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Synthesis and Characterization of Two New Cu(III) Compounds: $Ba_4LiCuO_4(CO_3)_2$ and $Ba_4NaCuO_4(CO_3)_2$

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Large single crystals of a new oxide–carbonate, $Ba_4NaCuO_4(CO_3)_2$, were grown in a $Ba(OH)_2$–$BaCl_2$ flux. Through the use of single crystal X-ray methods, it was found that the compound has $I4/mmm$ Laue symmetry. The structure was refined in the space group $I\bar{4}2m$: $a = 5.8322(6)$ Å, $c = 15.3712(9)$ Å, $Z = 2$, $R = 2.96\%$, and $R_w = 3.45\%$. The copper is present in the compound in isolated CuO_4 square planar units with short Cu–O distances of 1.85 Å. The stoichiometry, as determined from the crystal structure, and the short Cu–O distances suggest a formal oxidation state of Cu(III). Confirmation of this assignment was obtained by magnetic measurements which indicate that the compound is diamagnetic. $Ba_4LiCuO_4(CO_3)_2$ was prepared also and found to be isomorphous: $a = 5.7612(9)$ Å, and $c = 15.271(1)$ Å.

Introduction

Cuprates with mixed-valent copper in a formal oxidation state between Cu(II) and Cu(III) have attracted attention recently because several classes of these oxides are high temperature superconductors. In order to gain a better understanding of the electronic properties of these cuprates, it is important to have good model compounds for Cu(II) and Cu(III) coordinated to oxygen. For example, such model compounds are needed as standards for measurements of the oxidation state of copper in various mixed-valent cuprates by K-edge X-ray absorption spectroscopy. An "ideal" standard is a stoichiometric compound with isolated square-planar CuO_4 units; if the CuO_4 square planes are edge-shared or corner-shared, interactions between copper atoms will complicate the analysis. In addition, it is important that the model compound can be prepared as large single crystals, preferably under ambient conditions. We report here the synthesis and characterization of a new compound containing Cu(III) in isolated CuO_4^{-5} units: $Ba_4NaCuO_4(CO_3)_2$. $Ba_4LiCuO_4(CO_3)_2$ was prepared also and found to be isomorphous.

As discussed below, these two new copper oxide–carbonates have been crystallized from a $Ba(OH)_2$–$BaCl_2$ flux in an ambient atmosphere. Large plate-like crystals up to 1 cm across grew on the surface of the melt and were isolated easily. The structure was solved through the use of single crystal X-ray diffraction methods, and the oxidation state was verified by magnetic measurements.

Experimental Procedures

A mixture of 0.5 g of CuO, 0.33 g of Na_2CO_3, and 1.9 g of $BaCO_3$ was added to

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14.0 g of $Ba(OH)_2$ and 2.5 g of $BaCl_2 \cdot 2H_2O$. The anhydrous $Ba(OH)_2$ was used as purchased from Fisher Scientific, and the $BaCl_2 \cdot 2H_2O$ was dried at 110°C before use. The powders were mixed intimately, packed in a 20 ml silver crucible with a tightly-fitting lid, and placed in the furnace. The furnace was heated from room temperature to 750°C over 2.5 hr, held at 750°C for 5 hr, and cooled gradually to 600°C over 36 hr. The crucible was then removed and placed in a dry nitrogen atmosphere, in which all manipulations took place. The crystals formed a thick layer on the surface of the solidified melt, and were isolated mechanically. Any flux remaining on the crystals was removed by ultrasonic cleaning in absolute methanol. The crystals were a deep red color, but transparent when cut thinly, and were moisture-sensitive. $Ba_4LiCuO_4(CO_3)_2$ was prepared by similar methods by substituting Li_2CO_3 for Na_2CO_3. The potassium analog could not be prepared.

Magnetic measurements were obtained for the temperature range of 2.0 to 300 K in fields of 5 to 50 kG using a Quantum Design MPMS SQUID magnetometer. Data were corrected for the diamagnetism due to the Kel-f (polychlorotrifluoroethylene) container.

Crystal Structure Determination

Precession photos of single crystals of $Ba_4NaCuO_4(CO_3)_2$ showed $I4/mmm$ Laue symmetry, with no other systematic absences. Single crystal intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (*1*). Mo $K\alpha$ radiation and a monochromator of highly-oriented graphite were used. Automatic peak search and indexing procedures yielded a body-centered tetragonal cell which was used for all further work. Cell and data collection parameters are summarized in Tables I and II. The cell parameters were refined on the setting angles of 24 reflections with $2\theta > 36°$: $a = 5.8322(6)$ Å, and $c = 15.3712(9)$ Å. Precession photos of single crystals of $Ba_4LiCuO_4(CO_3)_2$ showed the same symmetry and intensity patterns as those of $Ba_4NaCuO_4(CO_3)_2$. The lattice parameters for the Li analog which were measured in an identical fashion to the Na compound are $a = 5.7612(9)$ Å and $c = 15.271(1)$ Å.

TABLE I

CRYSTAL PARAMETERS AT 25°C

$Ba_4NaCuO_4(CO_3)_2$

$a = 5.8322(6)$ Å
$b = 5.8322(6)$ Å
$c = 15.3712(9)$ Å
$\alpha = \beta = \gamma = 90°$
$V = 522.8(1)$ Å^3
$\mu(\text{calc.}) = 169\ \text{cm}^{-1}$
Space Group: $I\bar{4}2m$ (No. 121)
Crystal size: 0.14 × 0.18 × 0.24 mm
Transmission coefficient = 1.0–0.84
Formula weight: 819.9 amu
$Z = 2$
$\rho(\text{calc}) = 5.21\ \text{g cm}^{-3}$
$g = 4.13(5) \times 10^{-6}$
$R(F^2) = 2.96\%$
$R_w(F^2) = 3.45\%$
$GOF = 1.58$

Intensities for 729 reflections were measured ($+h$, $+k$, $\pm l$; $3° > 2\theta > 55°$) at 25°C for a small piece of an as-grown crystal of $Ba_4NaCuO_4(CO_3)_2$ and converted to structure factor amplitudes and their esd's by correction for scan speed, background, and Lorentz and polarization effects (*2*). The crystal was sealed in a capillary to prevent decomposition due to moisture. Correction for absorption was based on the azimuthal data (*3*), which showed a variation $I_{\text{min}}/I_{\text{max}} = 0.84$ for the average curve. Averaging the redundant data yielded 349 unique reflections. The R-value of agreement (*4*) for the observed data based on intensity was 3.3% and on structure factors was 1.6%.

The structure was solved by Patterson methods and refined via standard least-

TABLE II

DATA MEASUREMENT PARAMETERS

Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)
Monochromator: Highly oriented graphite ($2\theta = 12.2°$)
Detector: Crystal scintillation counter with PHA
Reflections measured: $+h$, $+k$, $\pm l$
2θ range: $3° \rightarrow 55°$
Scan type: θ–2θ
Scan width: $\Delta\theta = 0.65 + 0.35 \tan(\theta)$
Scan speed: $1.1 \rightarrow 6.7$ (θ, °/min)
Background: Measured over $0.25(\Delta\theta)$ added to each end of the scan
Aperture to crystal: 173 mm
Vertical aperture: 3.0 mm
Horizontal aperture: $2.0 + 1.0 \tan(\theta)$ mm (variable)
Intensity standards: (5 1 0), ($\bar{1}$ 5 0), (0 0 16); measured every 0.67 hr of X-ray exposure time: over the data collection period, no decrease in intensity was observed.
Orientation: Checked every 200 reflections. The crystal did not need reorientation during data collection.

squares and Fourier techniques. $I\bar{4}2m$ is a chiral space group; both enantiomers were refined, and the one with the lower R-value is reported here. The heavier atoms were refined with anisotropic thermal parameters, while the oxygen and carbon atoms were refined isotropically. The occupancy of the barium site was fixed at 100%. The site occupancies of the other atoms were checked by allowing them to refine individually; none deviated by more than 3σ from full occupancy and thus were fixed also at 100%.

The final residuals for 21 variables refined against the 347 independent reflections were $R = 2.96\%$, $R_w = 3.45\%$, and $GOF = 1.58$. All the data were included in the refinement, except for two reflections; one had a negative $F_{\rm obs}$ and the other had very poor agreement. The final refinement cycle converged with a shift/error = 0.005. The largest peaks in the difference Fourier were $+2.5$ and -4.6 electrons/Å^3 and were located near atoms. The p-factor used to reduce the weight of the intense reflections was set to 0.03 in the final stages of refinement; weighting was based on counting statistics. The secondary extinction parameter g was refined also (5), giving a maximum correction, $gI_{\rm max}$, of 0.97. The analytical forms of the scattering factors for the neutral atoms were used (6), and all scattering factors were corrected for both the real and imaginary components of the anomalous dispersion (7). Table III contains the refined positional and thermal parameters. Selected bond lengths and angles are given in Tables IV and V, respectively. A listing of the values of F_o and F_c are available from the authors upon request.

Results and Discussion

Figure 1 shows one unit cell of $Ba_4NaCuO_4(CO_3)_2$. The CuO_4 units are isolated and the closest Cu–Cu distance is 5.83 Å. Because the Cu atom occupies a site of $\bar{4}2m$ symmetry, the oxygen atoms coordinated to it (O1) are free to distort from a square planar environment around copper to a tetrahedral geometry. However, the oxygen atoms are only 0.082(7) Å above and below the Cu atom, forming O–Cu–O angles of 174.9(5)° and 90.11(2)°. The fact that these four oxygen atoms remain essentially coplanar confirms the strong stereochemical preference of Cu(III) for square planar geometry. The four short 1.851(1)

TABLE III

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	X	Y	Z	B_{iso}	Occupancy
Ba	0.0	0.5	0.11703(2)	0.545(6)	1.0
Cu	0.0	0.0	0.5	0.28(1)	1.0
Na	0.0	0.0	0.0	1.03(5)	1.0
C	0.0	0.0	0.2326(5)	0.82(9)[a]	1.0
O1	0.2758(4)	0.2758(4)	0.0054(5)	0.42(5)[a]	1.0
O2	0.0	0.0	0.1503(3)	1.37(8)[a]	1.0
O3	0.8664(7)	−0.8664(7)	0.2742(3)	2.24(9)[a]	1.0

[a] These atoms were refined with isotropic thermal parameters.

Å Cu–O bonds are similar to those found in other Cu(III) oxides: 1.84 Å (×4) in $KCuO_2$ (*8*), 1.85 Å (×4) in $NaCuO_2$ (*9*), and 1.84 Å (×2) in Li_3CuO_3 (*10*). Cu(II) oxides generally have Cu–O bond lengths of ~1.95 Å (*11*).

The sodium atoms lie at the center of a nearly perfect octahedron of oxygen atoms. The two axial bonds to the carbonate oxygen atoms (O2) are 2.310(4) Å and the four equatorial oxygen atoms (O1), which are part of the CuO_4 square planes, are at a distance of 2.277(2) Å. The barium atoms have eight close contacts to oxygen in an irregular coordination geometry, with Ba–O distances ranging from 2.692(5) to 2.961(1) Å.

Magnetic measurements on single crystal and powdered samples show that both $Ba_4LiCuO_4(CO_3)_2$ and $Ba_4NaCuO_4(CO_3)_2$ are diamagnetic. Cu(III) in a square planar coordination environment has no unpaired electrons, whereas Cu(II) has a single elec-

TABLE IV

SELECTED BOND LENGTHS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom 1	Atom 2	Distance (Å)
Ba	O1 (×4)	2.692(5)
Ba	O2 (×2)	2.961(1)
Ba	O3 (×2)	2.823(3)
Cu	O1 (×4)	1.851(1)
Na	O1 (×4)	2.277(2)
Na	O2 (×2)	2.310(4)
C	O2	1.266(9)
C	O3 (×2)	1.274(5)

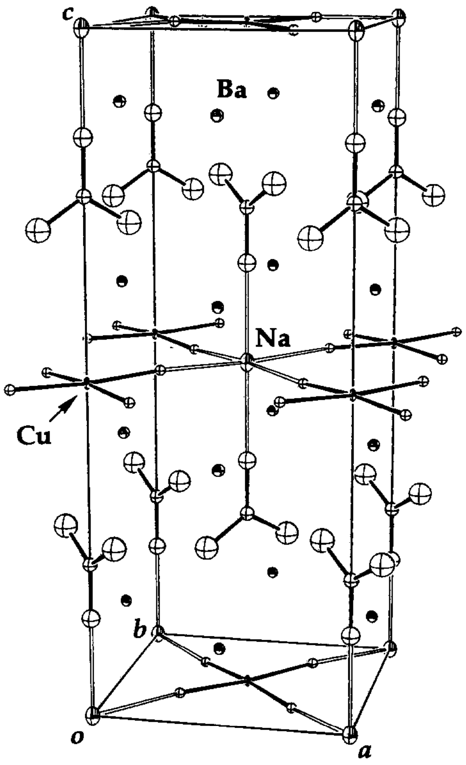

FIG. 1. Unit cell of $Ba_4NaCuO_4(CO_3)_2$. Cu–O and C–O bonds are shaded; Na–O bonds are unshaded.

TABLE V

SELECTED BOND ANGLES AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom 1	Atom 2	Atom 3	Angle (°)
O1	Cu	O1	174.9(5)
O1	Cu	O1	90.11(2)
O1	Na	O1	175.8(4)
O1	Na	O1	90.08(1)
O1	Na	O2	87.9(2)
O1	Na	O2	92.1(2)
O2	Na	O2	180
O2	C	O3	120.1(3)
O3	C	O3	119.7(7)

tron in the $d_{x^2-y^2}$ orbital and is paramagnetic.

These new materials represent the first examples of stoichiometric Cu(III) compounds with isolated CuO_4 square planes. Because they can be grown easily as large single crystals without the need for high pressures of oxygen, we believe they will be useful as a standard for the measurement of high oxidation states of copper.

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