average Cu–N bond length of 1.864 (7) Å is close to those in $[Cu_2(EDTB)]^{2+}$ (1.87 Å), which also has bis(benzimidazole) coordination to copper(I).[18] The conformation of the superstructure is significantly altered from that seen in mononuclear species. Instead of lying over the porphyrin ring the benzimidazoles stand in a relatively upright position such that the copper atom is 5.77 Å above the mean plane of the porphyrin. The planes of the benzimidazole rings intersect at an angle of 60°, which must be dictated at least in part by the minimization of steric interactions at copper. We note the presence of nonplanar phenyl amides in both the chelating arms and the pivalamido pickets even in the absence of obvious intramolecular interactions. Packing effects appear to be more energetically demanding than any π-delocalization stability that might occur if each *o*-amide was coplanar with its phenyl ring.

In conclusion, a binucleating porphyrin containing a certain degree of flexibility has been shown to form binuclear complexes whose structures can be definitively characterized by X-ray crystallography. The prospects appear good for the evolution of this approach into well-defined models for heterobinuclear sites of metalloproteins. Such models are essential for corroborating various structural proposals for binuclear active sites, particularly those based upon EXAFS data.

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Supplementary Material Available: Tables SI–SIV, giving atomic coordinates, bond distances and angles, and least-squares plane calculations for [Fe(PincerP)(4-*t*-BuHIm)], Tables SV–SX, listing atomic coordinates and anisotropic thermal parameters, calculated hydrogen atom positions, bond distances and angles, and least-squares plane calculations for Cu(PincerP′), and Tables SXI–SXV, giving atomic coordinates and anisotropic temperature factors, bond distances and angles, and least-squares plane calculations for $[(DMF)ZnCu(PincerP)]PF_6$ (36 pages). Ordering information is given on any current masthead page.

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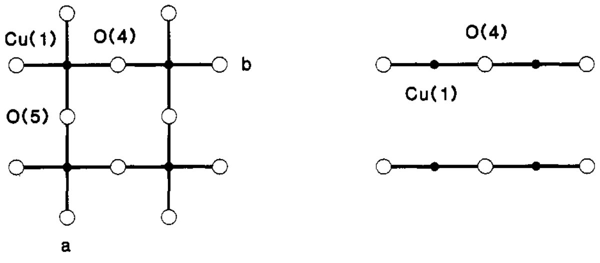
Oxygen Content and Site Distribution in High-T_c Superconducting $YBa_2Cu_3O_y$ Ceramics

Sir:

Since the initial report of Wu, et al.[1] on high-temperature superconductivity (T_c = 90–95 K) in a $YBa_2Cu_3O_y$ ceramic, a number of studies on the structural properties of this material have appeared. While the basic triple perovskite motif ($a \simeq b \simeq c/3$, orthorhombic, space group *Pmmm*) is now unquestioned, two fundamental queries remain for a particular preparative (annealing) scheme: (1) the total oxygen content (y); (2) the distribution of oxygen atoms between two sites, O(4)$[0, {}^1/_2, 0]$ and O(5)$[{}^1/_2, 0, 0]$ as in Figure 1.[2–16] In most preparations, it has been generally assumed that y is ca. 7, and models have been proposed in which there is a random distribution between sites O(4) and O(5) (Figure 1a) or O(4) is preferentially occupied [$P(0, {}^1/_2, 0) = 1$ in the limit, Figure 1b].



(a) (b)

Figure 1. $z = 0$ section of the structure of $YBa_2Cu_3O_y$: (a) random occupation of sites O(4) and O(5); (b) preferential occupation of site O(4) to the exclusion of site O(5).

It is suggested here that accurate determination of the unit cell lengths for a given preparation can give a good estimate of the total oxygen content (y) and the distribution [$P(0, {}^1/_2, 0) = 1 - P({}^1/_2, 0, 0)$] of oxygen atoms in sites O(4) and O(5). As an added advantage, the metrical properties of a unit cell can be determined with equal accuracy by either X-ray or neutron diffraction; thus, the relatively poor X-ray scattering amplitude for oxygen would not necessitate utilization of the less readily available neutron diffraction technique.

In Table I, cell parameters for an extensive set of syntheses of $YBa_2Cu_3O_y$ ceramics are presented. Members of the set were generally selected on the basis of good-to-excellent precision in the reported cell constants. Two of these studies are singled out: (a) the X-ray determination of Siegrist et al.[14] for which $a \simeq b$, the minimum value for c is given, and, apparently, $P(0, {}^1/_2, 0) \simeq {}^1/_2$; (b) the neutron study of Greedan et al.,[7] for which a is sizably smaller than b, and there is a clear site preference [O(4)], although this site is only about 70% occupied [$y \simeq 6.7$].

Given the $z = 0$ section of the structure of $YBa_2Cu_3O_y$ (Figure 1), a strong preference [$P(0, {}^1/_2, 0) \simeq 1$] for the O(4) site is expected to yield a b-axis length that is significantly larger than the a-axis length. In contrast, absence of a strong site preference

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Table I. Cell Parameters and Derived Oxygen Content (y) and Distribution $[P(0, {}^1/_2, 0]$ for $YBa_2Cu_3O_y$ Ceramics[a]

ref	a, Å	b, Å	c, Å	y	$P(0, {}^1/_2, 0)$
Beech[2]	3.8250 (1)	3.8864 (1)	11.6945 (4)	6.47	0.90 (na)^N
Beech[2]	3.8198 (1)	3.8849 (1)	11.6762 (3)	6.81	0.93 $(O_2)^N$
Beno[3]	3.8231 (1)	3.8864 (1)	11.6807 (2)	6.73	0.92 $(O_2)^N$
Cava[4]	3.8218 (7)	3.8913 (7)	11.677 (2)	6.79	0.96 $(O_2)^X$
David[5]	3.8187 (2)	3.8833 (2)	11.6687 (6)	6.95	0.93 $(O_2)^N$
Engler[6]	3.820	3.894	11.688	6.59	0.99 $(O_2)^X$
Greedan[7]	3.816 (2)	3.892 (2)	11.682 (9)	6.70[b]	1.00[b] $(O_2)^N$
Hewat[8]	3.8206	3.8851	11.6757	6.82	0.92 $(O_2)^N$
Hyde[9]	3.820	3.886	11.703	6.31	0.93 $(O_2)^X$
Izumi[10]	3.8282 (2)	3.8824 (2)	11.6878 (5)	6.59	0.86 $(O_2)^X$
Izumi[11]	3.8223 (3)	3.8829 (3)	11.690 (1)	6.55	0.90 $(O_2)^N$
Kini[12]	3.826 (2)	3.889 (2)	11.673 (4)	6.87	0.91 (air)^X
Kini[12]	3.844 (4)	3.889 (4)	11.685 (8)	6.64	0.80 $(O_2)^X$
LePage[13]	3.827 (1)	3.877 (1)	11.708 (6)	6.21	0.83 (air)^X
Siegrist[14]	3.856 (2)	3.870 (2)	11.666 (3)	7.00[b]	0.59 $(O_2)^X$
Steinfink[15]	3.824 (1)	3.891 (1)	11.685 (2)	6.64	0.94 (air)^X
Strobel[16]	3.841 (5)	3.889 (4)	11.736 (7)	5.69	0.82 (q,air)^X
Strobel[16]	3.828 (3)	3.891 (2)	11.679 (4)	6.76	0.91 $(O_2)^X$

[a] Key: na, not annealed; air, annealed in air; O_2, annealed under O_2; q,air, quenched in air; N, neutron diffraction; X, X-ray diffraction. [b] Assumed.

Table II. Comparison of Observed and Calculated y and $P(0, {}^1/_2, 0)$ Values for Refined Neutron Diffraction Studies

	y		$P(0, {}^1/_2, 0)$	
ref	obsd	calcd	obsd	calcd
Beech[2]	~6.9	6.81	~1	0.93
Beno[3]	6.81	6.73	~1	0.92
David[5]	6.85	6.95	~1	0.93
Izumi[11]	6.69	6.55	0.91	0.90

$[P(0, {}^1/_2, 0) \simeq {}^1/_2]$ should lead to a near equivalence of the a and b-axis lengths, to the limit of a tetragonal cell (probable space group $P4/mmm$). Thus, the difference in the a- and b-axis lengths can reasonably be taken as a measure of preferential site distribution. If one assumes (1) that the site preference is linear in the difference in the lengths of the a and b axes, (2) that only when $(b - a) = 0$ (tetragonal) is $P(0, {}^1/_2, 0) = {}^1/_2$ (by symmetry), and (3) that the site preference $P(0, {}^1/_2, 0) = 1$ (complete) for the determination of Greedan et al.;[7] then the very reasonable derived values, given the published preparative procedures,[2-16] for $P(0, {}^1/_2, 0)$ in Table I are obtained.

Similarly, if one assumes (1) that the sample of Siegrist et al.[14] has the formulation $YBa_2Cu_3O_7$ and that of Greedan et al.[7] is $YBa_2Cu_3O_{6.7}$ and (2) that there is a linear relationship between the length of the c axis and the total oxygen content; then the very rational values for y in Table I are derived.

To illustrate the utility and accuracy of the method, results from four powder neutron diffraction studies,[2,3,5,11] where oxygen atom site occupancies have been refined to give observed values (to an accuracy of about 0.04) for y and $P(0, {}^1/_2, 0)$, are compared to estimated values in Table II. In general, the calculated values for y and $P(0, {}^1/_2, 0)$ are in good accord with their experimental counterparts derived from the neutron results, strongly supporting the basic tenets of the method proposed here.

In summary, it is argued that if accurate cell constants are available (from X-ray, neutron, or electron diffraction), then semiquantitative estimates can be made for the oxygen atom site preference $[P(0, {}^1/_2, 0)]$ and the total oxygen content (y) of a particular $YBa_2Cu_3O_y$ ceramic. Qualitatively, if the difference between the lengths of the b and a axes is large (~0.07 Å), then a strong preference $[P(0, {}^1/_2, 0) > 90\%]$ is expected. If the difference in a and b is small (zero, in the limit of a tetragonal cell), then a weak site preference is anticipated $[P(0, {}^1/_2, 0) = {}^1/_2$ by symmetry in the limit of a tetragonal cell$]$. Additionally, if the c-axis length is small (~11.66 Å), then a formulation near $YBa_2Cu_3O_7$ is to be expected, with a diminishing oxygen content (y) denoted by an increasing c-axis length. Quite obviously, but apparently not always,[12] sample annealing in O_2 yields the highest total oxygen content (Table I). Finally, strong site preference $[P(0, {}^1/_2, 0) > 90\%]$ is predicted (Table I) for properly annealed (O_2) samples.

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Electronic Structure and Fermi Level Location in Defect Superconducting Solids $YBa_2Cu_3O_{7-\delta}$ and $La_2CuO_{4-\delta}$

Sir:

The recently discovered[1-4] high-transition-temperature T_c superconducting materials $YBa_2Cu_3O_{7-\delta}$ and $(La,Sr)_2CuO_{4-\delta}$ are extraordinarily sensitive to the concentration of oxygen. The parent or undoped lanthanum compounds exhibit antiferromagnetism[5] and possibly superconductivity[5,6] at $\delta = 0.03$. With increasing δ the yttrium compounds show[7] a decrease in T_c. The superconductivity appears to vanish near or at $\delta = 0.5$, at which point the material is also no longer metallic. These observations have motivated us to examine the nature of the oxygen defects in these two systems.

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