*Inorg. Chem.* **1996,** *35,* 7919−7921

# $Ba_3CuBr_3(P_2O_7)$: The First Copper(I) Halide Pyrophosphate

**Kristen M. S. Etheredge,[†] Richard Mackay,[‡]
George L. Schimek,[‡] and Shiou-Jyh Hwu*,[‡]**

Departments of Chemistry, Rice University, P.O. Box 1892,
Houston, Texas 77251, and Clemson University,
Clemson, South Carolina 29634

*Received April 26, 1996*

## Introduction

Copper(I)-containing phosphate chemistry is a remarkably unstudied field. The vast majority of copper phosphates contain a $Cu^{2+}$ cation,(1) except for a few electronically distinct compounds: two mixed-valence Cu(I/II) phases, $Cu_2PO_4$,(2) and $Na_2Cu_4P_2O_9Cl$,(3) as well as the arsenate, $Pb_2Cu_8(AsO_4)_6)$,(4) and one copper(I) phosphate, $CuPO_3$.(5) The structure of $CuPO_3$, to our knowledge, has not been reported. Otherwise, these compounds all contain Cu−O−P−O−Cu and/or Cu−O−Cu covalent linkages.

A new barium copper(I) compound, $Ba_3CuBr_3P_2O_7$, has been synthesized in a molten halide reaction. The title compound has been made by incidental incorporation of Ba and Br from the flux. The structural analysis shows that there is no direct bond interaction between $Cu^+$ and $P_2O_7^{4-}$. An interesting precessional disorder with respect to the pyrophosphate groups is identified. In this report, the synthesis, structure, and infrared spectrum of $Ba_3CuBr_3P_2O_7$ are presented.

## Experimental Section

**Synthesis.** Single crystals of $Ba_3CuBr_3P_2O_7$ were grown from a eutectic flux of 40% $BaBr_3$ (Strem, minimum 95%) and 60% NaBr (Strem, 99+%), which has a melting point of 600 °C.(6) The reactants, CuO (Strem, 99.999%), $Cu_2O$ (Aldrich, 97%), and $P_2O_5$ (Aesar, 99.99%), were ground together in a 1:1:1 ratio and then ground in a 1:5 ratio with the flux. This mix was loaded into a carbon-coated quartz ampule and heated to 800 °C for 4 days, cooled at 2 °C/h to 600 °C, and then cooled at 50 °C/h to room temperature. The pale red crystals were isolated from the flux by the suction filtration method using deionized water.

**Structure Determination.** An irregularly-shaped plate crystal was mounted on a glass fiber for single-crystal X-ray diffraction study. The diffraction data were collected on a Rigaku AFC7R four-circle diffractometer. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters were determined by a least-squares fit of 25 peak maxima in the range $36° < 2\theta < 47°$. There was no detectable decay during data collection, according to the intensities of three standard reflections (−1,3,−1; 2,1,−1; 3,−2 ,−1), which were measured every 100 reflections. Lorentz-polarization and empirical absorption corrections based on three computer-chosen azimuthal scans ($2\theta = 11.58, 23.28, 35.23$) were applied to the intensity data. On the basis of intensity statistics, extinction conditions, and correct structure solution, a centrosymmetric space group $P6_3/m$ (No. 176) was chosen. The structure was solved by direct methods with SHELXS-86(7) and refined on $|F|$ with TEXSAN(8) by least-squares, full-matrix techniques.(9) A model of static precessional disorder with respect to the $P_2O_7$ group was proposed (see below) to resolve the distorted thermal ellipsoids for oxygen atoms. The structural and thermal parameters were refined to $R = 0.030$, $R_w = 0.042$, and GOF = 3.39. Figures were drawn with SHELXTL-PLUS.(10) Table 2 lists the final positional and thermal parameters.

**Table 1.** Crystallographic Data for $Ba_3CuBr_3(P_2O_7)$

| | | | |
|---|---|---|---|
| chemical formula | $Ba_3CuBr_3(P_2O_7)$ | fw | 889.23 |
| *a*, Å | 10.1610 (8) | space group | $P6_3/m$ (No. 176) |
| *c*, Å | 7.044(2) | *T*, K | 155 |
| *V*, Å$^3$ | 629.9(1) | $\lambda$, Å | 0.710 73 |
| Z | 2 | $\rho_{calcd}$, g cm$^{-3}$ | 4.30 |
| R[a] | 0.030 | linear abs coeff, cm$^{-1}$ | 178.08 |
| $R_w$[b] | 0.042 | | |

[a] $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. [b] $R_w = [\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2]^{1/2}$.

**Table 2.** Positional and Equivalent Displacement Parameters for $Ba_3CuBr_3(P_2O_7)$

| atom | x | y | z | $B_{eq}$ (Å$^2$)[a] |
|---|---|---|---|---|
| Ba | 0.04523(6) | 0.39441(6) | 1/4 | 1.81(2) |
| Cu | 0 | 0 | 1/4 | 3.08(7) |
| Br | 0.2461(1) | 0.2417(1) | 1/4 | 1.81(3) |
| P | 1/3 | 2/3 | 0.9613(4) | 0.99(6) |
| O(1)[b] | 0.609(2) | 0.259(2) | 1/4 | 1.0(5) |
| O(2)[b] | 0.355(2) | 0.545(2) | 0.076(2) | 1.0(5) |
| O(3)[b] | 0.370(1) | 0.543(1) | −0.015(1) | 1.4(3) |

[a] Equivalent isotropic thermal parameters defined as $B_{eq} = (8\pi^2/3)$ trace *U*. [b] Multiplicity of O(1) and O(2) fixed at 1/3. Multiplicity of O(3) fixed at 2/3. See text.

**Infrared Spectroscopy.** The infrared absorption spectra of $Ba_3CuBr_3(P_2O_7)$ were studied in the range of 1600−400 cm$^{-1}$ and recorded on a Perkin-Elmer 1600 Series FTIR spectrometer with 16 scans and 2.0 cm$^{-1}$ increments. The samples for this study were selected single crystals which were ground with KBr and pressed into disks. The results were consistent with what would be expected on the basis of the X-ray structure. The spectrum shows bands at 935.5 and 720.0 cm$^{-1}$, which correspond to the P−O−P $\upsilon_a$ and $\upsilon_s$, respectively. There are also several bands in the 1150−1000 and 600−400 cm$^{-1}$ regions for the $\upsilon$(P−O) and $\delta$(O−P−O).(11)

## Results and Discussion

Figure 1 shows the unit cell of $Ba_3CuBr_3(P_2O_7)$ viewed along the c axis. The copper(I) cation coordinates to bromine in a regular trigonal planar arrangement. This is not an uncommon geometry for $Cu^+$ cations and can also be seen in $K[Cu(CN)_2]$.(12) The phosphorus atoms reside in a $P_2O_7$ configuration with O(1) as the bridging oxygen. The P−O(1)−P bridging angle is 131°, which is at the large end of the bond angle range adopted by the pyrophosphate groups.(13) The bonds to the barium cation

---

[†] Rice University.

[‡] Clemson University.

(1) See, for example: (a) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 1495. (b) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 3123. (c) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 1474 and references therein.

(2) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 5013.

(3) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 5278.

(4) Effenberger, H. *J. Solid State Chem.* **1995**, *114*, 413.

(5) Ball, M. C. *J. Chem. Soc.* **1968**, 1113.

(6) Levin, E. M.; Robbins, C. R.; McMurdie, H. F. *Phase Diagrams for Ceramists*; The American Chemical Society, Inc.: Columbus, OH, 1964; Figure 1243.

(7) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: London/New York, 1985; pp 175−189.

(8) (a) TEXSAN: Single Crystal Structure Analysis Software, Version 1.6b, Molecular Structure Corp., The Woodlands, TX, 1993. (b) Cromer, D. T.; Waber, J. T. Scattering Factors for Non-hydrogen Atoms. In *International Tables for X-ray Crystallography*; Kyroch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71−98.

(9) Busing, W. R.; Martin, K. O.; Levy, H. A. ORFLS, A FORTRAN Crystallographic Least Squares Program, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1962.

(10) Sheldrick, G. M. SHELXTL-PLUS: Siemens XRD, Madison, WI.

(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons, Inc.: New York, 1986.

(12) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons, Inc.: New York, 1988; p 756.

(13) (a) Cruickshank, D. W. *J. Chem. Soc.* **1961**, 5486. (b) Etheredge, K. M. S. Ph.D. Dissertation, Rice University, 1996.

S0020-1669(96)00461-2 CCC: $12.00

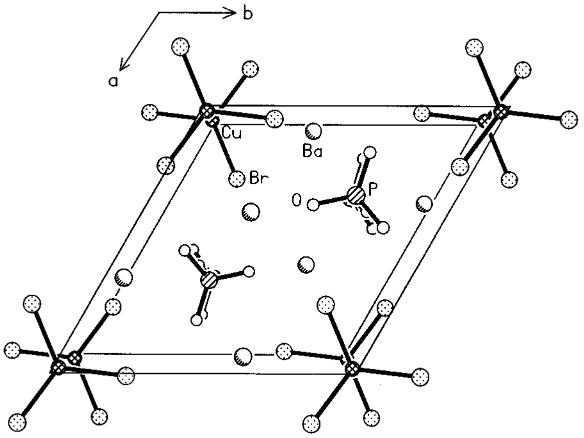

**Figure 1.** Projected view of the $Ba_3CuBr_3(P_2O_7)$ structure along the *c* axis. The $CuBr_3$ and $P_2O_7$ coordination geometries are outlined by thick lines; the Ba−(O,Br) bonds are omitted for clarity.

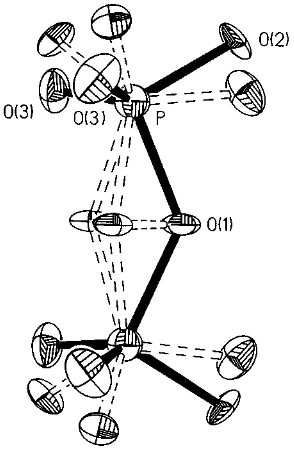

**Figure 2.** ORTEP drawing of the disordered $[P_2O_7]$ structure. The bent geometry of the pyrophosphate is outlined by solid lines (see text). The anisotropic thermal ellipsoids are drawn in 70% probability.

have not been drawn in this figure for clarity, but it resides in a $BaO_5Br_4$ geometry, which will be discussed in more detail later. The barium cation has the function of holding the isolated $CuBr_3$ and $P_2O_7$ groups in position and linking them together in the structure.

The pyrophosphate group shows an interesting static precessional disorder with respect to the 3-fold axis along the P−P vector. The bridging oxygen of the pyrophosphate group is randomly disordered over three sites on a triangular plane. Fourier maps through the plane of the bridging oxygen show this disorder (available in Supporting Information). In conjunction with the disorder of the bridging oxygen, the terminal oxygens are disordered to give different possible canting of the tetrahedra, as illustrated in Figure 2. When the bridging oxygen is at position O(1), the tetrahedra outlined in solid lines join to the corresponding occupied sites on the terminal oxygens. Each bridging site is one-third occupied. In a corresponding manner, each O(2) site is one-third occupied, and each O(3) site is two-thirds occupied. Occupancies were fixed at these ratios for all refinements.

Table 3 lists important bond distances and angles that describe the geometries of the $CuBr_3$ and $P_2O_7$ polyhedra. The $CuBr_3$ trigonal plane has three equivalent Cu−Br bond distances of 2.36 Å. Since there is no direct comparison with other three-coordinated copper(I) bromide, intuitively, this bond distance is reasonable in comparison with 2.46 Å for the four-coordinated copper(I) bromide in the zinc blende-type CuBr.[14] The $P_2O_7$ polyhedron has bond distances for the terminal oxygens, O(2) and O(3), of 1.58 and 1.49 Å, respectively, which are close to 1.52 Å, the sum of Shannon crystal radii for $P^{5+}$ (0.31 Å) and $O^{2-}$ (1.21 Å).[15] The bond distances to a bridging oxygen atom are typically longer than 1.52 Å. It is the same in this case, where the P−O(1) distance is 1.64 Å. These inhomogeneous bond distances can be qualitatively justified by the electrostatic interaction that each oxygen in the $P_2O_7$ unit undergoes with the equation given by Baur.[16] The analysis procedures are the same as those previously reported.[17] The resulting P−O bond distances ($d_{calc}$, Å), based on the bond strength that each cation contributes ($Ba^{2+}$, $P^{5+}$) to the coordinated oxygen atoms, are compared to the observed values in Table 4. The values of $|\Delta d|$ in Table 4 are slightly large compared to those reported previously,[17] which may be associated with the errors in estimating the electrostatic interaction of the disordered oxygen atoms.

**Table 3.** Important Bond Distances (Å) and Angles (deg) for $Ba_3CuBr_3(P_2O_7)$

| | | | |
|---|---|---|---|
| | $CuBr_3$ | | |
| Cu−Br | 2.3575(9) (3×) | Br−Cu−Br | 120 (3×) |
| | $P_2O_7$ | | |
| P−O(1) | 1.638(7) | O(1)−P−O(3) | 108.4(7) |
| P−O(2) | 1.58(2) | O(2)−P−O(3) | 107.9(7) |
| P−O(3) | 1.486(8) (2×) | O(2)−P−O(3) | 115.3(7) |
| O(1)−P−O(2) | 96.2(7) | O(3)−P−O(3) | 118.7(1) |
| O(1)−P−O(3) | 107.9(6) | P−O(1)−P | 131(1) |
| | $BaO_5Br_4$ | | |
| Ba−Br | 3.292(1) | 7-oxygen coordination[a] | |
| Ba−Br | 3.351(1) | Ba−O(1) | 2.89(2) |
| Ba−Br | 3.8059(9) (2×) | Ba−O(2) | 3.20(1) (2×) |
| 4-oxygen coordination[a] | | Ba−O(3) | 2.79(7) (2×) |
| Ba−O(3) | 2.681(8) (2×) | Ba−O(2) | 2.99(1) (2×) |
| Ba−O(2) | 2.54(1) (2×) | | |

[a] Coordination number is chosen on the basis of the two extreme static orientations of the pyrophosphate group.

**Table 4.** Observed and Calculated P−O Distances in $Ba_3CuBr_3(P_2O_7)$

| anion | $\rho_o$ | $\Delta\rho_o$ | $d_{obs}$(Å) | $d_{calc}$(Å) | $\|\Delta d\|$ |
|---|---|---|---|---|---|
| P(1)−O(1) | 2.72 | 0.66 | 1.64 | 1.61 | 0.03 |
| P(1)−O(2) | 2.13 | 0.07 | 1.58 | 1.54 | 0.04 |
| P(1)−O(3) (2×) | 1.69 | -0.37 | 1.49 | 1.50 | 0.01 |

[a] $\rho_o$ is the sum of the cation contributions for the bond interactions of a particular oxygen atom. $\Delta\rho_o$ is the difference between $\rho_x$ ((no. of positive charges)/ C.N.) of one individual oxide and the mean $\rho_o$ of all oxides in the coordination polyhedron. $d_{obs}$ (Å) is the observed P−O distance in the title compound. $d_{calc}$(Å) is the calculated bond distance from Baur's equation: $d_{calc}$ (Å) = 1.537 + 0.109$\Delta\rho_o$. Finally, $|\Delta d|$ is the difference between $d_{obs}$ (Å) and $d_{calc}$(Å). [b] The valences of the coordinated cations used in the above calculations are the following: $Ba^{2+}$ and $P^{5+}$. These cations contribute bond strengths, $\rho_x$, of 0.22, and 1.25, respectively.

The average coordination around barium is nine-coordinate $BaO_5Br_4$. The local coordination around a given barium atom can range from four to seven oxygen atoms, depending on the orientation of the surrounding pyrophosphate groups (Table 3). Considering site multiplicities and fractional occupancies, the average coordination number is five oxygen atoms. In Table 3, the Ba−O bonds range in length from 2.53 to 3.20 Å, with an average of 2.81 Å, which is quite close to 2.82 Å, the sum of the Shannon crystal radii for $Ba^{2+}$ (1.61 Å and $O^{2-}$ (1.21 Å). The Ba−Br bonds lie in the range of 3.30−3.80 Å and are

---

(14) West, A. R. *Solid State Chemistry and Its Applications*; John Wiley & Sons Ltd.: New York, 1984; p 237.

(15) Shannon, R. D. *Acta. Crystallogr.* **1976**, *A32*, 751.

(16) Baur, W. H. *Trans. Am. Crystallogr. Assoc.* **1970**, *6*, 129.

(17) Wang, S.; Hwu, S.-J. *J. Solid State Chem.* **1991**, *90*, 31.

all longer than the sum of $Ba^{2+}$ and $Br^-$, 3.23 Å. This Ba-centered polyhedron plays a very important role in the structure of the title compound, because it holds the isolated $CuBr_3$ and $P_2O_7$ groups in position by sharing oxygen atoms with the $P_2O_7$ group and bromine atoms with the $CuBr_3$ unit.

The assigned formal oxidation states for the cations are confirmed by the following bond valence sum analysis (BVS).[18] A value of +1.11 is calculated for the oxidation state of $Cu^+$ on the basis of the $CuBr_3$ coordination. $P^{5+}$ has a calculated value of +4.57. A value of +2.09 is calculated for $Ba^{2+}$ in its nine-coordinate environment.

In summary, the structure of a copper(I) halide pyrophosphate, $Ba_3CuBr_3(P_2O_7)$, is presented. This is the first example in the rarely studied Cu(I)-containing phosphate system where the Cu−O−P−O−Cu covalent linkage is broken down due to the incorporation of a bromide anion. The structure is saltlike, with a trigonal planar $CuBr_3$ and a $P_2O_7$ group being held together by the electropositive $Ba^{2+}$ cation. The static precessional disorder about the $P_2O_7$ group can be understood by considering the cooperative effect for a bent pyrophosphate configuration.

**Acknowledgment.** Financial support for this research (DMR-9612148) and the single-crystal X-ray diffractometer from the National Science Foundation is gratefully acknowledged.

**Supporting Information Available:** Tables of detailed crystallographic data and anisotropic thermal parameters, as well as figures showing the electron density contour map and nine-coordinate $BaO_5Br_4$ (5 pages). Ordering information is given on any current masthead page.

IC960461E

---

(18) Brese, N. E.; O'Keefe, M. *Acta Crystallogr.* **1991**, *B47*, 192.