

boat conformation is unfavourable for the *trans* isomer because one substituent would be equatorial, and only an approximately planar conformation is available, even though this involves angle strain in the B_2N_4 ring. In fact, the conformation is slightly towards the chair form, presumably to reduce the *peri* interactions still further, although the ring nitrogen atoms are then slightly pyramidal. However, the angle strain at these nitrogen atoms is probably small, because the constraining of the C–N–N angle to 107–108° should allow the B–N–N angle to open to the observed 124° fairly easily.

That the *trans* rather than the *cis* isomer is formed in the reaction is also to be expected, because the *cis* isomer in the boat conformation with both substituents pseudo-equatorial would have severe *peri* interactions, while if they were pseudo-axial there would be very large transannular interactions, and these would still be present, although less marked, if the molecule were planar.

The same B_2N_4 ring system has been examined (Thomas & Paul, 1968) in $(C_4H_{11}NB_2)_4$ and found to have a boat conformation. However this is not directly

comparable with the present structure as the ring is saturated, and the main controlling factor for its geometry is the overall cage structure of the molecule.

Bond lengths in the terminal pyrazole do not depart significantly from those in free pyrazole (Krebs Larsen, Lehmann, Søtofte & Rasmussen, 1970), while those in the ring pyrazole are similar but with equal C–C and C–N distances.

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Cadmium Fluorophosphate, $Cd_2(PO_4)F$

By J. R. REA* AND E. KOSTINER†

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, U.S.A.

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Abstract. Monoclinic, $C2/c$, $a = 13.879$ (2), $b = 6.693$ (1), $c = 10.519$ (1) Å, $\beta = 120.22$ (1)°, $Z = 8$, $D_x = 5.385$ g cm⁻³. The crystals were grown from a melt containing excess CdF_2 . $Cd_2(PO_4)F$ is isostructural with $Mn(PO_4)F$.

Introduction. Cadmium fluorophosphate was first reported by Engel (1970) to crystallize in the space group $C2/c$, who pointed out its structural relationship to the minerals of the wagnerite group $[M_2(PO_4)X]$. In a detailed investigation (Rea & Kostiner, 1972) of $Mn_2(PO_4)F$, a synthetic end member of the series represented by the mineral triplite $[(Mn, Fe)_2(PO_4)F]$, we discussed a possible explanation for the disorder found at the fluorine position in the mineral in terms of cation size. The fluorine atom in synthetic $Mn_2(PO_4)F$ is not disordered. To help resolve this question, we have

carried out a refinement of the crystal structure of $Cd_2(PO_4)F$.

Crystals were grown by cooling a melt of $Cd_3(PO_4)_2$ and excess CdF_2 from 1075°C at 20°C⁻¹. A sphere was ground to a radius of 0.0055 cm; precession photographs confirmed the space group as $C2/c$. The lattice parameters were determined in a PICK II least-squares refinement program using 48 reflections, each automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation.

Diffraction intensities were measured using Zr-filtered Mo $K\alpha$ radiation at a take-off angle of 2.5° with the diffractometer operating in the θ - 2θ scan mode. Scans were made at 1° per min over 1.5° with allowance for dispersion and with 40 s background counts taken at both ends of the scan. Of the 1411 independent data investigated in the angular range $2\theta < 62^\circ$, 1344 were considered observable according to the criterion $|F_o| > 0.8\sigma_F$, where σ_F is defined as $0.02|F_o| + [C + k^2B]^{1/2}/2|F_o|Lp$; the total scan count is

* Permanent address: Department of Chemistry, Mary Baldwin College, Staunton, VA, USA.

† To whom correspondence should be addressed.

C , k is the ratio of scanning time to the total background time and B is the total background count. Three reflections were systematically monitored and no random variations in intensity greater than 3% were observed over the data collection period; the mean variation was very much smaller.

Intensity data were corrected for Lorentz and polarization effects, and absorption corrections (*International Tables for X-ray Crystallography*, 1967) were applied for a spherical crystal with $\mu R = 0.57$. The maximum absorption correction applied was 8.0% of $|F_o|$.

Two cycles of full-matrix least-squares refinement (Busing, Martin & Levy, 1962) using the positional parameters for $Mn_2(PO_4)F$ as a trial structure, a $1/\sigma^2$ weighting scheme, zero-valent scattering factors for Cd, P, F and O (Cromer & Mann, 1968), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0.047$ and a weighted residual $R_w = 0.076$. The anisotropic refinement, based on a data:parameter ratio of 18 to 1 with 74 independently varied parameters yielded a final $R = 0.029$ and $R_w = 0.044$ for the observed data.* In the final refinement, the maximum extinction correction (Zachariasen, 1968) was 34% of $|F_o|$ for the 202 reflection.

Discussion. Table 1 presents the final atomic coordinates and anisotropic thermal parameters. The cadmium atoms lie at the centers of distorted octahedra. Cd(1) is coordinated by four oxygens at an average distance of 2.260 Å and two fluorines at 2.270 and 2.468 Å. Cd(2) is coordinated by four oxygens at an average distance of 2.244 Å and two fluorines at 2.281 and 2.414 Å. The fluorines are *cis* in both cases. Table 2 lists angles and distances for the cadmium polyhedra. The metal-oxygen distances are about 0.1 Å greater in $Cd_2(PO_4)F$ as compared with $Mn_2(PO_4)F$ which is in line with the difference of 0.12 Å in their ionic radii (Shannon & Prewitt, 1969). In each of the octahedra, one fluorine atom is about 0.15 Å more distant in the cadmium compound while the second

(longer) metal-fluorine bond is increased by only 0.04 Å in the Cd(2) polyhedron and actually decreases by 0.07 Å in the Cd(2) polyhedron (relative to the manganese compound).

Table 2. Bond distances, polyhedral edge lengths, and bond angles for cadmium polyhedra

Numbers in parentheses are estimated standard deviations in the last significant figure.

Cd(1)-O(2)	2.258 (4) Å	Cd(2)-O(1)	2.222 (4) Å
Cd(1)-O(3)	2.326 (4)	Cd(2)-O(1')	2.314 (4)
Cd(1)-O(3')	2.221 (4)	Cd(2)-O(2)	2.222 (4)
Cd(1)-O(4)	2.236 (4)	Cd(2)-O(4)	2.219 (4)
Cd(1)-F	2.270 (3)	Cd(2)-F	2.281 (3)
Cd(1)-F'	2.468 (3)	Cd(2)-F'	2.414 (4)
Cd(1) octahedron			
O(2)-O(3)	3.021 (6) Å	O(1)-O(1')	2.864 (8) Å
O(2)-O(4)	3.139 (5)	O(1)-O(2)	3.201 (5)
O(2)-F	2.828 (5)	O(1)-F	3.233 (5)
O(2)-F'	3.217 (5)	O(1)-F'	3.725 (5)
O(3)-O(3')	2.793 (7)	O(1')-O(2)	3.773 (6)
O(3)-O(4)	4.005 (5)	O(1')-O(4)	3.195 (6)
O(3)-F	3.236 (5)	O(1')-F	3.508 (5)
O(3')-O(4)	3.525 (5)	O(2)-O(4)	3.497 (5)
O(3')-F	3.454 (5)	O(2)-F'	2.828 (5)
O(3')-F'	3.946 (5)	O(4)-F	2.832 (5)
O(4)-F'	2.832 (5)	O(4)-F'	3.094 (5)
F-F'	2.756 (6)	F-F'	2.800 (7)
Cd(1) octahedron			
O(2)-Cd(1)-O(3)	82.4 (1)°	O(1)-Cd(2)-O(1')	78.3 (1)°
O(2)-Cd(1)-O(4)	88.6 (1)	O(1)-Cd(2)-O(2)	92.2 (1)
O(2)-Cd(1)-F	77.3 (1)	O(1)-Cd(2)-F	91.8 (1)
O(2)-Cd(1)-F'	85.7 (1)	O(1)-Cd(2)-F'	106.9 (1)
O(3)-Cd(1)-O(3')	75.8 (1)	O(1')-Cd(2)-O(2)	112.6 (1)
O(3)-Cd(1)-O(4)	122.8 (1)	O(1')-Cd(2)-O(4)	89.6 (1)
O(3)-Cd(1)-F	89.5 (1)	O(1')-Cd(2)-F	99.6 (1)
O(3')-Cd(1)-O(4)	104.6 (1)	O(2)-Cd(2)-O(4)	103.9 (1)
O(3')-Cd(1)-F	100.5 (1)	O(2)-Cd(2)-F'	75.1 (1)
O(3')-Cd(1)-F'	114.5 (1)	O(4)-Cd(2)-F	78.0 (1)
O(4)-Cd(1)-F'	73.9 (1)	O(4)-Cd(2)-F'	83.7 (1)
F-Cd(1)-F'	71.0 (1)	F-Cd(2)-F'	73.2 (1)
O(2)-Cd(1)-O(3')	158.1 (2)	O(1)-Cd(2)-O(4)	162.8 (1)
O(3)-Cd(1)-F'	159.1 (1)	O(1')-Cd(2)-F'	171.0 (1)
O(4)-Cd(1)-F	142.9 (1)	O(2)-Cd(2)-F	147.7 (1)

* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30637 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The phosphate tetrahedron is not as regular as that in $Mn_2(PO_4)F$; the average bond length is 1.537 Å (+0.011, -0.008 Å) and the average angle is 109.5° (+1.6, -2.4°). Table 3 lists the tetrahedral bond angles and distances. The standard deviations for all

Table 1. Fractional atomic coordinates and anisotropic thermal parameters

Numbers in parentheses are estimated standard deviations in the last significant figure.

	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd(1)	518.8 (3)	2611.8 (5)	9845.8 (4)	0.77 (2)	0.74 (2)	0.61 (2)	0.15 (1)	0.37 (1)	0.07 (1)
Cd(2)	3416.8 (3)	3997.6 (5)	6531.5 (4)	0.83 (2)	0.57 (2)	0.65 (2)	-0.12 (1)	0.40 (1)	-0.02 (1)
P	1763 (1)	4114 (2)	8056 (1)	0.52 (4)	0.50 (4)	0.39 (4)	-0.05 (3)	0.24 (3)	-0.03 (3)
O(1)	3100 (4)	798 (6)	5881 (4)	1.55 (14)	0.58 (12)	0.57 (12)	-0.03 (11)	0.35 (12)	0.27 (10)
O(2)	2109 (3)	1382 (6)	1815 (4)	0.77 (12)	1.29 (14)	0.95 (13)	0.10 (11)	0.59 (11)	0.22 (11)
O(3)	4098 (3)	290 (6)	3551 (4)	0.75 (12)	1.07 (14)	0.44 (11)	0.04 (10)	-0.08 (10)	0.29 (10)
O(4)	3680 (4)	2735 (6)	1517 (4)	1.42 (14)	0.44 (12)	0.97 (13)	-0.25 (10)	0.85 (12)	-0.01 (10)
F	145 (3)	859 (5)	3920 (4)	0.85 (11)	1.27 (12)	1.08 (12)	0.16 (9)	0.72 (10)	-0.04 (9)

bond lengths and angles were computed by the function and error program (*ORFFE*) of Busing, Martin & Levy (1964).

Table 3. *Bond distances, polyhedral edge lengths, and bond angles for the phosphate tetrahedron*

Numbers in parentheses are estimated standard deviations in the last significant figure.

P—O(1)	1.529 (4) Å	O(1)—O(2)	2.528 (6) Å
P—O(2)	1.537 (4)	O(1)—O(3)	2.511 (5)
P—O(3)	1.533 (4)	O(1)—O(4)	2.475 (5)
P—O(4)	1.548 (4)	O(2)—O(3)	2.503 (5)
		O(2)—O(4)	2.526 (5)
		O(3)—O(4)	2.511 (5)
O(1)—P—O(2)	111.1 (2)°	O(2)—P—O(3)	109.3 (2)°
O(1)—P—O(3)	110.2 (2)	O(2)—P—O(4)	110.0 (2)
O(1)—P—O(4)	107.1 (2)	O(3)—P—O(4)	109.2 (2)

As we predicted (Rea & Kostiner, 1972), $\text{Cd}_2(\text{PO}_4)\text{F}$ is isostructural with $\text{Mn}_2(\text{PO}_4)\text{F}$; the fluorine atom occupies a single position as opposed to the situation in both wagnerite [$\text{Mg}_2(\text{PO}_4)\text{F}$] and tripoidite [$\text{Mn}_{1.5}\text{Fe}_{0.5}(\text{PO}_4)\text{OH}$], in which the fluorine atom (or hydroxyl ion) half-occupies two sites in a doubled unit cell. Furthermore, it is undoubtedly the larger cadmium ion that causes a reduction in the unusually long

Table 4. *Bond distances and angles for the fluorine environment*

Numbers in parentheses are estimated standard deviations in the last significant figure.

F—Cd(1)	2.468 (3) Å	Cd(1)—F—Cd(1')	109.0 (1)°
F—Cd(1')	2.270 (3)	Cd(1)—F—Cd(2)	95.4 (1)
F—Cd(2)	2.281 (3)	Cd(1)—F—Cd(2')	109.9 (1)
F—Cd(2')	2.414 (4)	Cd(1')—F—Cd(2)	139.1 (1)
		Cd(1')—F—Cd(2')	95.5 (1)
		Cd(2)—F—Cd(2')	106.6 (1)

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Cyanomethyl 2-Picolyl Sulfone

BY R. L. HARLOW

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

M. P. SAMMES

University of Zambia, Box 2379, Lusaka, Zambia

AND S. H. SIMONSEN

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

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Abstract. $(\text{C}_3\text{H}_4\text{N})\text{CH}_2\text{SO}_2\text{CH}_2\text{CN}$, $(\text{C}_8\text{H}_8\text{N}_2\text{O}_2\text{S})$, $M = 196.32$, monoclinic, $P2_1/c$, $a = 10.609$ (1), $b = 9.964$ (1), $c = 9.124$ (1) Å, $\beta = 106.10$ (1)°, $V = 926.60$ Å³, $Z = 4$, $D_x = 1.406$, $D_m = 1.403$ g cm⁻³. Full-matrix least-squares

refinement of 1686 reflections [$I > 3\sigma(I)$] collected with θ - 2θ scans on a Syntex $P2_1$ diffractometer yielded a conventional R of 0.036. Expected C—H···O and/or C—H···N interactions were not found.

metal-fluorine distances for one of the two fluorines in each of the octahedra in $\text{Mn}_2(\text{PO}_4)\text{F}$. Table 4 presents the relevant bond angles and lengths about the fluorine atom. The cadmium ion, with a six-coordinated ionic radius of 0.95 Å (Shannon & Prewitt, 1969), most probably represents the largest divalent metal cation which forms a fluorophosphate with the wagnerite structure type. Calcium ($r = 1.00$ Å) does not form a fluorophosphate with the 2:1:1 stoichiometry, and the compound chlorospodiosite [$\text{Ca}_2(\text{PO}_4)\text{Cl}$] adopts an entirely different structure (Greenblatt, Banks & Post, 1967).

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