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Structure of BaCuP₂O₇

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Abstract. Barium copper pyrophosphate, $M_r = 374.8$, triclinic, $P\bar{1}$, $a = 7.353(2)$, $b = 7.578(2)$, $c = 5.231(1) \text{ \AA}$, $\alpha = 90.83(2)$, $\beta = 95.58(2)$, $\gamma = 103.00(2)^\circ$, $V = 282.5(1) \text{ \AA}^3$, $Z = 2$, $D_x = 4.41 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71069 \text{ \AA}$, $\mu = 112.5 \text{ cm}^{-1}$, $F(000) = 342$, $T = 298 \text{ K}$, $R = 3.4\%$ for 1207 observed reflections. The structure of

BaCuP₂O₇ is isostructural with that of BaCoP₂O₇. Both show planes of $[(MP_2O_7^{2-})_2]_\infty$, $M = \text{Cu, Co}$, composed of mixed MO_5 and PO_4 polyhedra and square-pyramidal coordination for M , linked together by interplanar Ba atoms.

Introduction. Two types of structures are found for solid-state diphosphates, $A_2P_2O_7$ ($A = \text{bivalent cation}$): thortveitite and dichromate (Cruickshank,

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Lynton & Barclay, 1962; Brown & Calvo, 1970). The anionic groups, $P_2O_7^{4-}$, are found in staggered conformation in thortveitite structures and eclipsed in dichromates.

For mixed diphosphates, AMP_2O_7 (A = alkaline-earth cation, M = transition metal), only the compounds $BaCoP_2O_7$, $BaNiP_2O_7$ and $CaCoP_2O_7$ have been examined by single-crystal X-ray analysis (Riou, Labbe & Goreaud, 1988*a,b*). $BaCoP_2O_7$ and $CaCoP_2O_7$ crystallize in a triclinic unit cell. $BaNiP_2O_7$ was found to be an incommensurate structure. $SrMgP_2O_7$, $SrCuP_2O_7$ and $CaCuP_2O_7$ (Calvo, 1968; Boukhari, Moqine & Flandrois, 1991) have been identified as isomorphous with α - $Ca_2P_2O_7$. For these structures, the unit cell is monoclinic and the space group is $P2_1/n$.

In a recent publication (Boukhari, Moqine & Flandrois, 1991) we have noted the resemblance of the powder pattern of $BaCuP_2O_7$ to those of $BaCoP_2O_7$ and $BaNiP_2O_7$. This would suggest that $BaCuP_2O_7$, like $BaCoP_2O_7$, crystallizes with dimers, $(MP_2O_7)_2$, in which metal atoms are bridged in pairs by two O atoms. However, magnetic measurements on powder samples of $BaCuP_2O_7$ show no maximum on the $\chi_M = f(T)$ curve, and thus suggest that the solid-state structure of $BaCuP_2O_7$ may differ from the dimeric grouping seen in $BaCoP_2O_7$. We have thus undertaken the single-crystal structural analysis of $BaCuP_2O_7$ in an effort to interpret the ferromagnetism observed for the powder.

Experimental. Single crystals of $BaCuP_2O_7$ have been prepared by fusion in the presence of a 3:1 molar excess of P_2O_5 . A mixture of $(NH_4)_2HPO_4$, $BaCO_3$ and CuO (of high purity) was heated slowly to liquidity at 1323 K. This product was then cooled slowly (10 K h^{-1}) to 1073 K. Below this temperature, the oven was turned off and cooling allowed to continue. The resulting product was placed in a 0.1 M solution of HCl for approximately 4 h to facilitate dissolution of the amorphous material, leaving well formed crystals in the form of narrow plates.

A crystal of $BaCuP_2O_7$ (dimensions $0.15 \times 0.2 \times 0.2$ mm) was mounted on a Syntex $P3$ automated diffractometer. Unit-cell dimensions were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 29^\circ$) during normal alignment procedures. Data (1658 independent points after removal of redundant data) were collected at room temperature using a variable scan rate, a θ - 2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60° . Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections.

As the intensities of these reflections showed less than 5% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects using the reflection profile peak analysis program, *DREAM* (Blessing, 1986). Equivalent reflections were averaged and showed a variance of 3%. An empirical absorption correction was applied using the data from ψ scans of 21 independent reflections with χ angles between 70 and 110° . Observed reflections [1207 with $F > 3.0\sigma(F)$] were used for solution and refinement of the structure. Direct methods (*MULTAN*; Main *et al.*, 1980) permitted location of the heavy-atom positions. A cycle of least-squares refinement followed by a difference Fourier synthesis allowed location of the $P_2O_7^{4-}$ groups. Refinement (*XRAY*; Stewart, 1978) of scale factor, positional and isotropic thermal parameters was carried out to convergence. Final cycles of least-squares refinement were completed with anisotropic thermal parameters [function minimized, $\sum[(F_o - |F_c|)^2]$ leading to a final agreement factor $R = 3.4\%$. Scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion corrections were made for Ba and Cu (*International Tables for X-ray Crystallography*, 1974, Vol. IV). In the final stages of refinement a weight of $1/\sigma(F)^2$ was used ($wR = 4.1\%$).

Discussion. A projection view of $BaCuP_2O_7$ is shown in Fig. 1, based on the positional parameters of Table 1. Bond distances and angles are listed in Table 2.*

The structure is characterized by isolated layers composed of mixed polyhedra: CuO_5 and PO_4 (Fig.

* Lists of structure factors, anisotropic thermal parameters and bond angles at the Ba atom have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54156 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

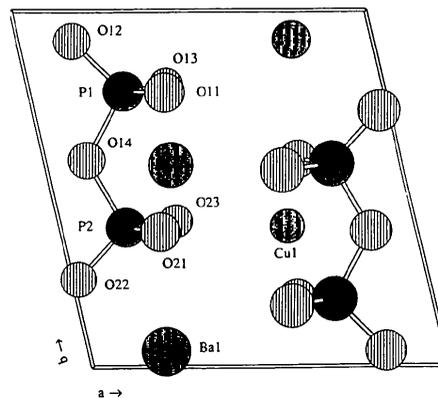


Fig. 1. View of $BaCuP_2O_7$, showing a projection of Cu dimer succession in the c direction.

Table 1. Positional parameters for BaCuP₂O₇

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
Ba1	-0.7759 (1)	0.0736 (1)	-0.2023 (1)	10.0 (1)
Cu1	-0.3582 (2)	0.4010 (1)	-0.8152 (2)	6.7 (2)
P1	-0.7327 (3)	0.7849 (2)	-0.6954 (4)	4.3 (5)
P2	-0.8130 (3)	0.4029 (3)	-0.7117 (4)	4.8 (4)
O11	-0.6153 (10)	0.7901 (9)	-0.4367 (12)	10.3 (1)
O12	-0.8433 (9)	0.9286 (8)	-0.7097 (12)	8.4 (1)
O13	-0.6108 (8)	0.7956 (8)	-0.9186 (11)	5.6 (1)
O14	-0.8794 (9)	0.5921 (8)	-0.7308 (12)	7.9 (1)
O21	-0.7177 (9)	0.4009 (8)	-0.4394 (12)	8.2 (1)
O22	-0.9802 (10)	0.2527 (9)	-0.7742 (13)	12.3 (1)
O23	-0.6724 (9)	0.4117 (8)	-0.9123 (12)	8.5 (1)

an adjacent chain (Table 2), Cu—O23 [2.337 (7) Å]. The O22 atom at 3.214 (6) Å represents a potential sixth coordination site. This distance is too long to be considered interactive. Elongation of the apical bond is consistent with the presence of two electrons in the *d_{z²}* orbital for Cu²⁺ (*d⁹*) (Goodenough, 1966). Similar square-pyramidal environments have been observed for Cu²⁺ in α-Cu₂P₂O₇ and Cu₃(PO₄)₂ (Robertson & Calvo, 1967; Shoemaker, Anderson & Kostiner, 1977).

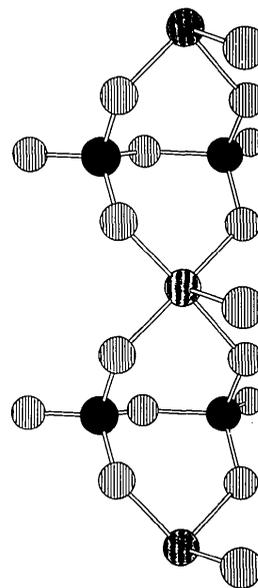
Table 2. Bond distances (Å) angles (°) for BaCuP₂O₇

Cu1—O11 ⁱ	1.962 (7)	O11 ⁱ —Cu1—O13 ⁱⁱ	86.6 (3)
Cu1—O13 ⁱⁱ	1.983 (6)	O11 ⁱ —Cu1—O21 ⁱ	94.9 (3)
Cu1—O21 ⁱ	1.939 (6)	O11 ⁱ —Cu1—O23	100.2 (2)
Cu1—O23	2.337 (7)	O11 ⁱ —Cu1—O23 ⁱⁱⁱ	177.0 (3)
Cu1—O23 ⁱⁱⁱ	2.019 (6)	O13 ⁱⁱⁱ —Cu1—O21 ⁱ	170.2 (3)
Ba1—O21	2.754 (6)	O13 ⁱⁱⁱ —Cu1—O23	89.8 (2)
Ba1—O13 ⁱ	2.798 (6)	O13 ⁱⁱⁱ —Cu1—O23 ⁱⁱⁱ	90.5 (2)
Ba1—O12 ⁱⁱⁱ	2.790 (5)	O21 ⁱ —Cu1—O23	99.4 (3)
Ba1—O12 ^{iv}	2.813 (6)	O21 ⁱ —Cu1—O23 ⁱⁱⁱ	87.7 (2)
Ba1—O11 ^{iv}	2.977 (6)	O23—Cu1—O23 ⁱⁱⁱ	80.8 (2)
Ba1—O23 ^v	2.868 (7)	O11—P1—O12	112.4 (4)
Ba1—O13 ^{vi}	3.001 (5)	O11—P1—O13	111.2 (4)
Ba1—O22 ^{vii}	2.702 (6)	O11—P1—O14	108.0 (3)
Ba1—O22 ^v	3.236 (6)	O12—P1—O13	111.1 (4)
Ba1—O12 ^{vi}	2.860 (5)	O12—P1—O14	107.5 (4)
P1—O11	1.528 (7)	O13—P1—O14	106.2 (4)
P1—O12	1.498 (7)	P1—O14—P2	122.1 (4)
P1—O13	1.532 (7)	O14—P2—O21	106.2 (3)
P1—O14	1.605 (6)	O14—P2—O22	108.2 (4)
P2—O14	1.617 (7)	O14—P4—O23	105.2 (4)
P2—O21	1.527 (6)	O21—P2—O22	113.9 (4)
P2—O22	1.482 (6)	O21—P2—O23	111.3 (4)
P2—O23	1.535 (7)	O22—P2—O23	111.4 (4)

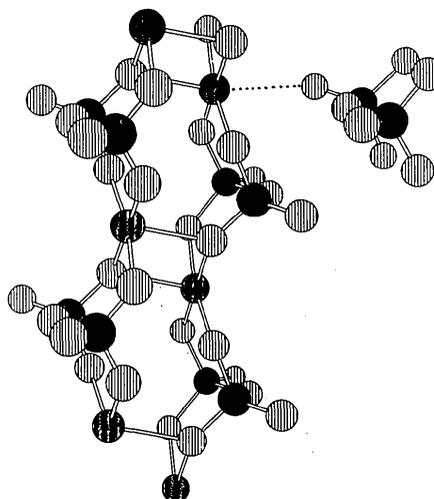
Symmetry codes: (i) $-1-x, 1-y, -1-z$; (ii) $-1-x, 1-y, -2-z$; (iii) $-2-x, 1-y, -1-z$; (iv) $x, -1+y, z$; (v) $x, y, 1+z$; (vi) $x, -1+y, 1+z$; (vii) $-2-x, -y, -1-z$.

1). These layers are approximately parallel to the (010) of the triclinic cell. Adjacent layers are linked by interactions with Ba²⁺ ions. Within the layers, PO₄³⁻ tetrahedra share a corner forming diphosphates, P₂O₇⁴⁻. These anions are grouped in pairs related by a center of inversion and with bridging O atoms extending towards each other. Repetition of this motif follows the *c* axis of the cell (Fig. 2).

Cu²⁺ atoms bridge two successive P₂O₇⁴⁻ groups, being linked to O atoms of each of the two P atoms of two successive groups. These four linkages form the square of the square-pyramidal Cu coordination [Cu—O average 1.976 (6) Å]. Cu atoms linked in this manner thus form chains, (CuP₂O₇²⁻)_∞ extending in the *c* direction. Two adjacent chains are related by centres of inversion which relate [(CuP₂O₇²⁻)₂]_∞ units of each polymeric chain. The same motif is found in the low-temperature form of Na₂CuP₂O₇ (Erragh, Boukhari, Abraham & Elouadi, 1991). Cu coordination is completed by a fifth linkage to an O atom of



(a)



(b)

Fig. 2. (a) Projection view of BaCuP₂O₇ on the (100) plane, showing Cu coordination in adjacent unit cells. (b) Projection view of BaCuP₂O₇, showing the chains (CuP₂O₇)₂²⁻ and the formation of Cu₂O₂ dimers. The broken line (---) indicates a sixth atom [O22(-1 + *x*, *y*, *z*)] at an extended distance from Cu.

$P_2O_7^{4-}$ is found in eclipsed conformation; P—O distances range from 1.482 (6) to 1.617 (7) Å with P—O_{terminal} distances averaging 1.517 (6) Å and P—O_{bridging} distances longer [average 1.611 (6) Å]. The P—O—P angle is 122.1 (4)°. These distances are comparable to the values seen for other similar groups. BaCuP₂O₇ thus belongs to the family of dichromate structures in which P₂O₇ shows an eclipsed conformation and P₂O₇⁴⁻ ions appear in groups of two with bridging O atoms directed towards each other.

Ba²⁺ ions show ninefold coordination with Ba—O distances between 2.702 (6) and 3.001 (5) Å [average 2.840 (6) Å]. These distances are similar to those observed for Ba in BaCoP₂O₇ (2.70–2.97 Å). In α -Sr₂P₂O₇ (Hagman, Jansson & Magnéli, 1968), isostructural with α -Ba₂P₂O₇ (Morris, McMurdie, Evans, Paretzkin, DeGroot, Hubbard & Carmel, 1979), Sr²⁺ shows ninefold coordination. Thus the structures of BaCuP₂O₇ and BaCoP₂O₇ are isostructural. Both display dimers of $MP_2O_7^{2-}$ in which pairs of metal atoms are bridged by two O atoms. The solid-state structure of BaCuP₂O₇, thus, does not lead to a complete interpretation of its low-temperature magnetic behavior.

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CsSbO(SiO₃)₂: A New {uB, 1_∞¹}[¹²SiO₃] Chain Silicate

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Abstract. CsSbO(SiO₃)₂, $M_r = 422.82$, orthorhombic, $Pna2_1$, $a = 21.024$ (2), $b = 13.602$ (2), $c = 7.1287$ (7) Å, $V = 2038.6$ (7) Å³, $Z = 12$, $D_x = 4.131$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 9.66$ mm⁻¹, $F(000) = 2280$, $T = 293$ K, $R = 0.044$, $wR = 0.047$ for 2576 independent reflections. The structure consists of chains of corner-sharing SbO₆ octahedra, running parallel to the c axis and cross-linked to chains of corner-sharing SiO₄ tetrahedra running parallel to the a axis. This covalent framework delimits tunnels which extend through the structure parallel to the a axis and wherein Cs

atoms are situated. The overall silicate anion topology is {uB, 1_∞¹}[¹²SiO₃].

Introduction. As part of a search for layered or skeleton structures with covalent networks built up from MO₆ octahedra (M : high valent cation) and XO₄ tetrahedra ($X = \text{P, Si, Ge}$) the first alkali antimony(V) silicates KSbOSiO₄ (Crosnier, Guyomard, Verbaere & Piffard, 1990) and NaSbOSiO₄ (Pagnoux, Guyomard, Verbaere, Piffard & Tournoux, 1991), which are both isomorphous derivatives of KTiOPO₄, have recently been characterized. This paper reports the crystal structure determination of a monopolysilicate isolated during the

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