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Synthesis, Structure, and Properties of the Orthoborate $SrCu_2(BO_3)_2$

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The new orthoborate $SrCu_2(BO_3)_2$ has been synthesized and its structure determined by single-crystal X-ray methods. It crystallizes in space group $I\bar{4}2m$ in a cell of dimensions $a = 8.995(1)$ Å, $c = 6.649(1)$ Å, and $V = 537.9(1)$ Å^3 with $Z = 4$. The structure was determined from 604 independent reflections and refined to the final residuals $R = 0.040$ and $R_w = 0.051$. It is composed of CuO_4 rectangles and BO_3 triangles that are connected by sharing vertices and edges to form two-dimensional sheets; Sr atoms are interleaved between successive sheets. The compound decomposes at 970(3)°C to CuO and amorphous strontium borate; the CuO is reduced to finely divided Cu metal by heating at 300°C in flowing H_2. The corrected molar susceptibility of the material is 2.16(3) BM at 22°C.

Introduction

Copper is widely used as a catalyst on various supports for the production of chemicals, including the preparation of methanol from synthesis gas (*1*) and the hydration of acrylonitrile to acrylamide (*2*). The activity and selectivity of the catalysts are largely determined by the surface area of the Cu species and their interactions with the support. Consequently, catalyst efficacy may be enhanced with new materials that afford effective methods for producing finely divided particles or desired catalyst–support interactions. As part of our effort to synthesize incongruent phases that will afford, on decomposition, Cu species impregnated on supports of varying acidities, we have discovered a new compound in the system $SrO–CuO–B_2O_3$. This simple orthoborate, $SrCu_2(BO_3)_2$, decomposes above 970°C to finely divided CuO and amorphous strontium borate. Subsequent heating at 300°C in a H_2/Ar flow reduces the CuO to Cu metal.

In this report we describe the preparation, crystal structure, and properties of the new compound $SrCu_2(BO_3)_2$ and the characteristics of the CuO and Cu metal that are produced after decomposition by heat treatment.

Experimental

The title compound was prepared by grinding a stoichiometric ratio of the reagents $Sr(NO_3)_2$ (reagent grade, Mallinckrodt), $Cu(NO_3)_2 \cdot 2\frac{1}{2}H_2O$ (reagent grade, Mallinckrodt), and B_2O_3 (99.99%, Morton Thiokol) under hexane to a fine powder, followed by heating at 600°C for 30 min and at 850°C for 18 hr with the heat treatment interrupted several times to grind the sample. Except for some weak lines attributable to CuO, the X-ray powder pattern indicated a single-phase product.

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TABLE I

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS FOR $SrCu_2(BO_3)_2$

Crystal data	Experimental conditions
Diffractometer	Rigaku AFC6R
Radiation	Graphite monochromated Mo$K\alpha$
Formula weight (amu)	332.33
a (Å)	8.995(1)
c (Å)	6.649(1)
V (Å^3)	537.9(1)
Space group	$I\bar{4}2m$
D_{calc} (g cm^{-3})	4.13
Crystal volume (mm^3)	0.0005
$F(000)$	616
Z	4
Linear absolute coefficient (cm^{-1})	175.33
p factor	0.05
No. unique data with $F_0^2 > 3\sigma(F_0^2)$	604
R_{int}	0.076
$R(F)$	0.040
$R_w(F)$	0.051
Error in observation of unit weight (e^2)	1.34

Single crystals were grown with $LiBO_2$ as a flux. A mixture in the solute : flux ratio of 7 : 1 by mass was heated in a Pt crucible to 850°C, cooled at 6°C/hr to 600°C, then quenched by removal from the furnace. Blue single crystals were physically separated from the crucible for structure determination.

A crystal of dimensions 0.20 × 0.08 × 0.03 mm was chosen for analysis. Lattice parameters were refined from 20 reflections in the range $30° < 2\theta < 40°$ that were automatically centered on a Rigaku AFC6R diffractometer equipped with monochromatic Mo$K\alpha$ radiation. Intensity data in the range of indices $-19 \leq h \leq 19, 0 \leq k \leq 19$, and $0 \leq l \leq 14$ were collected with the ω–2θ scan technique at a scan speed of 16°/min in ω and a scan width of $\Delta\omega = (1.25 + 0.3 \tan \theta)°$. From 2061 reflections measured to $2\theta = 100°$, 604 unique data having $F_0^2 \geq 3\sigma(F_0^2)$ were obtained. Three reflections monitored every 199 measurements exhibited no significant deviations throughout the data collection. Crystal data and experimental conditions are summarized in Table I.

All calculations were performed on a Microvax II computer with programs from the TEXSAN crystallographic software package (*3*). The Laue symmetry $4/mmm$ and the systematic absence hkl, $h + k + l = 2n + 1$, are consistent with the acentric groups $I422$, $I4mm$, $I\bar{4}m2$, and $I\bar{4}2m$ and the centric group $I4/mmm$. The statistical distribution of intensities indicated that the structure is acentric (*4*). Also, the Patterson vectors indicated that the structure was layered with the heavy Sr atoms separated from sheets of Cu, B, and O atoms by $z \approx \frac{1}{4}$. A successful solution was found by drawing numerous layers of appropriate composition in the four acentric space groups that were consistent with the Patterson map and afforded reasonable interatomic distances. A successful solution and refinement were achieved with the space group $I\bar{4}2m$.

Following refinement with isotropic thermal parameters, the data were corrected for absorption with the computer program DIFABS (*5*) and subsequently averaged. Final least-squares refinement on $|F_0|$ with data having $F_0^2 \geq 3\sigma(F_0^2)$ and anisotropic temperature factors on each atom resulted in the residuals $R = 0.040$ and $R_w = 0.051$. The largest peak in the final differences map has a height of 2.4% of a Sr atom.

Unit cell parameters were also determined from X-ray powder data by least-squares refinement of 2θ values. Powder samples were ground, sieved with a 100-mesh wire screen, and annealed at 700°C for 2 hr. Eight intense reflections in the range $30° < 2\theta < 60°$ were collected on a Philips diffractometer equipped with Cu$K\alpha$ radiation; elemental Si (NIST Standard Reference Material 640b) was used as the internal standard for the zero-point correction. The refined cell parameters $a = 8.991(1)$ Å and $c = 6.660(3)$ Å compare well to those obtained from the single-crystal data.

DTA data were obtained with a Harrop Model DT-726 differential thermal analyzer interfaced to a PC via a Metrabyte DAS-8 A/D converter and Series M1000 signal conditioner. The sample and reference (Al_2O_3) were enclosed in Pt cups and heated at 10°C/min. A strong endothermic signal observed at 970(3)°C corresponds to decomposition of the phase.

The effective magnetic moment was obtained at 22°C by the Guoy method. The measurement was made at a field strength of 5 kG by using an Alpha Model AL 7500 water-cooled magnet with 4-in. pole faces and a 1.5-in. gap. The Guoy tube was calibrated with $HgCo(SCN)_4$. Diamagnetic corrections to molar susceptibilities were made from reported values except for the Sr^{2+} ion, where interpolation of reported values was used (*6*).

Results and Discussion

Final atomic coordinates and thermal parameters are listed in Table II, and selected interatomic distances and angles are given in Table III. Views of the structure along the *a* and *c* axes are shown in Fig. 1.

The structure is a simple, new type exhibiting layers of interconnected triangular planar BO_3 and rectangular planar CuO_4 groups. These layers extend parallel to the plane (001) (Fig. 1); a portion of the sheet is depicted in Fig. 2. Adjacent CuO_4 rectangles share edge O1···O1 to form dimeric units. Opposite edges O2···O2 of the dimer are shared with BO_3 triangles that also bridge each dimer by sharing vertex O1. The connectivity affords hollows defined by four O2 atoms. Distorted cubes of O2 atoms are formed by successively stacking the sheets with application of the improper four-fold axis of rotation; the Sr atom occupies the O2 cube. We have observed a comparable layered structure in the pyroborate Ba CuB_2O_5, in which the Ba atoms interleave successive sheets comprised of vertex-sharing CuO_4 rectangles and B_2O_5 groups (*7*).

The average Cu–O distance of 1.94(1) Å is similar to values determined in other complex copper(II) borates, e.g., 1.930(6) Å in α-$Sr_2Cu(BO_3)_2$, 1.94(3) Å in β-$Sr_2Cu(BO_3)_2$ (*8*), and 1.95(2) Å in $Ba_2Cu(BO_3)_2$ (*9*). Bond angles reflect the distortion of the CuO_4 groups that arises from sharing the O2···O2 edge with a B atom and the O1···O1 edge with a Cu atom. The acute angle of 72.9(2)° for O2–Cu–O2 is similar to values observed in β-$Sr_2Cu(BO_3)_2$ and $Ba_2Cu(BO_3)_2$, where edges are shared between rectangular CuO_4 and triangular BO_3 polyhedra (*8*, *9*). The shared edge O1···O1 affords a larger angle, O1–Cu–O1 = 82.2(2)°. The planarity of the CuO_4 rectangle is slightly relieved as evidenced by the angle O1–Cu–O2 = 174.7(2)°. Inspection of the central portion of the cell sketched in Fig. 1 reveals that O1 atoms occupy positions over the Cu atoms along the *c* axis, affording the appearance of cubane-like fragments Cu_4O_4. The Cu–O1 distances parallel to the *c* axis are greater than 3.25 Å.

The orthoborate group is slightly irregular. The average B–O bond distance of 1.37(1) Å compares well to the expected distance of 1.365 Å for a 3-coordinate B atom (*10*). Bond angles are only slightly distorted because of the shared edge O2···O2 with

TABLE II

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR $SrCu_2(BO_3)_2$

Atom	Wyckoff notation	x	y	z	B_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	4(*c*)	0	1/2	0	0.71(2)	0.0108(3)	0.0107(3)	0.0054(2)	0	0	0
Cu	8(*i*)	0.11412(1)	0.11412	0.2783(2)	0.93(1)	0.0081(2)	0.0081	0.0191(4)	−0.0001(2)	0.0004(2)	0.0004
B	8(*i*)	0.2953(4)	0.2953	0.243(1)	0.74(9)	0.008(1)	0.008	0.012(2)	−0.000(1)	−0.001(1)	−0.001
O1	8(*i*	0.4004(4)	0.4004	0.212(1)	1.5(1)	0.009(1)	0.009	0.040(4)	0.000(1)	−0.007(1)	−0.007
O2	16(*j*)	0.3276(3)	0.1456(3)	0.254(1)	0.9(1)	0.009(1)	0.008(1)	0.018(1)	0.001(1)	0.001(1)	0.002(1)

Note. From symmetry constraints U_{12}, U_{13}, and U_{23} = O for Sr, and $U_{11} = U_{22}$ and $U_{13} = U_{23}$ for Cu, B, and O1.

the Cu atom. Thus, the O2–B–O2 angle is reduced from the ideal 120° to 114.1(1)° and the O1–B–O2 angle is increased to 122.9(2)°.

The Sr atom occupies a distorted cubic environment having D_2 symmetry (cf. Fig. 1). The O2–Sr–O2 angular values listed in Table III may be compared with the values 70.5° and 109.5° for an ideal centered cubic configuration. Adjacent Sr atoms share quadrilateral faces of O2 atoms to form one-dimensional chains that extend parallel to the *c* axis. The average Sr–O distance 2.62(2) Å compares to the expected value of 2.63 Å that is calculated from the crystal radii of 8-coordinate Sr^{2+} and 4-coordinate O^{2-} (*11*). Atom O2 is 4-coordinate, binding two Sr atoms, one Cu atom, and one B atom while atom O1 is 3-coordinate, binding two Cu atoms and one B atom.

The effective magnetic moment of the compound at 22°C is 2.16(3) BM. This value is less than the expected spin-only value of 2.83 BM for a compound with isolated transition-metal ions having d^9 electron configurations. The reduced moment likely results from antiferromagnetic interactions between the Cu ions that arise from exchange coupling through both the O1 atoms and the bridging orthoborate groups. Exchange interactions in di-μ-hydroxo-bridged copper(II) molecular dimers have been found to be sensitive to the Cu–O–Cu bridge angle (*12*, *13*). The Cu–O1–Cu angle in the borate is 97.7(2)°. In a hydroxo dimer this value would afford the small singlet–triplet splitting of $-12\ cm^{-1}$.

TABLE III

SELECTED DISTANCES (Å) and Angles (°) for $SrCu_2(BO_3)_2$

Sr–O2 × 4	2.608(4)	O2–Sr–O2	79.12(8)
Sr–O2 × 4	2.640(4)	O2–Sr–O2	66.34(4)
		O2–Sr–O2	108.0(2)
Cu–O1 × 2	1.929(3)	O1–Cu–O1	82.2(2)
Cu–O2 × 2	1.947(3)	O2–Cu–O2	72.9(2)
		O1–Cu–O2	102.4(1)
		O1–Cu–O2	174.7(2)
B–O1	1.353(7)	O1–B–O2	122.9(2)
B–O2 × 2	1.379(4)	O2–B–O2	114.1(4)

Samples were heated at 10°C/min to 1050°C on the DTA; a strong signal at 970°C indicated decomposition of the sample. Inspection of the samples revealed that they had melted and changed color from blue to black. Analysis of X-ray powder patterns of the black product revealed only peaks attributable to CuO, a result of incongruent melting. After reduction of the CuO to Cu metal under flowing H_2, the X-ray pattern exhibits only peaks attributable to Cu metal. Thus, the strontium borate remains amorphous throughout the heat treatment.

A primary concern in processing catalytic materials is maximizing the surface area of the active component. Results from previous studies have indicated that very active Cu catalysts can be produced from decomposition of a single-phase Cu–Zn mixed basic carbonate (*14*) which affords finely dispersed CuO.

The title compound also decomposes to

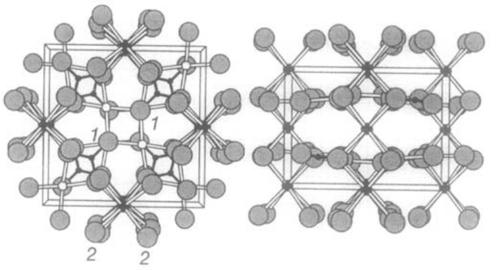

FIG. 1. (Left) sketch of structure viewed along [001]. (Right) sketch of structure viewed along [100]. The Sr atoms are represented as small filled circles with open bonds, Cu atoms as small open circles with open bonds, B atoms as small filled circles with filled bonds, and O atoms as large shaded circles. The labels 1 and 2 refer to atoms O1 and O2, respectively.

finely divided CuO which can be reduced to Cu metal. We used Scherrer's equation (1)

$$L_{hkl} = 0.89\lambda/\beta_{hkl} \cos \theta \qquad (1)$$

to determine the crystallite size of the products CuO and Cu; L_{hkl} is the particle dimension, λ is the radiation wavelength, and β_{hkl} is the difference in peak widths (radians) at half height between the sample and the internal standard NaCl (*15*), the standard having a crystallite dimension much greater than 2000 Å. It is assumed in Eq. (1) that peak broadening arises only from crystallite size and not from lattice distortions or stresses. Heating the title compound for 30 min at 1050°C afforded a sample of CuO with a mean crystallite dimension of 320 Å as measured by the widths of the $(11\bar{1})$–(002), (111)–(200), and $(20\bar{2})$ reflections. Subsequent heating at 300°C in 5% H_2/Ar for 3 hr resulted in Cu particles with an average dimension of 390 Å as determined from the widths of the (111), (200), and (220) reflections. Assuming that the Cu crystallite morphology is spherical, this size corresponds to a Cu surface area of 17 m^2/g. This value compares with surface areas of 38–77 m^2/g for mixed Cu–Zn oxides prepared from hydroxycarbonate precursors as determined by BET methods (*16*). Although the quantitative results from the Scherrer method are probably not highly accurate, the results do indicate that small particles are produced since annealed samples of CuO and Cu metal afford little broadening of the measured X-ray diffraction peaks.

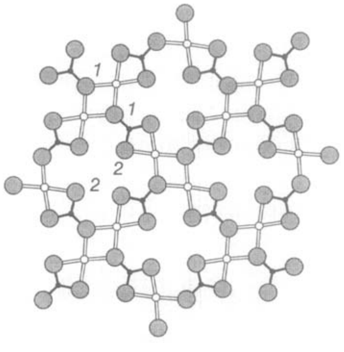

FIG. 2. Sketch of a portion of the Cu–B–O network parallel to the (001) plane.

Attempts to synthesize Ni and Pd analogs of the Cu compound were unsuccessful. Solid state reactions, coprecipitation methods, and freeze-drying techniques resulted in the mixtures SrB_2O_4 + 2 NiO and SrB_2O_4 + 2 Pd metal.

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References

1. G. C. CHINCHEN, P. J. DENNY, D. G. PORTER, G. D. SHORT, M. S. SPENCER, K. C. WAUGH, AND D. A. WHAN, *Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem.* **29**, 178 (1984); F. MARSCHNER AND F. W. MOELLER, *in* "Applied Industrial Catalysis" (B. E. Leach, Ed.), Vol. 2, p. 215, Academic Press, New York (1983); A. V. STILES, *AIChE J.* **23**, 362 (1987).

2. E. OTSUKA, T. TAKAHASHI, N. HASHIMOTO, AND F. MATSUDA, *Chem. Econ. Eng. Rev.* **7**(4), 29 (1975).

3. *TEXSAN*, Molecular Structure Corp., The Woodlands, TX (1985).

4. E. R. Howells, D. C. Phillips, and D. Rodgers, *Acta Crystallogr.* **3,** 210 (1950).
5. N. Walker and D. Stuart, *Acta Crystallogr., Sect. A* **24,** 214 (1968).
6. L. N. Mulay and E. A. Boudreaux, "Theory and Applications of Molecular Diamagnetism," pp. 306–307, Wiley, New York (1976).
7. R. W. Smith, Ph.D. dissertation, Oregon State University (1989).
8. R. W. Smith and D. A. Keszler, *J. Solid State Chem.* **81,** 305 (1989).
9. R. W. Smith and D. A. Keszler, *Acta Crystallogr., Sect. C* **46,** 370 (1990).
10. A. F. Wells, "Structural Inorganic Chemistry," 4th ed., p. 862, Oxford Univ. Press (Clarendon), Oxford (1975).
11. R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B* **25,** 925 (1969).
12. W. E. Hatfield, *in* "Magneto-Structural Correlations in Exchange-Coupled Systems" (R. D. Willey, O. Kahn, and D. Gatteschi, Eds.), *NATO ASI Ser.*, p. 555, Plenum, New York (1985), and references sited therein.
13. P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.* **97,** 4884 (1975).
14. G. Petrini, A. Bossi, and F. Garbassi, *Stud. Surf. Sci. Catal.* **16,** 735 (1983).
15. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures," p. 689, Wiley, New York (1974).
16. G. Moretti, G. Fierro, M. Lo Jacono, and P. Porta, *Surf. Interface Anal.* **14,** 325 (1989).