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Crystal Chemistry of $Cd_{2-x}Cu_xP_2O_7$, $0 \le x \le 2$ Structure of $CdCuP_2O_7$[1]

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The domains of the system, $Cd_{2-x}Cu_xP_2O_7$, $0 \le x \le 2$, have been established by powder diffraction methods. Two solid solutions have been found near $Cd_2P_2O_7$ ($0 \le x \le 0.40$) and $Cu_2P_2O_7$ ($1.60 \le x \le 2$). A new phase with $x = 1$ has been identified using single crystal X-ray diffraction. The mixed diphosphate $CdCuP_2P_7$ ($x = 1$) crystallizes in monoclinic space group $C2$ with $a = 6.806(7)$, $b = 8.665(4)$, $c = 4.504(2)$ Å, $\beta = 105.85(6)°$, $V = 255.5(3)$ Å^3, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu_{MoK\alpha} = 89.26$ cm^{-1}, $D_{calc} = 4.55$ g cm^{-3}, $D_{meas} = 4.59(5)$ g cm^{-3}, $Z = 2$, $F(000) = 326$, $T = 298$ K, $R = 3.9\%$, $R_W = 5.1\%$ for 247 observed reflections. P_2O_7 groups show staggered conformation identifying the solid state structure to be of the thortveitite type. The mixed Cd : Cu sites display sixfold coordination with average M–O distance 2.24(3) Å. © 1994 Academic Press, Inc.

INTRODUCTION

Cation size plays a role in determining the type of crystalline structure observed for diphosphate complexes with bivalent ions, $A_2P_2O_7$. Two structural types have been noted in the literature for these compounds (1). When A is a metallic ion of small size (A = Cu (0.73), Mg (0.72), Ni (0.69), Zn (0.74), Mn (0.83 high spin), Fe (0.78 high spin), Co (0.745 high spin); effective ionic radii (Å) for six coordinate ions in parentheses (2)), the phosphate complexes, $A_2P_2O_7$, belong to the thortveitite class (3–16). When the ion, A, is larger in size (Ba (1.35), Pb (1.19), Sr (1.18), Ca (1.0), Cd (0.95)), the structure is of the dichromate type (17–25). Cd^{2+} has an ionic radius which is among the smallest of those of the ions associated with dichromate structures and 0.22 Å larger than that of six coordinate Cu^{+2} which is expected to form thortveitite type structures.

The conformation of the P_2O_7 group is eclipsed in dichromate structures. Pairs of P_2O_7 groups crystallize about a center of symmetry or a pseudo-inversion center with the bridging oxygen atoms directed toward each other. $Cd_2P_2O_7$ (24) crystallizes in space group $P\bar{1}$ and displays a dichromate-type structure. Cadmium atoms show five- and sixfold coordination in sites of distorted trigonal bipyramidal, and octahedral geometry. The P–O–P angle is 132.3(7)° (24, 25).

In the thortveitite family of structures, P_2O_7 ions are isolated from each other and in staggered conformation. $Cu_2P_2O_7$ exists in two allotropic forms, α (low temperature) and β (high temperature), both of which are of the thortveitite type. The P–O–P angle at the bridging oxygen atom is 157° in α-$Cu_2P_2O_7$ (9). Transition between α and β forms occurs at 345 K. β-$Cu_2P_2O_7$ (10) is isostructural with β-$Mg_2P_2O_7$ (4), with a P–O–P angle of 180°. Cu^{2+} shows five- and sixfold coordination to oxygen in the α and β forms, respectively. (α-$Cu_2P_2O_7$, five Cu–O distances average 2.024(6) Å, β-$Cu_2P_2O_7$, six Cu–O distances 2.172(15) Å.)

The mixed $AA'P_2O_7$ diphosphates currently known and containing Cd^{2+} or Cu^{2+} are $CaCuP_2O_7$ (26, 27), $SrCuP_2O_7$ (28), $BaCuP_2O_7$ (29), $Cd_{1.25}Ca_{0.75}P_2O_7$ (30), $CdSrP_2O_7$ (31), $CdBaP_2O_7$ (31, 32), $PbCdP_2O_7$ (33), and $CdCoP_2O_7$ (34). All belong to the dichromate family, as does the parent compound, $A_2P_2O_7$, of the larger ion; A = Ca, Sr, Ba, Cd, Pb. $CaCuP_2O_7$ and $SrCuP_2O_7$, however, show a staggered arrangement of P_2O_7 oxygen atoms, which is inconsistent with the eclipsed arrangement observed in the parent compound, $A_2P_2O_7$, i.e., $Ca_2P_2O_7$ and $Sr_2P_2O_7$.

We report here a study of the system, $Cd_2P_2O_7$–$Cu_2P_2O_7$ and the single-crystal structure of $CdCuP_2O_7$. Cd^{2+} is one of the smaller of the ions that dictate dichromate-type structure ($Cd_2P_2O_7$ is a dichromate-type structure). Cu^{2+} is a cation 0.22 Å smaller in ionic radius (ionic radius six coordinate Cd^{2+} 0.95 Å,

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Cu^{2+} 0.73 Å), but which normally forms a diphosphate of thortveitite type. One aim of the study was to observe P_2O_7 conformation in an $AA'P_2O_7$ diphosphate when $A_2P_2O_7$ and $A'_2P_2O_7$ were different types.

CRYSTAL CHEMISTRY

The diphosphates $Cd_2P_2O_7$ and $Cu_2P_2O_7$ were synthesized by grinding together stoichiometric amounts of $(NH_4)_2HPO_4$, CuO, and $CdCO_3$ according to the following equations and heating them progressively to 1173 K with intermittent regrinding:

$$2CdCO_3 + 2(NH_4)_2HPO_4 \rightarrow Cd_2P_2O_7 + 4NH_3\uparrow + 2CO_2\uparrow + 3H_2O\uparrow$$

$$2CuO + 2(NH_4)_2HPO_4 \rightarrow Cu_2P_2O_7 + 4NH_3\uparrow + 3H_2O\uparrow .$$

Stoichiometric compounds of the $Cd_2P_2O_7$–$Cu_2P_2O_7$ mixture have been prepared according to the equation

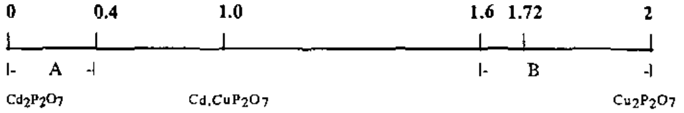
$$(1 - x/2)Cd_2P_2O_7 + (x/2)Cu_2P_2O_7 \rightarrow Cd_{2-x}Cu_xP_2O_7; \quad 0 \leq x \leq 2.$$

Appropriate mixtures were ground together, heated to 873 K and then to 1173 K for a period of 72 h with intermediate grinding.

Polycrystalline powder samples were characterized using a C.G.R. (Theta 60) powder diffractometer with $CuK\alpha_1$ radiation (λ = 1.54051 Å). *d* spacings have been calibrated using Si as an internal standard. Unit-cell parameters for the solid solutions have been refined using least-squares techniques. Densities have been determined experimentally using a picnometer in diethylorthophthalate at ambient temperature.

Single crystals of $CdCuP_2O_7$ were prepared using slow cooling techniques in the presence of excess P_2O_5 ((moles $CdCuP_2O_7$)/(moles P_2O_5) = 0.88). The stoichiometric mixture was heated to 1273 K, cooled at a rate of 4 K hr^{-1} to 1073 K and at a rate of 10 K hr^{-1} to 473 K; then the heating of the furnace was stopped, allowing cooling to room temperature.

Powder diffraction studies of the mixed diphosphates, $Cd_{2-x}Cu_xP_2O_7$, $0 \leq x \leq 2$, show the existence of two solid solutions, *A* ($0 \leq x \leq 0.40$) and *B*($1.60 \leq x \leq 2$), and a compound of composition $CdCuP_2O_7$ ($x = 1$). The other domains of the solid solution are mixtures of the adjacent compounds.



Domain A: $Cd_{2-x}Cu_xP_2O_7$, $0 \leq x \leq 0.40$, is structurally isotypical with $Cd_2P_2O_7$. A linear variation of unit-cell parameters is observed with changing Cd/Cu presence. The substitution of Cu^{2+} for Cd^{2+}, i.e., an increase in the value, *x*, results in a decrease of the volume of the unit cell (Fig. 1).

Domain B: The two allotropes, α and β-$Cu_2P_2O_7$, crystallize in monoclinic space groups *C2/c* and *C2/m*, respectively (9, 10). The $\beta \rightarrow \alpha$ transition is accompanied by a doubling of the *c* cell parameter without significant change in the density.

β-$Cu_2P_2O_7$	α-$Cu_2P_2O_7$
a = 6.827(8) Å	a = 6.876(5) Å
b = 8.118(10)	b = 8.113(5)
c = 4.576(6)	c = 9.162(5)
β = 108.85(10)°	β = 109.54(6)°

For this reason the powder X-ray diffraction spectra of the two forms are very similar. Only the weak diffraction arising from the planes $(11\bar{3})$ and $(22\bar{1})$, characteristic of the α form and not the β form, permits differentiation between the two phases. The form α-$Cu_2P_2O_7$ exists in the domain, $1.72 \leq x \leq 2$; β-$Cu_2P_2O_7$ is stabilized in the domain $1.60 \leq x < 1.72$ of the solid solution $Cd_{2-x}Cu_xP_2O_7$ by the substitution of Cd^{2+} for Cu^{2+} ions in α-$Cu_2P_2O_7$.

$CdCuP_2O_7$ STRUCTURE

A single crystal of $CdCuP_2O_7$ (0.1 × 0.1 × 0.1 mm), turquoise in color, was mounted on a Syntex P3 automated diffractometer. Unit-cell dimensions were determined by least-squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 25°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å, graphite monochromator). Data (266 independent points after removal of redundant data) were collected at room temperature using a variable scan

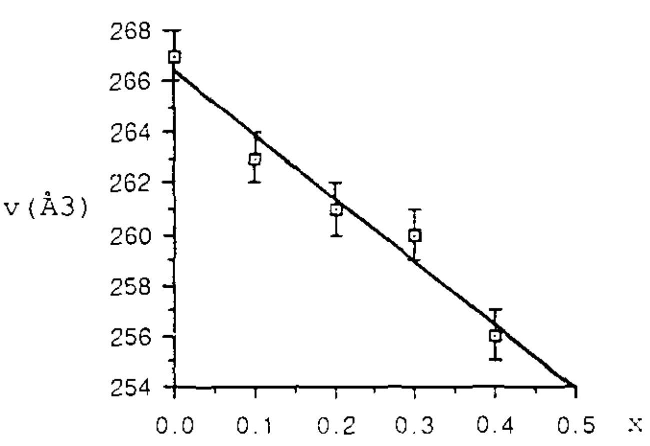


FIG. 1. Variation of unit-cell volume in Domain A, $Cd_{2-x}Cu_xP_2O_7$, $0 \leq x \leq 0.40$.

rate, a $\theta - 2\theta$ 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 (35). Observed reflections (247 points $[I > 3.0\sigma(I)]$ were used for solution of heavy atom positions by direct methods using MULTAN80 (36), P and O positions were determined from a difference Fourier synthesis following refinement of the heavy atom positions. Refinement (37) of scale factor, and positional and isotropic thermal parameters for all atoms was carried out to convergence. Thermal parameters for the heavy atom positions indicated partial occupancy at both sites. Cadmium and copper atoms were introduced in both positions with their x, y, z coordinates constrained and with population parameters (Cd population = n, Cu population $1 - n$). Final cycles of least-squares refinement were completed with anisotropic thermal parameters (each thermal parameter for Cu was constrained to equal that of the cadmium atom on the same site) (function minimized, $\Sigma(|F_o| - |F_c|)^2$), leading to a final agreement factor, $R = 3.9\%$ ($R = (\Sigma\omega||F_o| - |F_c||/\Sigma\omega|F_o|) \times 100$). Scattering factors were taken from Cromer and Mann (38). Anomalous dispersion corrections were made for Cu and Cd (39). In the final stages of refinement a weight of $1/\sigma(F)^2$ was used. $R_w = 5.1\%$.

The space group shows a symmetry close to $C2/m$. However, the positioning of the bridging oxygen atom, O14, on a twofold axis and not on a mirror also ($2/m$ symmetry) leads to the choice of space group, $C2$ and not $C2/m$.

The refined occupancies of 0.39(2) and 0.61(2) for Cd1 and Cd2, respectively (each of multiplicity 2), lead to 2.00 Cd per cell. The 0.61(2) and 0.39(2) occupancies for Cu1 and Cu2 lead to 2.00 copper atoms per unit cell. The P_2O_7 group occupies a position centered on the twofold axis in the cell ($Z = 2$), and thus the refined stoichiometry of the unit cell is $CdCuP_2O_7$, or $Cd_{2-x}Cu_xP_2O_7$, $x = 1.00$.

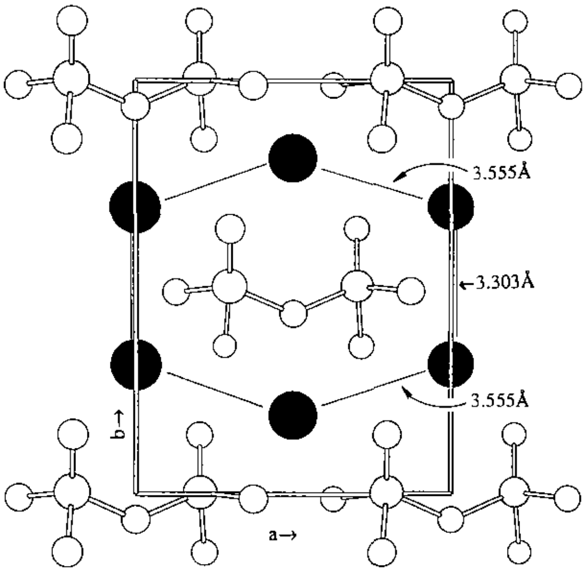


FIG. 2. View of $CdCuP_2O_7$ projected on the (001) plane.

A projection view of $CdCuP_2O_7$ based on the coordinates of Table 1 is shown in Fig. 2. Bond angles and distances are given in Table 2.

The structure of $CdCuP_2O_7$ is close to that of β-$Cu_2P_2O_7$ (10) and β-$Zn_2P_2O_7$ (12) (space group $C2/m$). All three show planes of octahedral metal atoms arranged in hexagons with adjacent metal atoms bridged by two bridging oxygen atoms (Fig. 3). α-$Cu_2P_2O_7$ crystallized with square

TABLE 1
Positional Parameters for $CdCuP_2O_7$

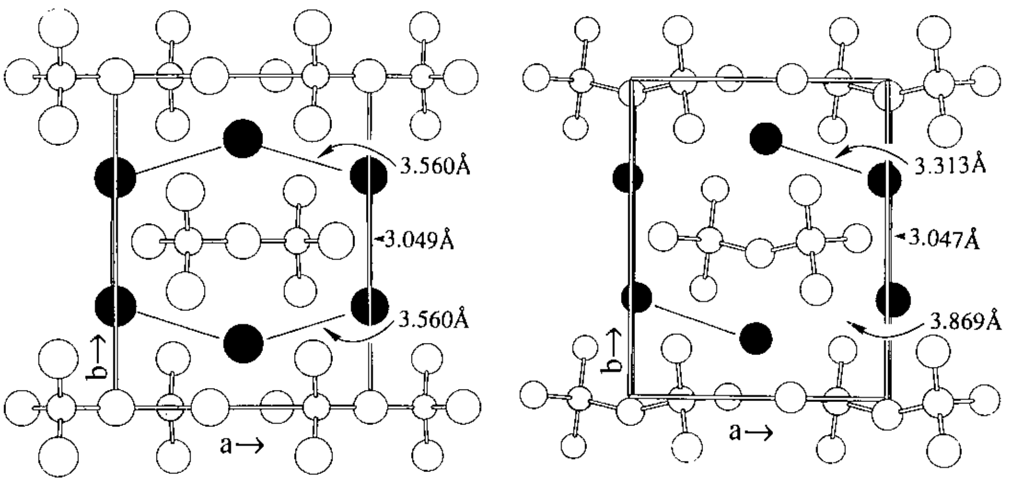
Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$	U_{eq}
Cd/Cu1	0.0000	0.3122	0.5000	10.7
Cd/Cu2	0.5000	0.1934(5)	0.5000	12.0
P1	0.2030(6)	0.004(2)	−0.0866(8)	23.3
O11	0.218(4)	−0.142(3)	−0.279(7)	25.6
O12	0.372(2)	−0.010(6)	0.220(3)	34.0
O13	0.201(6)	0.144(3)	−0.256(10)	63.2
O14	0.0000	−0.063(3)	0.0000	24.2

Note. $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

TABLE 2
Bond Angles (°) and Distances (Å) for $CdCuP_2O_7$

Cd1/Cu1–O13′	2.10(3)	Cd2/Cu2–O12	2.21(4)
Cd1/Cu1–O11″	2.42(3)	Cd2/Cu2–O11″	2.10(2)
Cd1/Cu1–O12^{iii}	2.03(4)	Cd2/Cu2–O12^{vii}	2.21(4)
Cd1/Cu1–O13^{iv}	2.10(3)	Cd2/Cu2–O11^{vi}	2.10(2)
Cd1/Cu1–O12^{v}	2.03(4)	Cd2/Cu2–O13^{vii}	2.60(3)
Cd1/Cu1–O11^{vi}	2.42(3)	Cd2/Cu2–O13′	2.60(3)
P1–O11	1.55(3)	O11–P1–O12	106(2)
P1–O12	1.54(1)	O11–P1–O13	112(2)
P1–O13	1.43(4)	O11–P1–O14	92(1)
P1–O14	1.55(3)	O12–P1–O13	116(2)
		O12–P1–O14	103(1)
		O13–P1–O14	123(2)
		P1–O14–P1^{iv}	138(2)

′ = $x, y, 1 + z$
″ = $0.5 + x, 0.5 + y, 1 + z$
^{iii} = $-0.5 + x, 0.5 + y, z$
^{iv} = $-x, y, -z$
^{v} = $0.5 - x, 0.5 + y, 1 - z$
^{vi} = $0.5 - x, 0.5 + y, -z$
^{vii} = $1 - x, y, 1 - z$



β-Cu2P2O7 α-Cu2P2O7

FIG. 3. Projection views of β-$Cu_2P_2O_7$ and α-$Cu_2P_2O_7$.

pyramidal coordination of copper atoms and "breaks" in the regularity of the hexagons on the metallic planes (Fig. 3). $CdCuP_2O_7$, β-$Cu_2P_2O_7$, and β-$Zn_2P_2O_7$ show a staggered conformation of isolated P_2O_7 groups. The average of the three dihedral angles, O–P ··· P–O (defined as the angle between planes, O–P1 ·· P1′ and O′–P′ ·· P such that one O–P ··· P–O angle spans the bridging oxygen atom and the other two involve the remaining alternate oxygen atoms) in $CdCuP_2O_7$ is 63.97°, close to the theoretical value of 60° for members of the thortveitite family. Space group symmetry mandates a 60° angle for those complexes observed in space group *C*2/*m*.

The two cationic sites are occupied unequally by Cd and Cu. Average *M*–O distances for the two sites, each of sixfold coordination, are 2.18(3) and 2.30(3) Å. Cd–O distances average 2.307(13) Å for the octahedral site in $Cd_2P_2O_7$ and 2.172(15) Å in β-$Cu_2P_2O_7$. Both sites show axial distortions of *M*–O distances.

P–$O_{terminal}$ distances in P_2O_7 range from 1.43(4) to 1.55(3) Å. The P–$O_{bridging}$ distances are both 1.64(1) Å. These distances are comparable to those observed for $Cd_2P_2O_7$ and $Cu_2P_2O_7$. The P–O–P angle of 138(2)° is similar to the angles observed in $A_2P_2O_7$ thortveitite structures as tabulated by Brown and Calvoin 1970 (1). The O–P–O angles range from 95(2)–122(2)° with an average value of 109(2).

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