.<sup>4</sup> Indeed, only minor effects have been reported, in terms of SC character, when Y or up to half the Ba was substituted by similar ions.<sup>5</sup> Subsequent work by Veal et al. did, however, show a systematic decrease in  $T_c$  in the solid solution  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_7$ , with increasing Sr content, and they ascribed this decrease to lattice distortions around the Ba, Sr site, which affect the adjacent Cu-O chains.<sup>6</sup> Also,  $\text{YBa}_2\text{Cu}_3\text{O}_6$  was found

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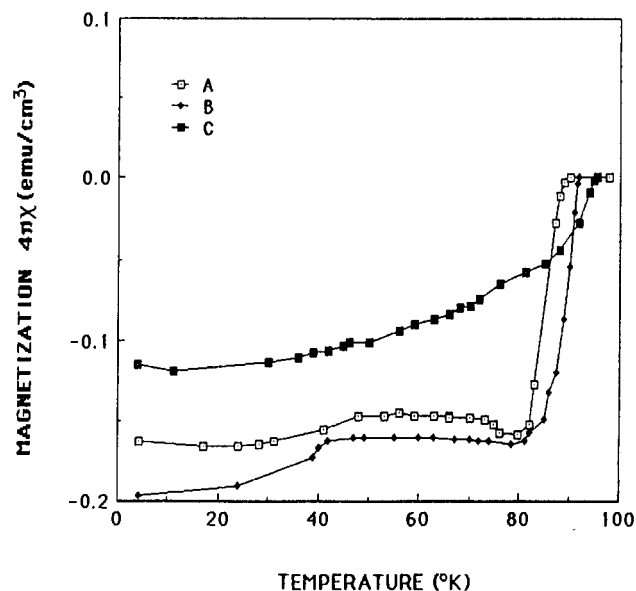
**Figure 1.** Plot of resistivity vs temperature for  $\text{YBa}(\text{Cu},\text{Ag})_3\text{O}_7$ : (A) 0.0 atom % Ag; (B) 0.7 atom % Ag; (C) 1.4 atom % Ag.

to be a semiconductor.<sup>7</sup> There the  $\text{CuO}_4$  arrangement is replaced by  $\text{CuO}_2$  linear bonds, not interconnected, with a formal Cu valency of +1.

In view of these results, the substitution of Cu by similar species will be important in determining the role of the Cu–O arrangements in the SC behavior. Solid-state and structural chemical comparisons provide a basis for choosing possible substituting elements. Silver appears to be a likely candidate even though Ag/Cu substitution is rare in oxides. The larger size of Ag in oxides, compared to that of Cu,<sup>8</sup> can be expected to limit substitution to low levels. Because only mono- and trivalent Ag occurs in oxides, and since  $\text{Ag}^{3+}$  prefers square-planar coordination, the Ag should substitute preferentially for the Cu in the  $\text{CuO}_4$  planes. Additionally, substitution of Ag for Y or Ba is unlikely to occur due to differences in preferred coordination environments.

In terms of electron energy levels, the Ag 4d shell lies considerably lower than the Cu 3d one and substitution might affect, and even disrupt, the electronic structure of the  $\text{CuO}_4$  chains. Here we report that up to ca. 1.5 atom % of Ag can be substituted for Cu. This substitution causes a broadening of the temperature range over which the sample becomes superconducting and a decrease in the superconducting fraction of the samples.<sup>9</sup>

**Materials and Methods.**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  was prepared from mixtures of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and CuO, according to published procedures.<sup>1-3,5,6</sup> Initial heating was for 6–24 h in air at ca. 950 °C; subsequent annealings were, in order, at 950 °C for 8–12 h and at 700–750 and/or 450–500 °C for 6–24 h, and samples were then slowly (50 °C/h) cooled to room temperature (all under a ca. 50  $\text{cm}^3/\text{min}$  flow of  $\text{O}_2$ ) with regrinding and pelletizing between annealings. Ag-substituted material was prepared by using a small amount of  $\text{Ag}_2\text{O}$  instead of the equivalent amount of CuO. Product characterization was done by X-ray powder diffraction<sup>10</sup> and by EDS microprobe analyses (for Y, Ba, Ag, and Cu). Four-probe resistivity measurements were done on pellets onto which evaporated Au contacts were applied. Qualitative magnetic measurements were done at 77 K and, in several cases, at room temperature. A number of samples were measured in a vibrating-sample magnetometer using a field of 45 G.



**Figure 2.** Plot of magnetization vs temperature for  $\text{YBa}(\text{Cu},\text{Ag})_3\text{O}_7$ : (A) 0.0 atom % Ag; (B) 0.7 atom % Ag; (C) 1.4 atom % Ag.

**X-ray Diffraction.** Several samples, with between 0 and 6 atom % of the Cu replaced by Ag, were prepared. X-ray diffraction data for the Ag-free material agree with published ones for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and correspond to unit cell parameters of  $a = 382.0$  pm,  $b = 388.6$  pm, and  $c = 1165.7$  pm. Inspection of diffraction intensities showed no evidence for the oxygen-poor ( $\text{YBa}_2\text{Cu}_3\text{O}_6$ ) phase or the tetragonal phase of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , for any of the samples with Ag content up to 1.5 atom %. Lattice parameters for the Ag-substituted samples were determined from the X-ray diffraction data by using the (200), (020), and (006) reflections. The data show no change in the  $a$  and  $b$  axes while the  $c$  axis increases with increasing Ag concentration. This led, in the 1.4 atom % Ag sample, to clear separation of the (006) and (020) peaks. For the 0.7 atom % Ag sample,  $a = 381.7$  pm,  $b = 388.5$  pm, and  $c = 1165.5$  pm. For the 1.4 atom % Ag sample,  $a = 382.0$  pm,  $b = 388.7$  pm, and  $c = 1168.6$  pm, corresponding to a 0.25% increase.

**Electrical Measurements.** Figure 1 shows a plot of resistivity measurements for samples with 0, 0.7, and 1.4 atom % Cu replaced by Ag. In these and other samples, no significant differences in  $T(\text{onset})$  were seen. However, the temperature interval over which the resistivity drops to zero (below  $3 \times 10^{-5}$   $\Omega$  resistance in our measurement system) widens considerably and, in the 1.4 atom % Ag sample, the transition is completed only at 32 K (not shown).

**Magnetic Measurements.** Figure 2 gives data for the volume magnetic susceptibility, measured after the samples were cooled in the magnetic field. The data are given directly as fractions of the ideal 100% Meissner effect ( $-1/4\pi$ ), i.e. as  $4\pi\chi$ . The decrease in the fraction of the sample that is superconducting when Ag/Cu exchange exceeds 0.7% is clear. Transition temperatures rise slightly, up to 1.4 atom %, but the subsequent decrease at higher levels of exchange makes the significance of this effect doubtful. Further experiments are in progress.

To be able to discuss the results, we need first to ascertain that Ag is indeed incorporated in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure. The increase in the  $c$  axis with increasing Ag concentration provides clear evidence for Ag substitution. If Ag were substituting for the Cu in the  $\text{CuO}_4$  pyramids, it would be expected that the  $a$  and  $b$  parameters would increase more than the  $c$  parameter, since the equatorial Cu–O bonds are substantially shorter than the apical Cu–O bond.<sup>3</sup> In the  $\text{CuO}_4$  square planes, the Cu–O bond along the  $c$  axis is shorter than the Cu–O bond along the  $b$  axis and, therefore, it would be expected that the  $c$  parameter would increase more than the  $b$  parameter. We observe that the  $c$  axis increases with increasing Ag concentration and therefore conclude that the Ag is substituting for Cu in the  $\text{CuO}_4$  chains. Also, at low Ag levels no additional phases are found, by XRD, while at higher

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Ag levels, clear diffraction evidence is seen for other phases. The case for Ag substituting for Cu, rather than for Y or Ba, has already been made above.

Linear coordination of the type found for Cu in  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is well-known for Ag(I). We did not find evidence in terms of diffraction intensities (cf. ref 7) for the O-poor compound, which contains Cu in the formal oxidation state of +1. However, on the basis of our electrical and magnetic measurements we cannot exclude the possibility that it is present, with Ag in it, although our synthetic procedure, under flowing  $\text{O}_2$ , argues against formation of the O-poor material.

Notwithstanding this uncertainty, our results are consistent with the assumption that Ag will preferentially substitute for Cu in the  $\text{CuO}_4$  chains. In that case our data suggest that interrupting these chains with  $\text{AgO}_4$  groups leads to a decrease in the superconducting fraction of the sample, without a clear effect on  $T_c$  (onset), which would still be the result of the Ag-free regions of the material (e.g. by electronic interaction with the  $\text{CuO}_5$  planes). Also, the temperature interval over which the transition occurs is broadened considerably. We cannot say if these effects are electronic, structural, or a combination of the two.

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**Registry No.**  $\text{Y}_2\text{O}_3$ , 1314-36-9;  $\text{BaCO}_3$ , 513-77-9;  $\text{CuO}$ , 1317-38-0;  $\text{Ag}_2\text{O}$ , 20667-12-3;  $\text{YBa}(\text{Cu}_{1-x}\text{Ag}_x)_2\text{O}_{7-y}$  ( $x = 0.7$  and  $1.7$  atom %), 110456-64-9;  $\text{YBaCu}_3\text{O}_{7-y}$ , 109064-29-1.

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## Articles

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### Synthetic Model Approach to the Active Site of Cytochrome *c* Oxidase: Studies of a Heterodinuclear Iron(III) Porphyrin-Copper(II) Tripeptide Complex

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The reaction in THF of iron(II) *meso*-tetraphenylporphyrin,  $\text{Fe}^{\text{II}}\text{TPP}$ , with  $\text{Cu}^{\text{III}}(\text{aib}_3)$ , where  $\text{aib}_3$  is the tripeptide of  $\alpha$ -aminoisobutyric acid, results in the formation of a neutral heterodinuclear complex,  $[\text{Fe}^{\text{III}}(\text{TPP})\text{Cu}^{\text{II}}(\text{aib}_3)]$  (1). Optical, conductance, electrochemical, magnetic, EPR, and Mössbauer data are reported for the dinuclear complex 1. Isosbestic behavior is exhibited at 600, 525, and 415 nm by solutions of  $\text{Fe}^{\text{II}}\text{TPP}$  to which varying amounts of  $\text{Cu}^{\text{III}}(\text{aib}_3)$  are added, indicating the formation of 1. EPR and Mössbauer spectra provide evidence for the presence of a high-spin ( $S = 5/2$ ) iron(III) and ( $S = 1/2$ ) copper(II) in complex 1. A weak antiferromagnetic interaction between the iron and copper is evident from the EPR measurements. While the magnetic interaction is weak, electrochemical and conductometric results indicate that the anionic  $\text{Cu}^{\text{III}}(\text{aib}_3)^-$  complex is moderately strongly bound to the  $\text{Fe}^{\text{III}}\text{TPP}^+$ .

#### Introduction

Cytochrome *c* oxidase, found in mitochondria of all aerobic organisms, is the respiratory enzyme that catalytically reduces  $\text{O}_2$  to  $\text{H}_2\text{O}$  with the concomitant release of energy [ $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{energy}$ ]. Despite extensive studies, the active site structure of cytochrome *c* oxidase remains one of the most enigmatic and controversial problems in chemistry.<sup>1</sup>

Anomalous magnetic and spectroscopic behavior is observed for one iron and one copper site in the fully oxidized enzyme. This behavior has typically been interpreted in terms of a strong antiferromagnetic coupling between Fe(III) and Cu(II) atoms in the oxygen-binding site.<sup>2</sup> Several possible structural models have been advanced to account for the proposed large antiferromagnetic coupling. In most instances a bridging ligand is envisaged between the two metal centers. With this view in mind, several workers have reported<sup>3,4</sup> the synthesis of compounds that are, to varying degrees, potential structural analogues of the oxidized active site. Most of these systems incorporate bridging ligands containing N, O, or S atom(s). We have reported<sup>4</sup> trinuclear  $\text{Fe}^{\text{III}}/\text{Cu}^{\text{II}}/\text{Fe}^{\text{III}}$  and tetranuclear  $\text{Fe}^{\text{III}}/\text{Cu}^{\text{II}}/\text{Fe}^{\text{III}}/\text{Cu}^{\text{II}}$  complexes that have

Table I. Mössbauer Data for Iron(III) Porphyrin Complexes

compd	spin state assign	$T_c$ , K	$\delta_c^a$ , mm/s	$\Delta E_Q$ , mm/s	ref
1	$S = 5/2$	77	0.51	1.04	c
$(\text{Fe}^{\text{III}}\text{TPP})_2[\text{Cu}^{\text{II}}(\text{MNT})_2]$	$S = 3/2$	b	0.24	3.13	4a
$\text{Fe}^{\text{III}}(\text{TPP})\text{OMe}$	$S = 5/2$	4.2	0.42	0.62	24
$\text{Fe}^{\text{III}}(\text{TPP})\text{Cl}$	$S = 5/2$	4.2	0.41	0.46	24
$\text{Fe}^{\text{III}}(\text{TPP})\text{ClO}_4$	$S = 5/2, 3/2$	77	0.38	3.48	19

<sup>a</sup>Reported relative to metallic iron. <sup>b</sup>Room temperature. <sup>c</sup>This work.

bridging S atoms between the iron(s) and copper(s). Presently, none of the potential synthetic model compounds, including our

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