

Ba₃A₂PtCu₂O₁₀ (A = Y or Ho): The Crystal Structure of a Reaction By-Product of High Transition Temperature Superconductors with Platinum Metal

URS GEISER, LEIGH C. PORTER, HAU H. WANG,
THOMAS A. ALLEN, AND JACK M. WILLIAMS*

*Chemistry and Materials Science Divisions, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439*

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Mixtures of CuO, BaCO₃, and A₂O₃ (A = Y, rare earth) react at temperatures between 600 and 1000°C with platinum containers to produce crystals of composition Ba₃A₂PtCu₂O₁₀. The crystal structures of the compounds with A = Y or Ho were determined from single-crystal X-ray diffraction data. They are isostructural, monoclinic, space group *C2/m*, with *Z* = 2. Lattice parameters for Ba₃Y₂PtCu₂O₁₀ are *a* = 12.520(3) Å, *b* = 5.817(1) Å, *c* = 7.357(1) Å, β = 105.53(2)°, *V* = 516.2(2) Å³. Lattice parameters for Ba₃Ho₂PtCu₂O₁₀ are *a* = 12.516(3) Å, *b* = 5.813(1) Å, *c* = 7.350(3) Å, β = 105.54(2)°, *V* = 515.2(3) Å³. The structure of these complex oxides has the four metal ions in five distinct coordination environments: two barium sites with coordination numbers (CN) 8 and 11, yttrium or holmium with CN 7, platinum(IV) with CN 6, and copper with CN 5. © 1988 Academic Press, Inc.

Introduction

Recent research in the field of mixed oxide materials has yielded materials with superconducting transition temperatures (*T_c*) much higher than the A15 compounds known for well over a decade. Following the initial reports of possible high-*T_c* superconductivity in the La-Ba-Cu-O system by Bednorz and Müller (1) dramatic progress has been made in two classes of materials: (i) the layered perovskite solid solutions La_{2-*x*}A_{*x*}CuO₄ (A = Ba, Sr; *x* ≈ 0.15) with *T_c*'s of 36-40 K (2-5), or up to 52.5 K when subjected to hydrostatic pressure (6);

and (ii) the line compounds (except for some deviation from stoichiometry due to oxygen defects) ABa₂Cu₃O_{7-*x*} (A = Y or rare earth metal; *x* < 0.5) (7), which are derived from the cubic perovskite (KNiF₃) structure (8, 9) and have *T_c*'s of over 90 K.

In our preparations of YBa₂Cu₃O_{7-*x*} (10) and HoBa₂Cu₃O_{7-*x*} (11) we have observed the formation of small single crystals of a different compound, especially near the platinum crucible walls. In this paper we report the single-crystal structure of this reaction by-product, identified as Ba₃A₂PtCu₂O₁₀ (A = Y, Ho).

Experimental

Crystals of Ba₃A₂PtCu₂O₁₀ (A = Y or Ho) formed along the platinum crucible wall when mixtures of Y₂O₃ or Ho₂O₃, BaCO₃,

* To whom correspondence should be addressed.

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and CuO in the molar ratios 0.5:2:3, were finely ground, intimately mixed, and calcined in air at ca. 900 K. The crystals are typically metallic looking and rarely develop regular faces, but are translucent green when extremely thin. The crystals grow up to a few tenths of a millimeter in size, and even irregular chunks are often of remarkably good crystalline quality, as evidenced by X-ray diffraction photographs.

Single-crystal X-ray diffraction data of both yttrium and holmium derivatives were collected (details are given in Table I). All intensity data were corrected for Lorentz,

polarization, and absorption effects. The structure refinement minimized the function $\sum w(F_o - F_c)^2$ by use of the full-matrix least-squares method. The computer programs used were part of a locally modified version of the UCLA program package (12), which utilizes standard scattering factors, including anomalous dispersion correction terms (13).

Based on a Patterson synthesis, a structural model for the yttrium compound was developed first, before the presence of platinum was recognized. However, this model refined only if several of the metal site oc-

TABLE I
CRYSTAL DATA AT 295 K, INTENSITY DATA COLLECTION, AND STRUCTURE REFINEMENT
PARAMETERS FOR $Ba_3A_2PtCu_2O_{10}$ ($A = Y, Ho$)

	A = Y	A = Ho
a (Å)	12.520(3)	12.516(3)
b (Å)	5.817(1)	5.813(1)
c (Å)	7.357(1)	7.350(3)
β (°)	105.53(2)	105.54(2)
V (Å ³)	516.2(2)	515.2(3)
Crystal system, space group	Monoclinic, $C2/m$	Monoclinic, $C2/m$
Z (formula units/unit cell)	2	2
Diffractometer	Syntex P2 ₁	Nicolet P3/F
Wavelength	MoK α , graphite monochromator, 0.7107 Å	
Data collected	$h \geq 0, \pm k, \pm l$	$\pm h, \pm k, l \geq -1$
$2\theta(\max)$, $\sin(\theta)/\lambda$ (max)	55°, 0.650	80°, 0.904
Scan type, speed (°/min)	$\theta/2\theta$, 2–12	$\theta/2\theta$, 1.5–12
Total No. incl. standards	1285	7737
Unique, allowed refl. (NO)	656	1723
R_{av}	0.042	0.051
Absorption, μ (cm ⁻¹)	402	444
Crystal shape, dimensions	Irregular, ca. 0.15 mm dia	Approximated plate, 0.21 × 0.20 × 0.08 mm ³
Absorption correction	Empirical	Gaussian integration
NV, refined parameters ^a	52	53
R^b	0.049	0.060
R_w^c	0.059	0.075
Goodness of fit (GOF) ^d	3.8	4.92
Extinction parameter ^e	0.000023(2)	0.000065(8)

^a Includes anisotropic thermal parameters for all atoms, one ($A = Y$) or two ($A = Ho$) scale factors, and an isotropic extinction parameter.

^b $R = \sum |F_o - F_c| / \sum F_o$.

^c $R_w = \sqrt{[\sum w(F_o - F_c)^2 / \sum w F_o^2]}$, $w = 1/\sigma^2(F_o)$.

^d $GOF = \sqrt{[\sum w(F_o - F_c)^2 / (NO - NV)]}$.

^e Ref. (14).

cupancies were changed considerably from their theoretical values. Because of these difficulties, the data collection of the isostructural holmium analog was extended to much higher scattering angles, in order to obtain a larger number of reflections and to minimize cutoff problems in subsequent Fourier maps. With these extra high-angle data it became possible to apply direct methods for the structure solution. After oxygen atoms were found by use of difference Fourier techniques, it became clear that the metal atom in quasioctahedral coordination ($M-O \approx 2.0 \text{ \AA}$) corresponding to the highest peak of an electron density map had to be heavier than barium or holmium. Based on the synthesis conditions and the coordination geometry, platinum was the obvious choice, and subsequent structure refinement proceeded smoothly for both compounds. The presence of platinum in these samples was later confirmed from an inductively coupled plasma/atomic emission spectroscopy analysis. Structural and thermal parameters for both compounds are given in Tables II and III and interatomic distances and angles in Tables IV and V, respectively.¹

Crystal Structure Description

As expected from the very similar ionic radii of Y and Ho (15), the structures of Ba₃Y₂PtCu₂O₁₀ and Ba₃Ho₂PtCu₂O₁₀ are essentially identical. Minor differences, especially of the thermal parameters, may be

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TABLE II
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS IN Ba₃Y₂PtCu₂O₁₀

Atom	x	y	z	$U_{eq} \times 10^4$
Ba1	0.15065(9)	0.0000	0.5327(2)	125(4)
Ba2	0.0000	0.0000	0.0000	102(4)
Y	0.31050(14)	0.0000	0.1270(2)	83(5)
Pt	0.5000	0.0000	0.5000	69(3)
Cu	0.4079(2)	0.0000	0.7934(3)	88(6)
O1	0.4836(7)	0.222(2)	0.2833(13)	118(25)
O2	0.3171(7)	0.232(2)	0.8696(14)	139(27)
O3	0.3347(11)	0.0000	0.454(2)	101(37)

Note. The complete temperature factor is $\exp(-8\pi^2 U_{eq} \sin^2\theta/\lambda^2)$, where $U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i \cdot a_j$ in units of \AA^2 .

attributed to absorption correction problems (high μ 's, irregular crystal shapes). The structure is built from a complex packing of metal polyhedra and does not conform to any of the simple prototype structure types or a superstructure thereof. However, some of the structural details bear a striking resemblance to the family of compounds A₂BaCuO₅ (A = Y, Sm, Eu, Gd, Dy, Ho, Er, or Yb) whose crystal structure was determined first by powder X-ray diffraction (16) and recently confirmed (for A = Y) from single-crystal X-ray diffraction data (17).

The coordination polyhedra, with either

TABLE III
ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS IN Ba₃Ho₂PtCu₂O₁₀

Atom	x	y	z	$U_{eq} \times 10^4$
Ba1	0.15058(6)	0.0000	0.53284(11)	88(2)
Ba2	0.0000	0.0000	0.0000	64(2)
Ho	0.31066(4)	0.0000	0.12673(7)	47(1)
Pt	0.5000	0.0000	0.5000	37(2)
Cu	0.40766(12)	0.0000	0.7927(2)	62(3)
O1	0.4820(5)	0.2210(11)	0.2805(8)	75(13)
O2	0.3165(5)	0.2308(12)	0.8713(9)	92(14)
O3	0.3349(7)	0.0000	0.4563(13)	85(20)

Note. The complete temperature factor is $\exp(-8\pi^2 U_{eq} \sin^2\theta/\lambda^2)$, where $U_{eq} = \frac{1}{3} \sum_{ij} U_{ij} a_i^* a_j^* a_i \cdot a_j$ in units of \AA^2 .

TABLE IV
INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN Ba₃Y₂PtCu₂O₁₀

Ba1–O3	2.522(13)	Ba1–O1 ⁱ	2.880(9)	Ba1–O3 ⁱⁱ	2.9143(10)
Ba1–O1 ⁱⁱⁱ	2.914(9)	Ba1–O2	3.090(10)	Ba1–O2 ⁱⁱⁱ	3.462(10)
O3–Ba1–O1 ⁱ	113.9(3)	O3–Ba1–O3 ⁱⁱ	87.4(3)	O3–Ba1–O3 ⁱⁱⁱ	141.5(2)
O3–Ba1–O2	73.9(3)	O3–Ba1–O2 ⁱⁱⁱ	58.7(3)	O1 ⁱ –Ba1–O1 ^{iv}	68.3(4)
O1 ⁱ –Ba1–O3 ⁱⁱ	127.6(3)	O1 ⁱ –Ba1–O3 ⁱⁱⁱ	59.3(3)	O1 ⁱ –Ba1–O1 ⁱⁱⁱ	64.8(3)
O1 ⁱ –Ba1–O1 ^v	101.3(2)	O1 ⁱ –Ba1–O2	167.2(3)	O1 ⁱ –Ba1–O2 ^{vi}	118.9(2)
O1 ⁱ –Ba1–O2 ⁱⁱⁱ	55.6(2)	O1 ⁱ –Ba1–O2 ^v	86.5(3)	O3 ⁱⁱ –Ba1–O3 ⁱⁱⁱ	172.8(5)
O3 ⁱⁱ –Ba1–O1 ⁱⁱⁱ	125.2(3)	O3 ⁱⁱ –Ba1–O1 ^v	58.0(3)	O3 ⁱⁱ –Ba1–O2	60.9(3)
O3 ⁱⁱ –Ba1–O2 ^{vi}	122.7(3)	O3 ⁱⁱ –Ba1–O2 ⁱⁱⁱ	117.2(3)	O3 ⁱⁱ –Ba1–O2 ^v	63.9(3)
O1 ⁱⁱⁱ –Ba1–O1 ^v	67.4(4)	O1 ⁱⁱⁱ –Ba1–O2	102.6(3)	O1 ⁱⁱⁱ –Ba1–O2 ^{iv}	74.5(2)
O1 ⁱⁱⁱ –Ba1–O2 ⁱⁱⁱ	111.2(2)	O1 ⁱⁱⁱ –Ba1–O2 ^v	149.4(2)	O2–Ba1–O2 ^{vi}	51.9(4)
O2–Ba1–O2 ⁱⁱⁱ	132.42(13)	O2–Ba1–O2 ^v	106.3(2)	O2 ⁱⁱⁱ –Ba1–O2 ^v	53.4(3)
Ba2–O1 ⁱ	2.688(9)	Ba2–O2 ^{viii}	2.722(10)		
O1 ⁱ –Ba2–O1 ^{viii}	106.1(4)	O1 ⁱ –Ba2–O1 ^{iv}	73.9(4)	O1 ⁱ –Ba2–O2 ^{vii}	72.4(3)
O1 ⁱ –Ba2–O2 ⁱⁱⁱ	67.4(3)	O1 ⁱ –Ba2–O2 ^v	107.6(3)	O1 ⁱ –Ba2–O2 ^{ix}	112.6(3)
O2 ⁱⁱⁱ –Ba2–O2 ^{vii}	110.3(4)	O2 ^{viii} –Ba2–O2 ^{ix}	69.7(4)		
Y–O2 ^x	2.235(9)	Y–O2 ⁱⁱⁱ	2.346(10)	Y–O3	2.341(4)
Y–O1	2.521(9)				
O2 ⁱⁱⁱ –Y–O2 ^v	88.3(5)	O2 ⁱⁱⁱ –Y–O2 ^x	126.1(2)	O2 ⁱⁱⁱ –Y–O2 ^{xi}	77.7(4)
O2 ⁱⁱⁱ –Y–O3	83.4(3)	O2 ⁱⁱⁱ –Y–O1	151.9(3)	O2 ⁱⁱⁱ –Y–O1 ^{vi}	99.7(3)
O2 ^x –Y–O2 ^{xi}	70.4(5)	O2 ^x –Y–O3	143.7(3)	O2 ^x –Y–O1	82.0(3)
O2 ^{xi} –Y–O1	116.9(3)	O2–Y–O1	70.9(3)	O1–Y–O1 ^{vi}	61.7(4)
Pt–O3	2.006(13)	Pt–O1	2.020(9)		
O3–Pt–O1	89.1(4)	O3–Pt–O1 ^{xii}	90.9(4)	O1–Pt–O1 ^{xii}	100.4(5)
O1–Pt–O1 ^{vi}	79.6(5)				
Cu–O2	1.944(10)	Cu–O1 ^{xii}	2.060(9)	Cu–O3	2.419(14)
O2–Cu–O2 ^{vi}	88.2(6)	O2–Cu–O1 ^{xii}	97.0(4)	O2–Cu–O1 ^{xiii}	174.3(4)
O2–Cu–O3	102.1(4)	O1 ^{xii} –Cu–O1 ^{xiii}	77.7(5)	O1 ^{xii} –Cu–O3	79.2(3)
Ba1–Cu	3.277(3)	Ba1–Pt ⁱ	3.4397(9)	Ba2–Cu ⁱⁱ	3.3409(13)
Y–Cu ^x	3.019(3)	Y–Pt	3.110(2)	Y–Cu ^{xii}	3.416(3)
Pt–Cu	2.706(2)	Cu–Cu ^{xv}	3.288(5)		
Pt–O1–Cu ^{xii}	83.1(3)	Pt–O1–Y	85.7(3)	Cu ^{xii} –O1–Y	95.9(4)
Cu–O2–Y ⁱⁱ	164.3(5)	Cu–O2–Y ^{xiv}	88.9(4)	Y ⁱⁱ –O2–Y ^{xiv}	102.3(4)
Pt–O3–Y	91.0(5)	Pt–O3–Cu	74.7(4)	Y–O3–Cu	165.8(6)

Note. Symmetry codes: (i) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $x, -y, z$; (vii) $-\frac{1}{2} + x, -\frac{1}{2} + y, -1 + z$; (viii) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$; (ix) $-\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$; (x) $x, y, -1 + z$; (xi) $x, -y, -1 + z$; (xii) $1 - x, y, 1 - z$; (xiii) $1 - x, -y, 1 - z$; (xiv) $x, y, 1 + z$; (xv) $1 - x, y, 2 - z$.

mirror (Ba1, Ho/Y, Cu) or $2/m$ site symmetry (Ba2, Pt), are shown in Fig. 1. The copper ion possesses distorted square-pyramidal geometry, where the axial Cu–O3 bond forms an angle of 14.9° with the normal to the basal plane through the O1 and O2 atoms. The tilt direction is towards the O1

oxygen atoms, which form Cu–O bonds 0.1 Å longer than the corresponding O2 atoms and with a more acute O–Cu–O angle. These geometrical constraints are imposed because the triangle O1–O1–O3 is shared between the copper and platinum coordination spheres. The other triangular faces are

TABLE V
 INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) IN Ba₃Ho₂PtCu₂O₁₀

Ba1–O3	2.517(9)	Ba1–O1 ⁱ	2.903(6)	Ba1–O3 ⁱⁱⁱ	2.9121(8)
Ba1–O1 ⁱⁱⁱ	2.913(6)	Ba1–O2	3.087(7)	Ba1–O2 ⁱⁱⁱ	3.478(6)
O3–Ba1–O1 ⁱ	114.2(2)	O3–Ba1–O3 ⁱⁱ	87.2(2)	O3–Ba1–O1 ⁱⁱⁱ	141.0(2)
O3–Ba1–O2	73.8(2)	O3–Ba1–O2 ⁱⁱⁱ	58.9(2)	O1 ⁱ –Ba1–O1 ^{iv}	67.9(2)
O1 ⁱ –Ba1–O3 ⁱⁱⁱ	127.2(2)	O1 ⁱ –Ba1–O3 ⁱⁱⁱ	59.3(2)	O1 ⁱ –Ba1–O1 ⁱⁱⁱ	65.3(2)
O1 ⁱ –Ba1–O1 ^v	101.8(2)	O1 ⁱ –Ba1–O2	167.0(2)	O1 ⁱ –Ba1–O2 ^{vi}	119.3(2)
O1 ⁱ –Ba1–O2 ⁱⁱⁱ	55.6(2)	O1 ⁱ –Ba1–O2 ^v	86.4(2)	O3 ⁱⁱ –Ba1–O3 ⁱⁱⁱ	173.0(3)
O3 ⁱⁱ –Ba1–O1 ⁱⁱⁱ	125.6(2)	O3 ⁱⁱ –Ba1–O1 ^v	58.0(2)	O3 ⁱⁱ –Ba1–O2	61.3(2)
O3 ⁱⁱ –Ba1–O2 ^{vi}	112.8(2)	O3 ⁱⁱ –Ba1–O2 ⁱⁱⁱ	116.9(2)	O3 ⁱⁱ –Ba1–O2 ^v	63.5(2)
O1 ⁱⁱⁱ –Ba1–O1 ^v	67.7(2)	O1 ⁱⁱⁱ –Ba1–O2	102.0(2)	O1 ⁱⁱⁱ –Ba1–O2 ^{iv}	73.9(2)
O1 ⁱⁱⁱ –Ba1–O2 ⁱⁱⁱ	111.4(2)	O1 ⁱⁱⁱ –Ba1–O2 ^v	149.9(2)	O2–Ba1–O2 ^{vi}	51.5(2)
O2–Ba1–O2 ⁱⁱⁱ	132.50(8)	O2–Ba1–O2 ^v	106.5(1)	O2 ⁱⁱⁱ –Ba1–O2 ^v	53.5(2)
Ba2–O1 ⁱ	2.679(6)	Ba2–O2 ^{vii}	2.731(7)		
O1 ⁱ –Ba2–O1 ^{viii}	105.5(3)	O1 ⁱ –Ba2–O1 ^{iv}	74.5(3)	O1 ⁱ –Ba2–O2 ^{vii}	71.5(2)
O1 ⁱ –Ba2–O2 ⁱⁱⁱ	67.8(2)	O1 ⁱ –Ba2–O2 ^v	108.5(2)	O1 ⁱ –Ba2–O2 ^{ix}	112.2(2)
O2 ⁱⁱⁱ –Ba2–O2 ^{vii}	110.1(3)	O2 ^{vii} –Ba2–O2 ^{ix}	69.9(3)		
Ho–O2 ^x	2.234(6)	Ho–O2 ⁱⁱⁱ	2.325(7)	Ho–O3	2.359(10)
Ho–O1	2.496(6)				
O2 ⁱⁱⁱ –Ho–O2 ^v	88.9(4)	O2 ⁱⁱⁱ –Ho–O2 ^x	125.9(1)	O2 ⁱⁱⁱ –Ho–O2 ^{xi}	77.1(2)
O2 ⁱⁱⁱ –Ho–O3	83.6(2)	O2 ⁱⁱⁱ –Ho–O1	152.2(2)	O2 ⁱⁱⁱ –Ho–O1 ^{vi}	99.4(2)
O2 ^x –Ho–O2 ^{xi}	70.5(3)	O2 ^x –Ho–O3	143.7(2)	O2 ^x –Ho–O1	81.9(2)
O2 ^{xi} –Ho–O1	117.0(2)	O3–Ho–O1	71.1(2)	O1–Ho–O1 ^{vi}	62.0(3)
Pt–O3	2.004(9)	Pt–O1	2.027(6)		
O3–Pt–O1	89.0(3)	O3–Pt–O1 ^{xii}	91.0(3)	O1–Pt–O1 ^{xii}	101.4(4)
O1–Pt–O1 ^{vi}	78.6(4)				
Cu–O2	1.947(6)	Cu–O1 ^{xiii}	2.060(6)	Cu–O3	2.395(9)
O2–Cu–O2 ^{vi}	87.1(4)	O2–Cu–O1 ^{xiii}	97.7(3)	O2–Cu–O1 ^{xiii}	174.0(3)
O2–Cu–O3	102.4(2)	O1 ^{xiii} –Cu–O1 ^{xiii}	77.2(4)	O1 ^{xiii} –Cu–O3	80.0(2)
Ba1–Cu	3.272(2)	Ba1–Pt ⁱ	3.4373(7)	Ba2–Cu ⁱⁱ	3.341(1)
Ho–Cu ^x	3.016(2)	Ho–Pt	3.108(1)	Ho–Cu ^{xii}	3.415(2)
Pt–Cu	2.701(2)	Cu–Cu ^{xv}	3.294(3)		
Pt–O1–Cu ^{xii}	82.7(2)	Pt–O1–Ho	86.1(2)	Cu ^{xii} –O1–Ho	96.6(2)
Cu–O2–Ho ⁱⁱ	163.7(3)	Cu–O2–Ho ^{xiv}	89.4(3)	Ho ⁱⁱ –O2–Ho ^{xiv}	102.9(2)
Pt–O3–Ho	90.5(4)	Pt–O3–Cu	75.2(3)	Ho–O3–Cu	165.6(4)

Note. Symmetry codes: (i) $-\frac{1}{2} + x, -\frac{1}{2} + y, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (iii) $\frac{1}{2} - x, -\frac{1}{2} - y, 1 - z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (vi) $x, -y, z$; (vii) $-\frac{1}{2} + x, -\frac{1}{2} + y, -1 + z$; (viii) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$; (ix) $-\frac{1}{2} + x, \frac{1}{2} - y, -1 + z$; (x) $x, y, -1 + z$; (xi) $x, -y, -1 + z$; (xii) $1 - x, y, 1 - z$; (xiii) $1 - x, -y, 1 - z$; (xiv) $x, y, 1 + z$; (xv) $1 - x, y, 2 - z$.

shared with three neighboring Ba1 atoms, which form much longer *M*–O bonds than platinum and therefore do not require as much steric crowding of the oxygen atoms. The basal plane of the pyramid is not shared but rather lies opposing a basal plane of a symmetry-related copper–oxy-

gen polyhedron. A CuO₅ polyhedron with similar dimensions and distortions was found in Y₂BaCuO₅ and related compounds (16).

The platinum coordination geometry is a distorted octahedron with very small deviations from local *mmm* symmetry. How-

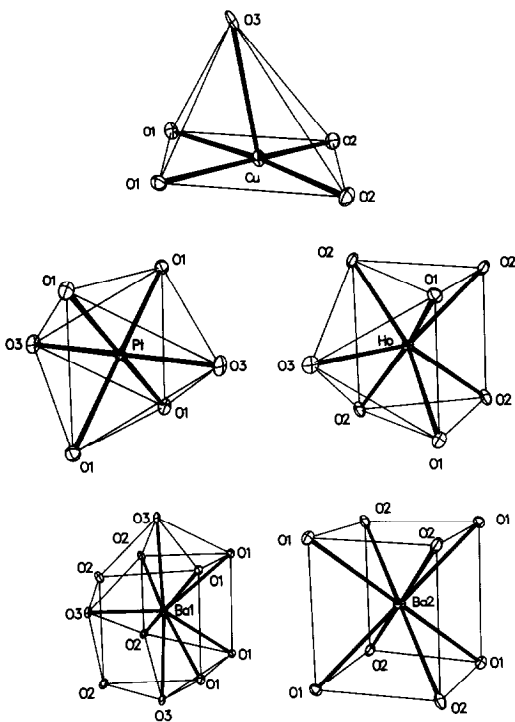


FIG. 1. Coordination polyhedra around the metal ions in $\text{Ba}_3\text{Ho}_2\text{PtCu}_2\text{O}_{10}$. Metal–oxygen bonds shorter than 2.5 Å (Cu, Pt, Ho) or 3.1 Å (Ba) are drawn with heavy lines. Temperature ellipsoids are drawn at the 50% probability level for $T = 295$ K. The polyhedra are essentially the same in the yttrium analog.

ever, large deviations from cubic local symmetry exist, as evidenced by the O1–Pt–O1 angle of 78.6° instead of 90° as in a regular octahedron. All faces of the platinum coordination polyhedron are shared by two copper, two yttrium or holmium, and four Ba1 cations. All O–Pt–O angles involving oxygen atoms of a triangle shared by copper atoms are acute (78.6 and 89.0°) for the same reasons as with the copper coordination geometry. The oxidation state of the platinum ion is deduced to be +4, both from the chemical formula and from the observed coordination geometry: Pt^{II} is usually observed in square planar environment, as in PtO (18), whereas Pt^{IV} is normally found with octahedral surroundings. For exam-

ple, the platinum ion in $\beta\text{-PtO}_2$ (19) has the same site symmetry, $2/m$, very similar bond lengths (1.98 and 2.02 Å), and an analogous rhombic distortion with a set of very acute O–Pt–O angles (74.8°), as in the title compounds.

The trivalent ion, A ($A = \text{Ho}, \text{Y}$), is surrounded by seven oxygen atoms, in the form of a monocapped distorted triangular prism, similar to that found in $A_2\text{BaCuO}_5$ ($A = \text{Y}$, lanthanide ion) (16), but also in the monoclinic B-form of some rare earth sesquioxides, e.g., Sm_2O_3 (20), and for the NbF_7^{2-} and TaF_7^{2-} ions in their potassium salts (21). The bond lengths range from 2.23 to 2.50 Å for the prismatic oxygen atoms ($2 \times \text{O1}$ and $4 \times \text{O2}$), and 2.36 Å for the capping O3 atom. The A–O3 bond is tilted 9.9° with respect to the normal to the prism face capped by the O3 atom, in the direction toward the O1 atoms. This distortion is again due to the sharing of the O1–O1–O3 face with the platinum coordination polyhedron, whereas the other triangular faces containing the O3 atom are shared with Ba1. None of the other faces are shared. In comparison with the samarium coordination geometry in $B\text{-Sm}_2\text{O}_3$ (20), where there are two crystallographically independent capped trigonal–prismatic Sm sites (in addition to a capped octahedral site), the O–M–O angles are quite comparable on the average, but in the title compounds the mirror plane is perpendicular to the prism axis, whereas in Sm_2O_3 the prism axis lies on the mirror plane. In contrast, the lanthanide cations in $A_2\text{BaCuO}_5$ (16) possess a mirror plane along the same direction as the title compound. In neither structure does the polyhedron assume crystallographic mm symmetry although the local oxygen environment would permit it.

Two distinct barium sites with much different stereochemistry are found in $\text{Ba}_3\text{A}_2\text{PtCu}_2\text{O}_{10}$. The simpler coordination geometry of the two is afforded by the atom labeled Ba2. That metal ion is surrounded by

eight oxygen atoms in the arrangement of a slightly distorted cube of crystallographic symmetry $2/m$. Two slightly different oxygen–barium bond lengths are found: 2.68 and 2.73 Å. Distortions of up to 4° in the O–Ba–O bond angles from the values for an ideal cube (i.e., 70.5 and 109.5°) are observed. The polyhedron around atom Ba2 is the only one in the structure of Ba₃A₂PtCu₂O₁₀ not involved in any face-sharing, although all its edges are shared with various other coordination spheres.

Atom Ba1 is surrounded by eleven oxygen atoms at distances ranging from 2.52 to 3.48 Å in a fashion very similar to that found in A₂BaCuO₅ (16). The oxygen atoms with the longest distances are probably not very strongly bonded to the barium atom, but they are useful in the description of the surroundings of that cation. Table VI summarizes some of the features of the Ba1 coordination geometry. The complex polyhedron may be thought of as a much distorted cube (the O2 atoms are much more separated from each other than the O1 atoms), with three faces capped by extra oxygen atoms, O3. Three rectangular, two rhomboidal, and eight triangular faces are thus formed whereof all but two (numbers 6 and 8 of Table VI) are shared by other metal

TABLE VI
FACES OF THE COORDINATION POLYHEDRON
AROUND ATOM Ba1

Face	Number	Vertices	Shape	Shared with	Symmetry ^a
1	2	O1, O1, O3	Triangle	Pt	1
2	2	O1, O2, ^b O3	Triangle	Y/Ho	1
3	2	O1, O2, ^c O3	Triangle	Cu	1
4	2	O2, ^b O2, ^c O3, O3	Rhomboid	Ba1	$\bar{1}$
5	1	O2, ^b O2, ^b O3	Triangle	Cu	m
6	1	O1, O1, O2, ^b O2 ^b	Rectangle	—	m
7	1	O1, O1, O1, O1	Rectangle	Ba1	$2/m$
8	1	O1, O1, O2, ^c O2 ^c	Rectangle	—	m
9	1	O2, ^c O2, ^c O3	Triangle	Y/Ho	m

^a Site symmetry at face center.

^b M–O2 = 3.09 Å (bond drawn in Fig. 1).

^c M–O2 = 3.48 Å (no bond drawn in Fig. 1).

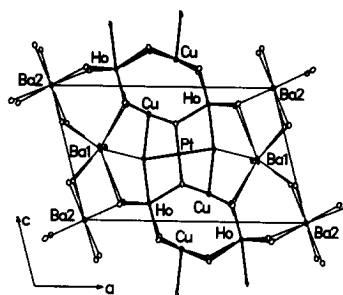


FIG. 2. Section of the crystal structure of Ba₃Ho₂PtCu₂O₁₀ near $y = 0$ showing the close connectivity of the copper, platinum, and holmium atoms. Unlabeled, open ellipses represent oxygen atoms.

ions. Coordination number eleven is observed only very rarely (22), and one could object against including the present case as an example because of some of the long Ba–O distances involved. We feel, however, that even the oxygen atoms at 3.5 Å separation (O2^c in Table VI) should be included in the first coordination shell, since otherwise the coordination sphere would have a gaping hole, with ligand–ligand distances well above the sum of their ionic and even van der Waals radii (2.8 and 3.0 Å, respectively, for oxygen): $d(O1 \cdots O3) = 4.55$ Å.

The observed packing in the crystal structure is shown in Figs. 2 and 3. Figure 2 emphasizes the atomic connectivity around the mirror planes at $y = 0$ and $y = 0.5$. All metal atom positions are located on these mirror planes. The area around $x \approx 0.5$ (in the $y = 0$ plane) is dominated by the small cations, Cu²⁺, Pt⁴⁺, and Y³⁺ or Ho³⁺, whereas the barium ions are found near $x \approx 0$. In the next layer, at $y = 0.5$, the situation is reversed. The oxygen atoms O1 and O2, near $y \approx 0.25$, connect the layers along the b direction. Figure 3 shows a stereoscopic view of the three-dimensional polyhedron packing of one unit cell with its surroundings. Most easily distinguished are the cubes around atom Ba2, at the corners of the unit cell. The Ba1 undecahedra are

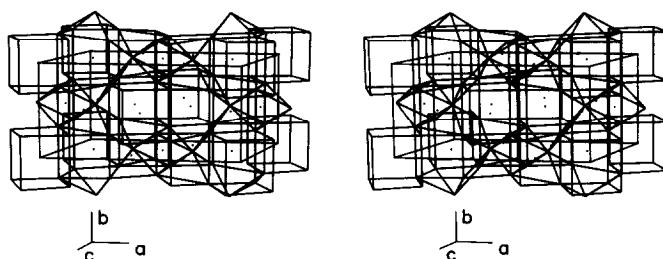


FIG. 3. Stereoview, in polyhedron representation, of the crystal structure of $\text{Ba}_3\text{Ho}_2\text{PtCu}_2\text{O}_{10}$. The large rectangular box is one unit cell.

characterized by their pyramidal "hats" protruding out above and below the crystal volume drawn in Fig. 3. An additional pair of adjoining Ba1 polyhedra is drawn around the center of the unit cell. Of the smaller polyhedra, the four platinum octahedra are clearly seen, surrounded by the copper and yttrium or holmium polyhedra.

Discussion

The most significant finding of this study in the context of high- T_c superconducting oxides is the observation that mixtures of CuO , BaCO_3 , or BaO (depending on the temperature), and A_2O_3 ($A = \text{Y}$, rare earth) react with platinum containers. This undesirable effect must be circumvented if high-purity samples of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ are to be obtained. This may be done either by minimizing the contact area between the starting oxides and the container walls, or by the choice of different crucible materials such as inert ceramics. Since the reaction is an oxidation process, oxides containing metal ions in their highest oxidation states, e.g., Al_2O_3 , are suggested. At least one research group in this area (23) reports the use of alumina boats in their synthesis procedure for $\text{ABa}_2\text{Cu}_3\text{O}_{7-x}$ ($A = \text{Y}$, rare earth).

The title compounds themselves, while not superconducting (24), possess a number of interesting and unusual features. The compounds are stoichiometric oxides of

four different metal ions with distinct positions in the unit cell. A more common situation is where two or more elements have a given crystallographic site. The reason for the separation in the present case lies in the individual sizes of the cations involved: the ionic radii for Ba^{2+} , Ho^{3+} , Y^{3+} , Pt^{4+} , and Cu^{2+} are 1.42 Å (coordination number 8) or ~ 1.6 Å (CN 11), ~ 0.95 , 0.96, 0.625, and 0.65 Å, respectively (15), for the coordination numbers observed in $\text{Ba}_3\text{A}_2\text{PtCu}_2\text{O}_{10}$. Barium is by far the largest cation involved and may not be substituted easily by any of the other metals. While yttrium and holmium are of the same size, they were never present simultaneously in the reactions described in this work. Presumably, one could prepare solid solutions of varying Ho:Y ratios. Platinum and copper ions are still smaller, and they are the only pair with similar radii. However, because of the higher charge on the Pt^{4+} ion, it is found in the cavity with the larger number of oxygen atoms. In addition, Cu^{2+} is known to be found in less symmetric environments because of its particular electronic structure (Jahn-Teller effect).

The title compounds present an interesting variety of coordination polyhedra with coordination numbers 5, 6, 7, 8, and 11. The structure is remarkably compact with many polyhedra sharing faces. This is equivalent to the observation that most interstices in the oxygen atom packing are filled. Only one significant "hole," near

(0.15, 0, 0.9), with a trigonal-prismatic environment, is found in the structure. In addition, the point at ($\frac{1}{2}$, 0, 0) is at the midpoint of a relatively short (3.3 Å) Cu · · · Cu contact. No direct bonding between the copper atoms is to be expected, however, because the frontier orbital, $d_{x^2-y^2}$, only allows δ -type interactions in the present geometrical arrangement which are negligible at this separation.

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