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$CaCuP_2O_7$: a Structure Closely Related to α-$Ca_2P_2O_7$

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Abstract. Calcium copper diphosphate, $CaCuP_2O_7$, $M_r = 277·56$, monoclinic, $P2_1/n$, $a = 5·2104\,(4)$, $b = 8·0574\,(5)$, $c = 12·344\,(1)$ Å, $\beta = 91·356\,(6)°$, $V = 518·1\,(2)$ Å^3, $Z = 4$, $D_x = 3·56$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71073 Å, $\mu_l = 59·00$ cm^{-1}, $F(000) = 540$, $T = 293$ K, $R = 0·029$, $wR = 0·034$ for 1581 independent reflections, $I_o \geq 3\sigma(I_o)$. The structure of $CaCuP_2O_7$ is closely related to that of α-$Ca_2P_2O_7$ [Calvo (1968). *Inorg. Chem.* **7**, 1345–1351], differing in the coordination of the cations. The coordination about Cu is square pyramidal and P atoms form diphosphate [P_2O_7] units. Each [CuO_5] polyhedron shares its five corners with five different disphosphate groups. The Ca atoms lie inside cages where they realize a 6 + 2 coordination with Ca—O distances ranging from 2·399 (2) to 2·846 (2) Å.

Introduction. Former investigations of the AMP_2O_7 diphosphates series, where M is a divalent metal and A an alkaline earth, have shown the existence of two structural types. The first group is represented by $BaCoP_2O_7$ and $BaNiP_2O_7$ (Riou, Labbe & Goreaud, 1988*a*), the second by $CaCoP_2O_7$ (Riou, Labbe, & Goreaud, 1988*b*). All these structures present a mixed framework of corner-sharing [MO_6] octahedra and [P_2O_7] diphosphate units. In both series, the [MO_6] octahedra are paired by edge sharing, but $CaCoP_2O_7$ is a cage structure with Ca^{2+} ions inside the cages and $BaCoP_2O_7$ is a sheet structure stabilized by the large Ba^{2+} ions which ensure the cohesion between the sheets.

The well known original behaviour of the Cu^{2+} ions and their tendency to realize an intermediate coordination between the octahedral and the square models were good reasons to choose this divalent metal for the synthesis of new $A^{II}M^{II}P_2O_7$ diphosphates.

The present paper deals with $CaCuP_2O_7$ which shows structural relationships to α-$Ca_2P_2O_7$.

Experimental. A mixture of $CaCO_3$, CuO and $(NH_4)_2HPO_4$ in ratios 1:1:2 was first heated in a platinum crucible at 973 K to decompose the phosphate and the carbonate. The resultant product was ground and heated for nine days at 1333 K in an evacuated sealed silica ampoule. After quenching at room temperature, a fragment with indefinite facies was chosen for the crystallographic study.

Green crystal, symmetry $2/m$ with systematic absences $0k0$, $k = 2n + 1$ and $h0l$, $h + l = 2n + 1$; space group $P2_1/n$. Enraf–Nonius CAD-4 diffractometer using Mo $K\bar{\alpha}$ radiation isolated by a graphite monochromator. 25 reflections ($36 \leq 2\theta \leq 50°$) for refining cell parameters. ω–2θ scan of $(1 + 0·35\tan\theta)°$ and counter slit aperture of $(1 + \tan\theta)$ mm. 3472 measured reflections ($-10 \leq h \leq 10$, $0 \leq k \leq 16$, $0 \leq l \leq 24$), $\theta_{\max} = 45°$, 1581 positive reflections with $I/\sigma(I) \geq 3$ corrected for Lorentz and polarization effects and used to solve the structure. 3 reference reflections (10,0,0, 0,16,0, 0,0,24) for intensity every 3000 s and for orientation every 600 reflections: no decay. No absorption or extinction corrections were performed. Crystal size 72 × 48 × 48 μm. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Calculations on MicroVAX II with *SDP* system (Frenz, 1985) using the heavy-atom method: Cu and Ca atoms were deduced from the Patterson function then the P and O from Fourier synthesis; all atoms refined on F anisotropically. The unusual space group $P2_1/n$ was chosen for comparison with α-$Ca_2P_2O_7$. $(\Delta/\sigma)_{\max} = 0·0$, $R = 0·029$, $wR = 0·034$, $S = 1·429$, $w = 1/\sigma^2F$. Max. peak height in the final difference Fourier synthesis 0·836 e Å^{-3} in the vicinity of the Cu atom. Atomic parameters are given in Table 1.† A projection along [100] is drawn in Fig. 1.

Discussion. The structure of $CaCuP_2O_7$ is built up from corner-sharing [CuO_5] square pyramids and [P_2O_7] diphosphate groups. The [PO_4] tetrahedra present the features usually observed in the classical

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52741 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional parameters and equivalent isotropic thermal parameters and their e.s.d.'s*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (ab\cos\gamma)\beta_{12} + (ac\cos\beta)\beta_{13} + (bc\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq} (Å)
Cu	0·79798 (8)	0·14058 (6)	0·11019 (4)	0·503 (5)
Ca	0·2878 (1)	0·32276 (9)	0·27641 (6)	0·673 (8)
P(1)	0·7523 (2)	0·5280 (1)	0·16483 (7)	0·40 (1)
P(2)	0·3116 (2)	0·2020 (1)	0·98402 (7)	0·42 (1)
O(1)	0·6608 (5)	0·3508 (3)	0·1542 (2)	0·66 (3)
O(2)	0·6524 (5)	0·3979 (3)	0·4005 (2)	0·63 (3)
O(3)	0·9384 (5)	0·1207 (3)	0·2653 (2)	0·64 (3)
O(4)	0·7641 (5)	0·1067 (3)	0·4535 (2)	0·69 (4)
O(5)	0·4747 (5)	0·0450 (3)	0·2929 (2)	0·79 (4)
O(6)	0·0980 (5)	0·3338 (3)	0·4715 (2)	0·65 (3)
O(7)	0·2124 (5)	0·1867 (4)	0·0967 (2)	0·72 (4)

Table 2. *Interatomic distances* (Å) *and angles* (°)

$[P_2O_7]$ group

P(1)	O(1)	O(3^{v})	O(4^{v})	O(5^{v})
O(1)	1·510 (2)	2·451 (3)	2·490 (3)	2·534 (3)
O(3^{v})	107·7 (1)	1·526 (2)	2·517 (3)	2·523 (3)
O(4^{v})	106·7 (1)	107·6 (1)	1·593 (2)	2·512 (3)
O(5^{v})	114·1 (1)	112·4 (1)	108·1 (1)	1·510 (2)

P(2)	O(2^{vi})	O(4^{vii})	O(6^{vi})	O(7^{ii})
O(2^{vi})	1·536 (2)	2·501 (3)	2·516 (3)	2·528 (3)
O(4^{vii})	105·6 (1)	1·605 (2)	2·531 (3)	2·448 (3)
O(6^{vi})	110·2 (1)	107·6 (1)	1·531 (2)	2·569 (3)
O(7^{ii})	112·7 (1)	104·0 (1)	115·8 (1)	1·500 (2)

$[CuO_5]$ square pyramid

Cu	O(1)	O(2^{viii})	O(3)	O(6^{iv})	O(7^{i})
O(1)	1·922 (2)	3·841 (3)	2·705 (3)	2·715 (3)	3·257 (3)
O(2^{viii})	160·16 (9)	1·978 (2)	2·755 (3)	2·960 (3)	3·005 (3)
O(3)	86·06 (9)	86·59 (9)	2·040 (2)	4·016 (3)	2·606 (3)
O(6^{iv})	87·78 (9)	96·40 (9)	169·33 (8)	1·994 (2)	3·526 (3)
O(7^{i})	104·16 (9)	91·82 (9)	75·72 (8)	114·31 (8)	2·201 (2)

Coordination of Ca

Ca—O(5^{ix})	2·399 (2)	Ca—O(7)	2·497 (2)
Ca—O(3^{iii})	2·444 (2)	Ca—O(1)	2·498 (2)
Ca—O(5)	2·447 (2)	Ca—O(6)	2·626 (2)
Ca—O(2)	2·487 (2)	Ca—O(3)	2·846 (2)

Symmetry code: (i) $1 + x, y, z$; (ii) $x, y, 1 + z$; (iii) $x - 1, y, z$; (iv) $1/2 + x, 1/2 - y, z - 1/2$; (v) $3/2 - x, 1/2 + y, 1/2 - z$; (vi) $1/2 + x, 1/2 - y, 1/2 + z$; (vii) $x - 1/2, 1/2 - y, 1/2 + z$; (viii) $3/2 - x, y - 1/2, 1/2 - z$; (ix) $1/2 - x, 1/2 + y, 1/2 - z$.

$M_2P_2O_7$ pyrophosphate compounds and the $A_xM'P_2O_7$ series (A = alkaline or alkaline earth; M' = Mo, Ti, Al, Fe, Co, Ni): a long P–O distance with the bridging oxygen O(4) from $[P_2O_7]$ and three shorter distances with terminal O atoms (Table 2). As in $BaCoP_2O_7$ and $CaCoP_2O_7$ each diphosphate unit has a free apex which can participate in the coordination of Ca. The conformation of the disphosphate group is staggered and the P(1)—O(4)—P(2) angle of 127·0 (1)° is near that observed in α-$Ca_2P_2O_7$ at 130·0 (4)°, where the $[P_2O_7]$ has an almost eclipsed conformation. On the other hand, α-$Cu_2P_2O_7$ (Robertson & Calvo, 1967) shows a larger P—O—P angle of 156° with a staggered configuration. The coordination about Cu is square pyramidal 4 + 1 with four bond lengths close to 1·98 Å and one longer at 2·201 (2) Å (Table 2). The Cu environment of the O atoms can be considered as a strong distortion of the octahedral coordination if we take account of a sixth oxygen at 2·949 (2) Å which is in fact the free apex O(5) of the diphosphate group. The polyhedra of coordination about Cu already known in the literature often differ and such a distorted octahedral coordination exists in $Ba_2Cu(PO_3)_6$ (Laugt & Guitel, 1975) and α-CuP_2O_7. The $[CuO_5]$ square pyramids are isolated from each other but are linked to six other $[CuO_5]$ through the edges of $[PO_4]$ tetrahedra. So, the Cu–Cu distances are rather long, the two shorter ones, 4·1516 (8) and 4·6664 (8) Å, inducing only weak interactions between the metal atoms.

The framework of $CaCuP_2O_7$ can be described as simply resulting from a particular mode of stacking of enantiomorphic chains running in the [010] direction (Fig. 1). These chains are formed by the alternate corner sharing of a $[P_2O_7]$ group and a $[CuO_5]$ pyramid. Adjacent chains are linked through O atoms which are always common apices between a tetrahedron and a pyramid. The chains correspond to one another through a centre or a 2_1 screw axis. The connections between these chains realize layers as drawn in Fig. 1. The framework of $CaCuP_2O_7$ is built up from these layers stacked perpendicularly to the a axis. The stacking mode defines tunnels running along [100] whose section is delimited by pentagonal windows formed by the edges of three $[PO_4]$ tetrahedra and two $[CuO_5]$ square pyramids. The windows are narrow, the shortest distances between

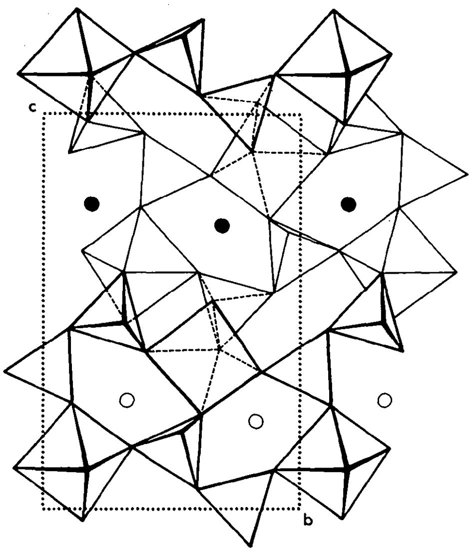

Fig. 1. Projection along [100] of the atomic arrangement of $CaCuP_2O_7$. Full circle for Ca at $x \sim 0·75$. Open circle for Ca at $x \sim 0·25$.

opposite O atoms are O(2)–O(3) = 3·180 (3) and O(1)–O(2) = 3·065 (3) Å; the Ca^{2+} ions are located in cages situated between two successive windows where they realize a 6 + 2 coordination with O atoms and Ca–O distances similar to those observed in α-$Ca_2P_2O_7$ (Table 2). Systematic geometrical calculations prove there is no pathway for the Ca^{2+} (or Mg^{2+}) ions through the framework. The coordination about Cu and Ca is geometrically quite different but the substitution of one Cu^{2+} for one Ca^{2+} is possible, involving a decrease of the lattice volume: 574·77 and 518·10 Å^3 for α-$Ca_2P_2O_7$ and $CaCuP_2O_7$, respectively. However, a progressive substitution of Cu^{2+} for Ca^{2+} is not expected due to the different behaviour of the two metals especially in their coordination with oxygen. In MoP_2O_7 (Leclaire, Borel, Grandin & Raveau, 1988) the arrangement of the [MoO_6] octahedra and the [P_2O_7] groups is similar to that of the [CuO_5] pyramids and the diphosphate groups in $CaCuP_2O_7$, but the layers are staggered and so the tunnels are not linear contrary to those of $CaCuP_2O_7$.

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Structure of Ta_5SnGa_2

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Abstract. Digallium pentatantalum tin, M_r = 1162·87, tetragonal, $I4/mcm$, a = 10·354 (2), c = 5·1795 (6) Å, V = 555·3 Å^3, Z = 4, D_x = 13·91 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 118·2 mm^{-1}, $F(000)$ = 1908, room temperature, final R = 0·053, wR = 0·055 for 336 [$|F_o| > 3\sigma(F_o)$] unique reflections. The title compound is isomorphous with W_5Si_3. The main characteristic of the structure is the existence of $(Ga_2Ta_8)_\infty$ columns parallel to the c axis. These columns are connected by Sn and Ga atoms to form a three-dimensional framework. There are two distinct sites for Ga atoms with one of them being shared equally and statistically between Ga and Sn atoms.

Introduction. In the project to study the crystal chemistry, structure and superconductivity of V*a*–Sn–Ga (V*a* = Ta, Nb, V) ternary systems, we have recently succeeded in synthesizing single crystals of a new ternary compound, Ta_5SnGa_2, in the Ta–Sn–Ga system (Shishido, Ye, Toyota, Ukei, Sasaki, Horiuchi & Fukuda, 1989). The present paper reports the crystal structure of this compound. Studies on the other members of the systems have also been made; the crystal growth and structure have been reported for Nb–Sn–Ga by Ukei, Shishido & Fukuda (1989) and for V–Sn–Ga by Ye, Horiuchi, Shishido & Fukuda (1990).

Experimental. Ta_5SnGa_2 crystals were synthesized by the self-component flux method from the melt of Ta, Sn and Ga (Shishido *et al.*, 1989). The crystal used for the single-crystal X-ray work was a cube with side ~0·04 mm. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were determined from 25 reflections with $28 < 2\theta < 36°$. A total of 2554 reflections in the range $2 < 2\theta < 70°$ ($-16 \le h \le 16$, $-16 \le k \le 16$, $0 \le l \le 8$) were collected under the following conditions: ω–2θ scan, scan width $\Delta\omega = (1{\cdot}1 + 0{\cdot}4\tan\theta)°$, scan speed 0·5° min^{-1}. The intensities of

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