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A Novel Honeycomb-like Copper(II) Phosphate Framework, [BaCl][$CuPO_4$]

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Introduction

Copper(II) phosphate chemistry is interesting because of the structural multiplicity attributed to the Jahn−Teller distortion (d^9) of Cu-centered oxygen polyhedra. While most early transition metal oxides prefer octahedral coordination geometry, copper(II) oxides frequently form distorted octahedra, *e.g.*, CuO_{6-x} (x = 0−2), that give rise to the wide variety of frameworks observed in ternary and quaternary phosphates as well as silicates.[1] These reported compounds have been synthesized by either conventional high-temperature, solid-state precursor methods or hydrothermal techniques. Altered synthetic methods have led to new discoveries due to changes in reaction conditions, *e.g.*, temperature, reaction mechanism, and basicity/acidity. By the employment of a low-temperature eutectic NaCl/CuCl flux, for example, a new layered sodium copper(II) pyrophosphate compound, $Na_2CuP_2O_7$, was recently discovered, possessing a unique wave-like $[CuP_2O_7]_\infty$ ribbon framework which has been recognized for the first time.[2] This observed low-dimensional framework is different from the complex structures of copper(II) compounds referenced above in the sense that these new structures have extra framework flexibility and low packing density. Here there exists another novel structure with a honeycomb-like low-dimensional framework constructed of an unusually seen $[CuPO_4]_\infty$ spiral framework. In this report, the synthesis, structure, and infrared spectrum of the newly synthesized barium copper(II) phosphate chloride, $BaCuPO_4Cl$, are presented.

Experimental Section

Synthesis. Single crystals of $BaCuPO_4Cl$ were grown from a reaction mixture containing Cu_2O (Aldrich, 97%) and P_2O_5 (Aesar, 99+%) with the nominal composition $Cu_2P_2O_6$. This mixture was loaded in a eutectic flux of 38% $BaCl_2$ (dried from $BaCl_2{\cdot}2H_2O$, EM Science, 99+%) and 62% NaCl (EM Science, 99%), mp= 660 °C, with a charge to flux ratio of 1:5. The starting materials and flux were placed in a carbon-coated silica ampule and heated to 800 °C for 4 days, cooled at 2 °C/h to 600 °C, and then cooled quickly (50 °C/h) to room temperature. Green, chunky crystals (few)[3] of the title compound were isolated by washing the reaction product with deionized water using a suction filtration method.

Table 1. Crystallographic Data[a] for $BaCuPO_4Cl$

chem formula	$BaCuPO_4Cl$	fw	331.30
a, Å	7.885(2)	space group	$P2_12_12_1$ (No. 19)
b, Å	8.650(1)	T, °C	23
c, Å	7.270(1)	λ, Å	0.710 73
V, Å^3	495.9(2)	ϱ_{calcd}, g cm^{-3}	4.439
Z	4	linear abs coeff, cm^{-1}	64.853
$R(F_o)$[b]	0.027	$R_w(F_o)$[c]	0.039

[a] The cell constants are refined in the orthorhombic crystal system with use of 25 high-angle reflections (30.93° ≤ 2θ ≤ 39.73°). [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R_w = [\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Positional and Thermal Parameters[a] for $BaCuPO_4Cl$

atom	x	y	z	B_{eq}, Å^2
Ba	0.01585(5)	0.29447(4)	0.37290(4)	0.71(2)
Cu	0.0161(1)	0.1839(1)	0.8645(1)	0.97(3)
P	0.3144(2)	0.0792(1)	0.1268(2)	0.50(5)
Cl	0.2340(2)	0.4607(2)	0.6732(2)	1.51(6)
O(1)	0.4209(6)	0.1531(5)	0.9743(5)	1.0(2)
O(2)	0.1237(5)	0.0840(5)	0.0801(6)	1.0(2)
O(3)	0.1396(5)	0.0903(5)	0.6630(6)	0.9(1)
O(4)	0.3500(5)	0.1856(4)	0.2936(6)	0.7(1)

[a] Equivalent isotropic thermal parameters defined as $B_{eq} = (8\pi^2/3)$ trace U.

Structure Determination. A light green, chunk crystal (0.50 × 0.30 × 0.30 mm) was mounted on a glass fiber for single-crystal X-ray diffraction study. The diffraction data were collected at room temperature on a Rigaku AFC5S four-circle diffractometer (Mo Kα, λ = 0.710 69 Å) equipped with a graphite monochromator. Crystallographic data for the title compound are summarized in Table 1. The unit cell parameters and the orientation matrix for data collection were determined by a least-squares fit of 25 peak maxima with 7° < 2θ <30°. There was no detectable decay during data collection, according to the intensities of three standard reflections (−1,−1,1; −1,0,1; 0,1,2) which were measured every 150 reflections. A total of 1408 reflections ($2\theta_{max}$ = 55°) were collected, of which 1132 unique reflections with $I > 3\sigma(I)$ were used for the structure determination. The TEXAN software package was used for crystal structure solution and refinement.[4] Redundant data were collected so that Friedel pair analysis could be performed to determine the correct enantiomorph. Data reduction, intensity analysis, and extinction conditions were determined with the program PROCESS. Lorentz−polarization and empirical absorption corrections based on three computer-chosen azimuthal scans (2θ = 9.43, 19.74, 29.02°) were applied to the intensity data. On the basis of extinction conditions and correct structure solution, space group $P2_12_12_1$ (No. 19) was chosen. The atomic coordinates of Ba, Cu, Cl, and P were determined using the SHELXS-86 program,[5] and those of oxygen atoms were resolved using a difference Fourier map. The structural and thermal parameters were refined by the full-matrix least-squares method to R = 0.027, R_w = 0.039, and GOF = 2.24. (The refinement based on the alternate enantiomorph gave rise to R = 0.035, R_w = 0.052, and GOF = 2.97.) Table 2 lists the final positional and thermal parameters.

Infrared Spectroscopy. The infrared (IR) absorption spectrum of $BaCuPO_4Cl$ was studied in the range 1600−400 cm^{-1} and recorded

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(1) (a) Robertson, B. E.; Calvo, C. *Acta Crystallogr.* **1967**, *22*, 665. (b) Robertson, B. E.; Calvo, C. *Can. J. Chem.* **1968**, *46*, 605. (c) Shoemaker, G. L.; Kostiner, E. *Am. Mineral.* **1981**, *66*, 176. (d) Shoemaker, G. L.; Anderson, J. B.; Kostiner, E. *Am Mineral.* **1981**, *66*, 169. (e) Spirlet, M. R.; Rebizant, J.; Liegeois-Duyckaerts, M. *Acta Crystallogr.* **1993**, *C49*, 209. (f) Shoemaker, G. L.; Anderson, J. B.; Kostiner, E. *Acta Crystallogr.* **1977**, *B33*, 2969. (g) Anderson, J. B.; Shoemaker, G. L.; Kostiner, E. *J. Solid State Chem.* **1978**, *25*, 49. (h) Brunel-Laügt, M.; Durif, A.; Guitel, J. C. *J. Solid State Chem.* **1978**, *25*, 39. (i) Brunel-Laüt, M.; Guitel, J. C. *Acta Crystallogr.* **1977**, *B33*, 3465. (j) Kawamura, K.; Kawahara, A.; Iiyama, J. T. *Acta Crystallogr.* **1978**, *B34*, 1978. (k) Kawamura, K.; Kawahara, A. *Acta Crystallogr.* **1976**, *B32*, 2419. (l) Senga, Y.; Kawahara; A. *Acta Crystallogr.* **1980**, *B36*, 2555. (m) Martin Pozas, J. M.; Rossi, G.; Tazzoli, V. *Am Mineral.* **1975**, *60*, 471. (n) Shoemaker, G. L.; Kostiner, E.; Anderson, J. B. *Z. Kristallogr.* **1980**, *152*, 317. (o) Effenberger, H. *Z. Kristallogr.* **1987**, *180*, 43. (p) Anderson, J. B.; Kostiner, E.; Ruszala, F. A. *J. Solid State Chem.* **1981**, *39*, 29. (q) Pabst, A. *Acta Crystallogr.* **1959**, *12*, 733. (r) Ito, J.; Peiser S. *J. Res. Natl. Bur. Stand.* **1969**, *73A*, 69. (s) Moqine, A.; Boukhari, A.; Darriet, J. *J. Solid State Chem.* **1993**, *107*, 362.

(2) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 1495.

(3) In a second reaction, CuO (Strem, 99.9999%) was added to this reaction mixture with the nominal composition $Cu_4P_2O_8$ and the same flux. The result was a much greater yield (ca. 50%) of the title compound.

(4) (a) *TEXSAN: Single Crystal Structure Analysis Software*, Version 5.0; Molecular Structure Corp.: The Woodlands, TX 1989. (b) Scattering factors for non-hydrogen atoms: Cromer, D. T., Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A, pp 71−98.

(5) 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.

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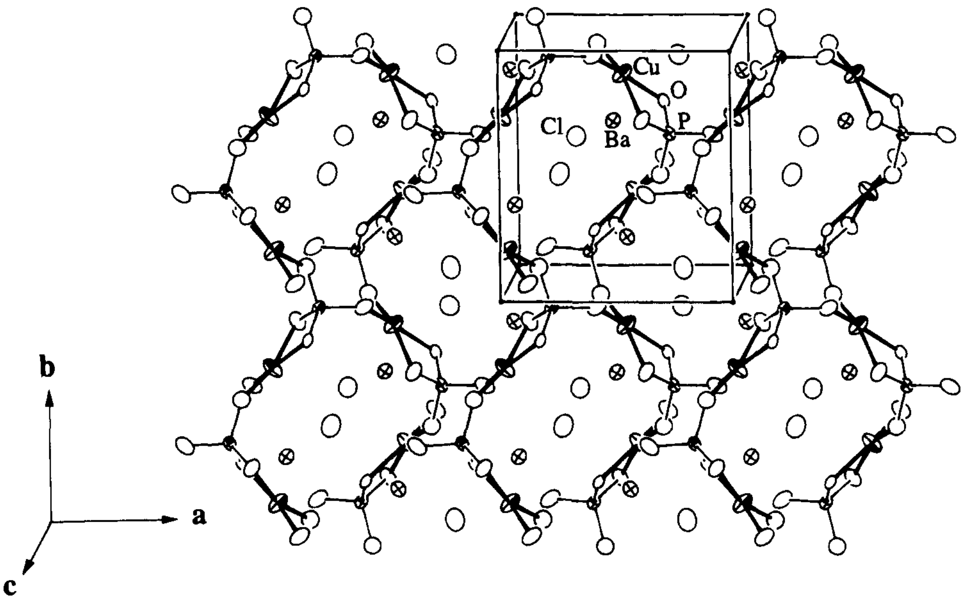

Figure 1. Extended structure of $BaCuPO_4Cl$ viewed approximately along the *c* axis. The unit cell is shown by the box. The $[CuPO_4]$ framework is outlined by Cu−O (in thick lines) and P−O (in thin lines) bonds. The barium (cross-hatched circles) and chlorine (open circles) atoms are drawn with bonds omitted for clarity. The anisotropic atoms are presented at 90% probability.

on a Perkin-Elmer 1600 Series FTIR spectrometer with 16 scans and 2.0 cm^{-1} increments. The samples for this study were from ground single crystals which were pressed into disks with KBr. The results were consistent with what would be expected on the basis of the X-ray structure. The spectrum shows several bands in 1100−900 cm^{-1} region corresponding to the characteristic ν(P−O) of the $[PO_4]$ group as well as multiple bands in the 650−500 cm^{-1} region for the ν(P−O) and δ(O−P−O) modes.[6]

Results and Discussion

An ORTEP[7] drawing in Figure 1 presents the extended structure of the title compound viewed approximately down the *c* axis. A honeycomb-like open-framework structure is seen with approximately rectangular-shaped windows. The quasi-one-dimensional channels are made by the $[CuPO_4]$ framework that is formed by corner and edge sharing between the CuO_4 and PO_4 polyhedra, as depicted by Cu−O (in thick lines) and P−O (in thin lines) bonds. The barium chloride ions reside in channels leading to a structural formula of $[BaCl]^+[CuPO_4]^-$. Although there are no bonds drawn, one should expect a weak interaction between Cu and Cl as the closest Cu−Cl distance is 2.77 Å, which is longer than 2.46 Å, the sum of Shannon crystal radii of 5-coordinated Cu^{2+} (0.79 Å) and Cl^- (1.67 Å).[8] The widths of the two differently sized windows are ca. 5.15 and 5.40 Å, across the narrow side. These distances may be large enough to allow a chemical modification via ion-exchange reactions to take place.

A detailed structural analysis has suggested that the $[CuPO_4]$ framework is characterized by a spiral structure propagating around the 2_1-screw axis, as shown in Figure 2. The $[CuPO_4]_\infty$ spiral is formed by square planar CuO_4 and tetrahedral PO_4 connected in an alternating fashion of corner and edge sharing. Intuitively, this type of connectivity would result in a "dangling" framework unless it can be "tied" together by external bonds. The barium cations, in this case, reside in the spiral framework, as shown by the cross-hatched circle with Ba−O bonds drawn in dashed lines, to support and maintain the distance between rotations. This demonstrates another special framework exhibited in copper(II) phosphate structures, in addition to the wave-like $[CuP_2O_7]_\infty$ ribbon identified in the previously reported $Na_2CuP_2O_7$ structure.

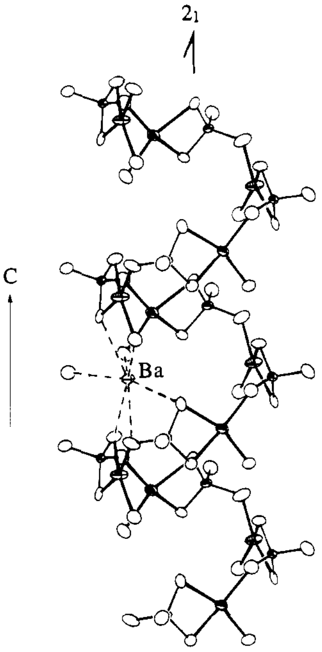

Figure 2. A single $[CuPO_4]_\infty$ spiral framework centered around the 2_1-screw axis of the unit cell. Only one barium atom is drawn for clarity, demonstrating the function of Ba−O bonds to with regard to the flexible framework; see text. The anisotropic atoms are presented at 90% probability.

With respect to the copper center, each CuO_4 square plane in the title structure shares one edge with a PO_4 and two corners with two different PO_4 groups. Specifically, O(2) joins unit cells along the *c* axis and O(3) joins unit cells along the *b* axis. This arrangement, accompanied by the bent configuration of the corner oxygen atoms, facilitates the observed curvature which is necessary for the spiral framework found in the extended lattice. One of the corner-shared PO_4 groups provides an essential element allowing the spiral chain to propagate along

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

(7) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

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

Table 3. Important Bond Distances (Å) and Angles (deg) for $BaCuPO_4Cl^a$

	CuO_4		
$Cu^a-O(1)^b$	1.981(4)	$Cu^a-O\ (3)^a$	1.937(4)
$Cu^a-O(2)^c$	1.981(4)	$Cu^a-O(4)^d$	2.076(4)
O(1)−Cu−O(2)	90.3(2)	(2)−Cu−O(3)	101.6(2)
O(1)−Cu−O(3)	159.4(2)	O(2)−Cu−O(4)	161.0(2)
O(1)−Cu−O(4)	72.6(2)	O(3)−Cu−O(4)	97.2(2)
	PO_4		
$P^a-O(1)^e$	1.531(4)	$P^a-O(3)^f$	1.53(4)
$P^a-O(2)^a$	1.542(4)	$P^a-O(4)^a$	1.548(4)
O(1)−P−O(2)	111.4(2)	O(2)−P−O(3)	107.1(2)
O(1)−P−O(3)	113.2(3)	O(2)−P−O(4)	109.5(2)
O(1)−P−O(4)	102.7(2)	O(3)−P−O(4)	113.0(2)

[a] Symmetry codes: (a) x, y, z; (b) $x - {}^1/_2, {}^1/_2 - y, 2 - z$; (c) $x, y, 1 + z$; (d) $x - {}^1/_2, {}^1/_2 - y, 1 - z$; (e) $x, y, z - 1$; (f) ${}^1/_2 - x; -y, z - {}^1/_2$.

the *c* axis, while the second one serves to link the neighboring spiral chains, as can be seen in Figure 1.

Table 3 lists important bond distances and angles that describe the geometries of the CuO_4 and PO_4 polyhedra. The CuO_4 square plane is distorted in that the angles between opposite oxygen atoms, such as O(1) and O(3) or O(2) and O(4), are far from linear, 159.4 and 161.0°, respectively. One of the rectangular angles associated with the oxygen atoms of the shared edge is particularly small, e.g., 72.6° for O(1)−Cu−O(4). The PO_4 tetrahedron, on the other hand, is less distorted, considering the angles are in a rather small range, 102.7−113.2°. In any event, the Cu−O and P−O bond distances are reasonable compared to those reported previously.[1,2]

The formal oxidation state for the copper atom is 2+ on the basis of the structural information and the following bond valence sum (BVS) analysis.[9] A value of 1.73 is calculated for the oxidation state of Cu on the basis of CuO_4 coordination, whereas a larger value, 1.87, is determined when one chlorine is considered as an extra coordinate. A lower BVS value, 1.81, for the oxidation state of divalent Ba is also calculated on the basis of BaO_7Cl_3 coordination as shown in Figure 3. This observed deviation from their formal oxidation states is due in part to the distortion of the polyhedra, an intrinsic difficulty in this type of calculation. If the polyhedron is less distorted, as in the PO_4 case, a nearly perfect value, 4.96, is calculated for the pentavalent P.

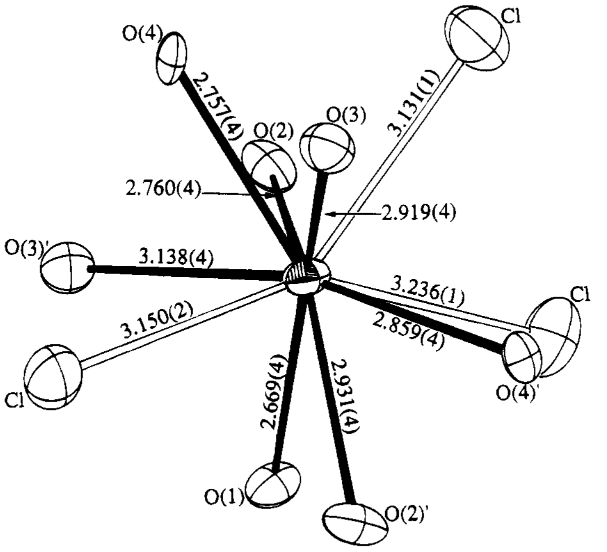

Figure 3. ORTEP drawing of the BaO_7Cl_3 polyhedron. The viewed orientation is the same as that shown in Figure 2, except in this case the chlorine atoms are included. The bond distances are in angstroms. The anisotropic atoms are presented at 90% probability.

In conclusion, the synthesis of $BaCuPO_4Cl$ is a result of inclusion of the $BaCl_2$ flux enroute to the formation of the honeycomb-like copper phosphate framework. From the above structure description, one can view the extended lattice as a $BaCl^+$ ion pair around which the flexible $[CuPO_4]$ framework revolves. This is reminiscent of some recent examples of supramolecular architecture using organic molecules as templating agents.[10] While incorporation of cations and/or anions from the flux is incidental, it provides much variety in the structural features of the final product.

Acknowledgment. Financial support for this research (Grant DMR-9208529) and the single-crystal X-ray diffractometer from the National Science Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of detailed crystallographic data and anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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