JOURNAL OF SOLID STATE CHEMISTRY **133,** 572–575 (1997)
ARTICLE NO. SC977515

BRIEF COMMUNICATION

Synthesis and Crystal Structure of $La_2Cu(SeO_3)_4$

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Received November 6, 1996; in revised form June 12, 1997; accepted June 23, 1997

Synthetic $La_2Cu(SeO_3)_4$ is built up from infinite anionic sheets of square-planar CuO_4 and pyramidal SeO_3 groups, connected *via* Cu–O–Se bonds. Ten-coordinate La^{III} species and a second selenite group complete the structure. $La_2Cu(SeO_3)_4$ is isostructural with $Bi_2Cu(SeO_3)_4$-II. Crystal data: $La_2Cu(SeO_3)_4$, M_r = 849.19, monoclinic, space group $P2_1/c$ (No. 14), a = 10.512(1) Å, b = 7.136(1) Å, c = 8.431(1) Å, β = 110.610(8)°, V = 591.9(2) Å^3, Z = 2, $R(F)$ = 2.89%, $R_w(F)$ = 2.89% [899 observed reflections with $I > 3\sigma(I)$].

INTRODUCTION

Copper and selenium, in combination with oxygen, are interesting candidates for new framework compounds built up from polyhedral units. Both elements have more than one stable oxidation state and copper has a substantial degree of flexibility in its coordination preference. Conversely, selenium(IV) always shows a distinctive pyramidal coordination geometry (1–3) as the selenite [SeO_3^{2-}] group. A hydrothermal investigation of the barium/copper/selenite system (4) revealed a striking number of different phases. In this paper we report the hydrothermal synthesis and single-crystal structure of $La_2Cu(SeO_3)_4$. This phase is isostructural with $Bi_2Cu(SeO_3)_4$-II (5).

EXPERIMENTAL

$La_2Cu(SeO_3)_4$ was prepared from the hydrothermal reaction of 5.855 g $La(NO_3)_3$, 3.404 g $Cu(NO_3)_2 \cdot 5H_2O$, and 1.999 g SeO_2. The solid components were sealed with 10 cc of water in a 23-cc capacity Teflon-lined stainless steel bomb and heated to 150°C for 72 h, followed by removal from the oven and cooling in air. Upon opening the bomb, a mass of brilliant blue rods of $La_2Cu(SeO_3)_4$ of maximum linear dimension ~ 0.5 mm were recovered by vaccum filtration and drying in air. Thermogravimetric analysis (ramp at 5°C/min to 1000°C in flowing O_2 atmosphere) was carried out on a Rigaku Thermoflex instrument.

The crystal structure of $La_2Cu(SeO_3)_4$ was established from single-crystal diffraction data: rod, $\sim 0.08 \times 0.08 \times 0.4$ mm; Siemens P4 diffractometer; $2^\circ < 2\theta < 60^\circ$; hkl limits $-6 \rightarrow 6$, $0 \rightarrow 9$, $-14 \rightarrow 14$; empirical absorption correction from ψ scans (min., max. equivalent transmission factors = 0.035, 0.107); R_{int} = 8.5% (Table 1). During data reduction, the setting of the unit cell was transformed from space group $P2_1/a$ to the standard setting of $P2_1/c$ (No. 14). Because of the similarity between $La_2Cu(SeO_3)_4$ and $Bi_2Cu(SeO_3)_4$-II (*vide infra*), starting coordinates for the atoms in $La_2Cu(SeO_3)_4$ were taken from Ref. (5), with La substituting for Bi. Refinement with CRYSTALS (6) proceeded satisfactorily to convergence. The low-angle 00l reflections showed a systematic $F_{obs} < F_{calc}$ trend, probably due to extinction. Supplementary crystallographic data are available from the authors.

RESULTS AND DISCUSSION

Crystal structure. Final atomic positional and thermal parameters for $La_2Cu(SeO_3)_4$ are listed in Table 2, with selected geometrical data in Table 3. $La_2Cu(SeO_3)_4$ is the first well-characterized lanthanum copper selenite and is isostructural with $Bi_2Cu(SeO_3)_4$-II (5). $La_2Cu(SeO_3)_4$, which has layered character with respect to Cu–O–Se bonds, is built up from irregularly coordinated lanthanum cations, square planar CuO_4 groups, and pyramidal SeO_3 groups. A fragment of the $La_2Cu(SeO_3)_4$ structure and atom labeling scheme is illustrated using CAMERON (7) in Fig. 1.

The lanthanum cation in $La_2Cu(SeO_3)_4$ is coordinated by ten oxygen atoms within 3 Å in irregular geometry (d_{av}[La(1)–O] = 2.622(3) Å). The bond valence sum (BVS) (8) for La is 3.11 (expected value, 3.00). In $Bi_2Cu(SeO_3)_4$-II, the corresponding Bi^{III} cation shows a sterically active lone

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0022-4596/97 $25.00

TABLE 1
Crystallographic Parameters for $La_2Cu(SeO_3)_4$

Empirical formula	$Se_4La_2CuO_{12}$
Formula weight	849.19
Crystal system	Monoclinic
a(Å)	10.512 (1)
b(Å)	7.136 (1)
c(Å)	8.431 (1)
β (deg)	110.610 (8)
V (Å^3)	591.9 (2)
Z	2
Space group	$P2_1/c$ (No. 14)
T(°C)	25 (2)
λ (Mo$K\alpha$) (Å)	0.71073
ρ_{calc} (g/cm^3)	4.76
μ (cm^{-1})	211.4
Total data	3191
Observed data[a]	899
Parameters	89
min., max. $\Delta\rho$ (e/Å^3)	-1.3, $+1.6$
$R(F)$[b]	2.82
$R_w(F)$[c]	2.87

[a] $I > 3\sigma(I)$ after data merging to 1213 reflections.
[b] $R = 100 \times \sum ||F_o| - |F_c|| / \sum |F_o|$.
[c] $R_w = 100 \times [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ with $w_i = 1/\sigma^2(F)$.

TABLE 2
Atomic Positional/Thermal Parameters for $La_2Cu(SeO_3)_4$

Atom	x	y	z	U_{eq}[a]
La(1)	0.41375 (5)	0.16865 (8)	0.26353 (6)	0.0108
Cu(1)	0	0	0	0.0210
Se(1)	0.12612 (8)	0.1644 (2)	0.3718 (1)	0.0189
Se(2)	0.31079 (8)	0.6797 (1)	0.3689 (1)	0.0119
O(11)	0.0531 (9)	0.378 (1)	0.3322 (9)	0.0495
O(12)	0.1437 (6)	0.1266 (9)	0.1797 (8)	0.0185
O(13)	0.2910 (6)	0.2136 (9)	0.4721 (7)	0.0183
O(21)	0.3792 (6)	0.5161 (9)	0.2806 (7)	0.0178
O(22)	0.3464 (7)	0.6134 (9)	0.5707 (8)	0.0214
O(23)	0.4388 (6)	0.8448 (8)	0.4072 (7)	0.0134

[a] U_{eq}(Å^2) = $\frac{1}{3}[U_1 + U_2 + U_3]$.

pair of electrons and is nine coordinated by O atoms within 3.2 Å in [4 + 5] geometry (5) with d_{av}[Bi–O] = 2.58 Å. The copper atom [site symmetry $\bar{1}$, d_{av}[Cu(1)–O] = 1.921(4) Å] in $La_2Cu(SeO_3)_4$ is in square planar geometry with respect to its four O atom neighbors (Fig. 2), each of which also makes a linkage to a selenium atom (θ_{av}[Cu–O–Se] = 120.2°). There are no further Cu ⋯ O contacts within 3 Å. The two distinct Se^{IV} atoms show their characteristic pyramidal geometry (1, 2) with respect to their three oxygen atom neighbors (the fourth tetrahedral vertex of Se is assumed to be occupied by an unobserved lone pair of electrons) with d_{av}[Se(1)–O] = 1.689(5) Å, BVS[Se(1)] = 4.17, d_{av}[Se(2)–O] = 1.696(4) Å, and BVS[Se(2)] = 4.09. Two out of three O atoms of the Se(1)O_3 group make Se–O–Cu bonds, whereas the Se(2)O_3 group does not participate in

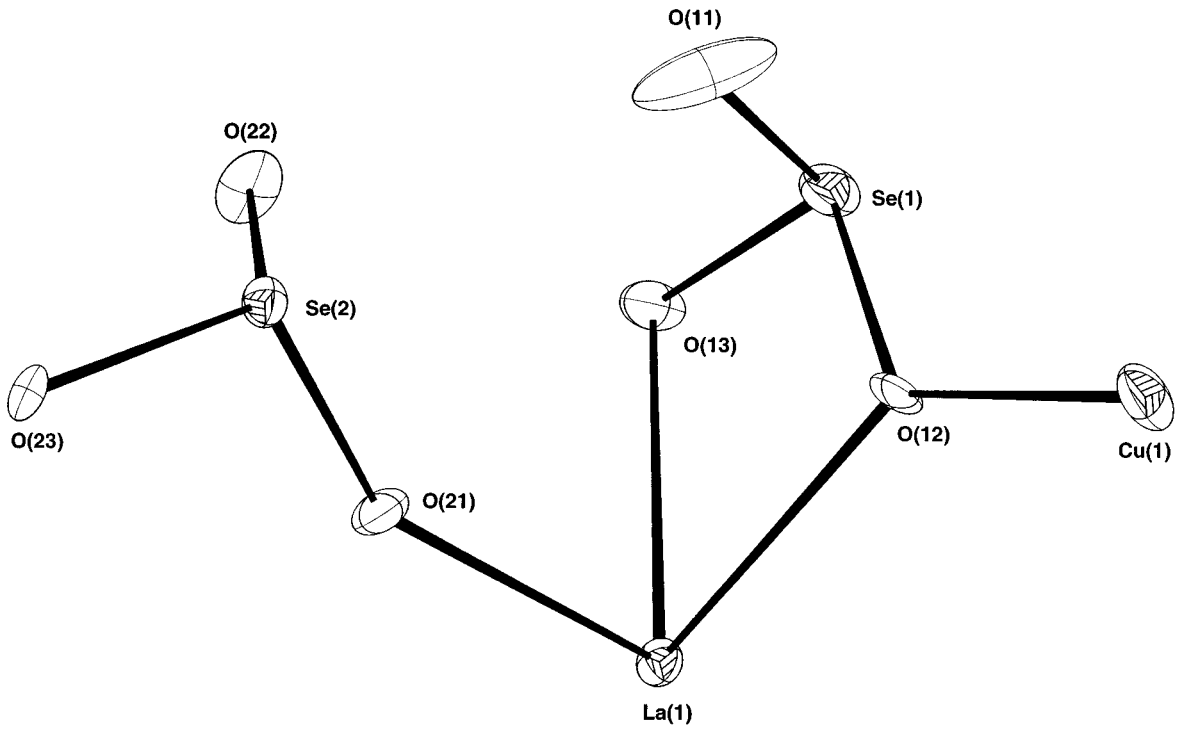

FIG. 1. CAMERON view of the building unit of $La_2Cu(SeO_3)_4$ showing the atom labeling scheme (50% thermal ellipsoids).

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $La_2Cu(SeO_3)_4$

La(1)–O(12)		2.690(6)	La(1)–O(13)		2.541(6)
La(1)–O(13)		2.485(6)	La(1)–O(21)		2.517(7)
La(1)–O(21)		2.575(6)	La(1)–O(22)		2.872(7)
La(1)–O(22)		2.527(7)	La(1)–O(23)		2.579(6)
La(1)–O(23)		2.662(6)	La(1)–O(23)		2.762(6)
Cu(1)–O(11)	×2	1.904(7)	Cu(1)–O(12)	×2	1.945(6)
Se(1)–O(11)		1.687(8)	Se(1)–O(12)		1.715(6)
Se(1)–O(13)		1.677(6)	Se(2)–O(21)		1.677(6)
Se(2)–O(22)		1.676(6)	Se(2)–O(23)		1.731(6)
O(11)–Cu(1)–O(11)		180	O(11)–Cu(1)–O(12)		89.1(3)
O(11)–Cu(1)–O(12)		90.9(3)	O(11)–Se(1) – O(12)		98.5(3)
O(11)–Se(1)–O(13)		103.2(4)	O(12)–Se(1) – O(13)		94.2(3)
O(21)–Se(2)–O(22)		106.0(3)	O(21)–Se(2) – O(23)		97.5(3)
O(22)–Se(2)–O(23)		97.0(3)	Cu(1)–O(11) – Se(1)		119.9(4)
Cu(1)–O(12)–Se(1)		119.8(3)			

any Se–O–Cu bridges. All the oxygen atoms except O(11) bond to the lanthanum cation.

The polyhedral connectivity of the $Cu(1)O_4$ and $Se(1)O_3$ units in $La_2Cu(SeO_3)_4$ leads to a layered *motif*, in which puckered anionic sheets of stoichiometry $[Cu(SeO_3)_2]^{2-}$ propagate normal to [100] (Fig. 2). Eight-ring "windows" (i.e., a loop consisting of eight nodal Cu and Se atoms) are formed, with the CuO_4 and SeO_3 polyhedra alternating around each ring. Similar Cu/Se/O sheets (with a protonated selenite group) have been seen in $Cu(HSeO_3)_2$ (1) and $Cu(HSeO_3)_2 \cdot H_2O$ (9). $[Cu(SeO_3)_2]^{2-}$ sheets with a different connectivity have been observed in $BaCu(SeO_3)_2$-I and $BaCu(SeO_3)_2$-II (4). Lanthanum cations and a second SeO_3 group complete the $La_2Cu(SeO_3)_4$ structure [compare Fig. 2 of Ref. 5]. This second component of the structure might be regarded as a cationic $[La_2(SeO_3)_2]^{2+}$ sheet to charge balance the anionic $[Cu(SeO_3)_2]^{2-}$ layers; the layers are actually connected by Se–O–La bonds. Both edge and triangular-face sharing linkages are apparent between the LaO_{10} polyhedra and both the SeO_3 groups make an edge-shared linkage to the lanthanum species. Similar crystallochemical behavior for the La/SeO_3 combination was seen in $LaH(SeO_3)_2$ (3). When the structure of $La_2Cu(SeO_3)_4$ is viewed down [001], small voids are apparent in the regions between the $[Cu(SeO_3)_2]^{2-}$ and $[La_2(SeO_3)]^{2+}$ sheets. The presumed lone pairs of the Se(2) atom project into these spaces.

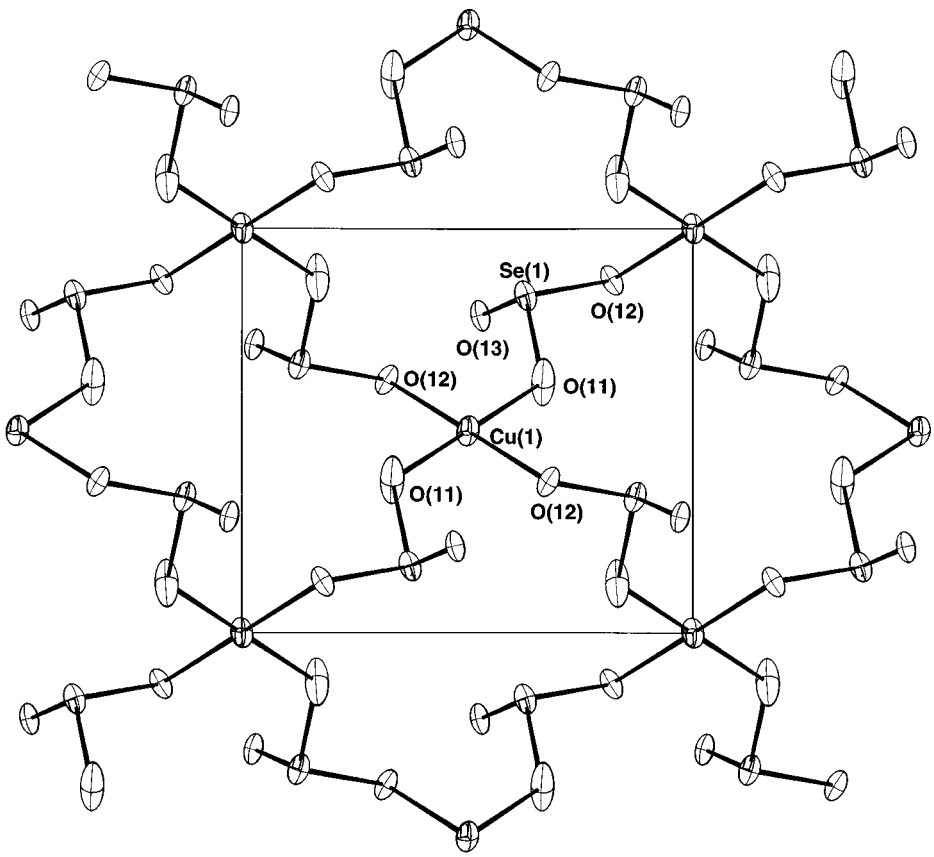

FIG. 2. View of a slice of the $La_2Cu(SeO_3)_4$ structure normal to [100] ($-0.3 < x < 0.3$) showing the $Cu(SeO_3)_2$ sheets, formed from 8-ring windows of alternating copper and selenium-centered units.

Physical data. TGA data for $La_2Cu(SeO_3)_4$ revealed thermal stability until $\sim 600°C$, then a weight loss of $\sim 50\%$ in three broad but discernible steps to 1000°C, the maximum operating temperature of the instrument. The expected percentage weight loss for the decomposition reaction $La_2Cu(SeO_3)_4$ (s) $\rightarrow La_2CuO_4$ (s) + 4 SeO_2 (g) is 52.3%, suggesting that decomposition is incomplete at 1000°C, which represents an unusual degree of thermal stability for Se(IV) containing materials.

ACKNOWLEDGMENTS

We thank Lakshitha Hannooman, Dave Faithfull, and Tony Littler for assistance. This work is financially supported by the Australian Research Council.

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