Reinvestigation of cadmium diphosphate

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Key indicators

Single-crystal X-ray study
$T = 292$ K
Mean σ(P–O) = 0.003 Å
R factor = 0.022
wR factor = 0.055
Data-to-parameter ratio = 11.8

For details of how these key indicators were
automatically derived from the article, see
http://journals.iucr.org/e.

The crystal structure of the title compound, $Cd_2P_2O_7$, has been reinvestigated by means of an image-plate diffraction system. The study confirms the previously determined structure [Calvo & Au (1969). *Can. J. Chem.* **47**, 3409–3417], but provides a less biased model and higher precision. The structure consists of alternating layers of isolated P_2O_7 groups and edge-sharing CdO_6 octahedra forming corrugated chains along [1$\bar{1}$0]. The layers and the parallel chains interconnect by means of corner-sharing. This room-temperature structure is actually the average of a modulated structure, which might partly rectify the unusual bond valences.

Comment

Although the structure of $Cd_2P_2O_7$, (I), has already been reported (Calvo & Au, 1969) (CA hereinafter), a re-determination appears justified because of several flaws in CA. Their refinement converged to $R(F) = 0.093$, but yielded two unusually high isotropic displacement parameters for atoms O3 and O7. Also, a rather doubtful absorption correction was applied (spherical for crystals said to be parallelepipeds). Finally, their intensities were only visually estimated from films. Since we had obtained crystals of (I) as a by-product of a synthesis aimed at another product, we took the opportunity this presented and redetermined the crystal structure.

A comparison seems all the more appropriate since our (WB henceforth) and CA's samples were both quenched from virtually the same temperature [1373 K (WB) and 1393 K (CA)]. Nevertheless, the unit cells are more disparate than one is willing to accept: $a_{CA} = 6.672$ (8), $b_{CA} = 6.623$ (8) and $c_{CA} = 6.858$ (7) Å, and $\alpha_{CA} = 95.8$ (1), $\beta_{CA} = 115.38$ (8) and $\gamma_{CA} = 82.38$ (8)°. Notwithstanding the suspicion raised by CA's cell, we undertook a comparision of their and our geometrical data (bond distances and angles) by means of a normal probability plot (NPP) (Wilk & Gnanadesikan, 1968; Gnanadesikan & Wilk, 1970; Abrahams & Keve, 1971). This plot (Fig. 1) shows three roughly linear segments with different slopes and non-zero ordinate intercepts, but with quite symmetrical wings. These features imply a significant departure from the hypothesis of normality in the differences between the two data sets. Thus, the NPP confirms that CA's data are somehow biased and that our determination of the structure (Fig. 2) provides improved information.

The structure of (I) can be considered as a layer structure (Fig. 3), with CdO_4 layers alternating with P_2O_7 layers. The CdO_4 layers consist of corrugated chains running along [1$\bar{1}$0] (Fig. 4) formed of edge-sharing CdO_6 octahedra. Parallel chains further interconnect by means of corner-sharing. In the loops of these meandering chains the P_2O_7 groups attach themselves, by sharing corners, to the CdO_6 octahedra to link
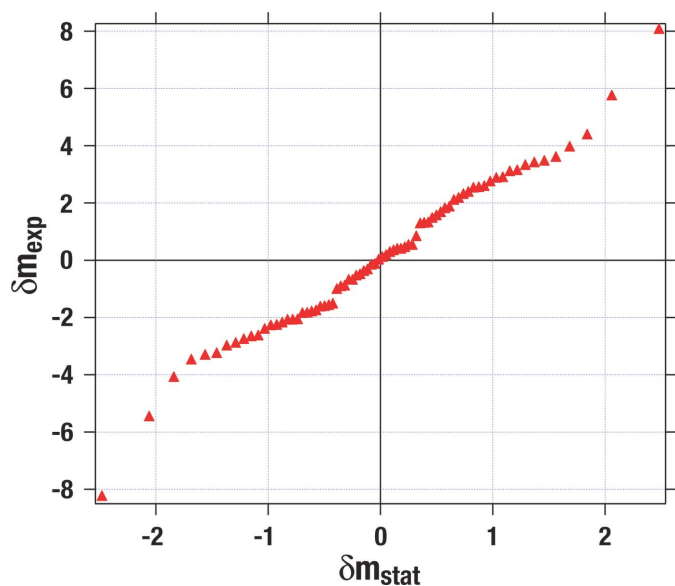
Figure 1
A normal probability plot for (I), comparing 76 pairs of distances or angles.

Figure 3
Projection of the structure of (I) along $[\bar{1}10]$, displaying its quasi-layer character.
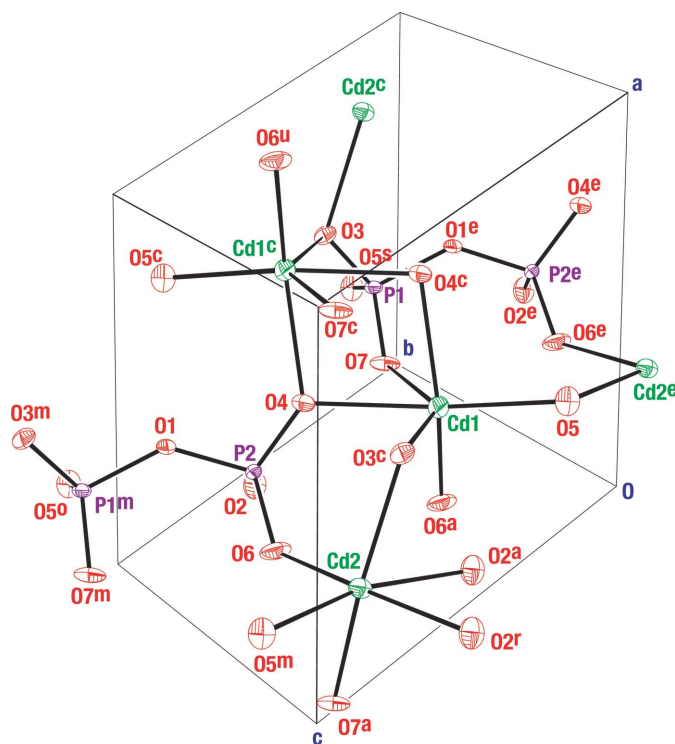

Figure 2
The structure of (I), drawn with anisotropic displacement parameters at the 80% probability level. [Symmetry operators: (a) $-x, 1 - y, 1 - z$; (c) $1 - x, 1 - y, 1 - z$; (e) $x, y, z - 1$; (m) $x, y, z + 1$; (o) $x, y + 1, z + 1$; (r) $x, y - 1, z$; (s) $x, y + 1, z$; (u) $x + 1, y, z$.]

Figure 4
Projection of the structure of (I) along $[\bar{2}\bar{2}1]$. The corrugated $[1\bar{1}0]$ chains (green) are seen horizontally. The P_2O_7 groups linking the layers are blue in front and red at the back of the layer.

neighbouring layers. The P—O distances and O—P—O angles are in the typical ranges found for diphosphate groups: P—O 1.505 (3)–1.626 (3) Å and O—P—O 102.09 (14)–114.94 (16)° for P1, and P—O 1.516 (3)–1.597 (3) Å and O—P—O 103.60 (14)–114.55 (16)° for P2. The PO_4 tetrahedra are almost regular, with O—O distances of 2.447 (3)–2.567 (4) Å, but atoms P1 and P2 are displaced by 0.144 (4) and
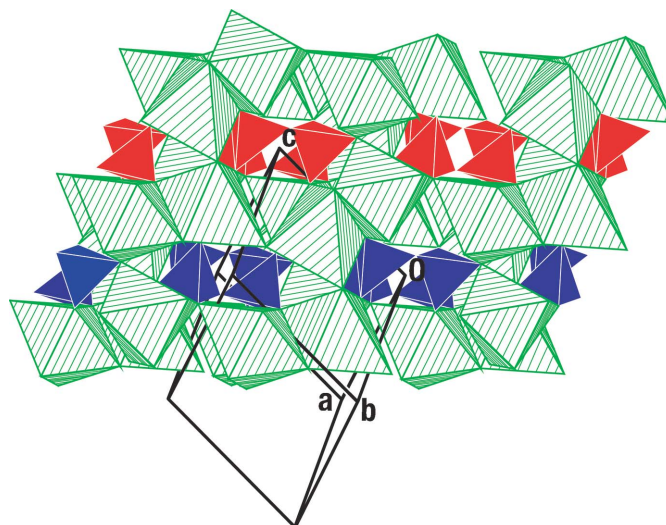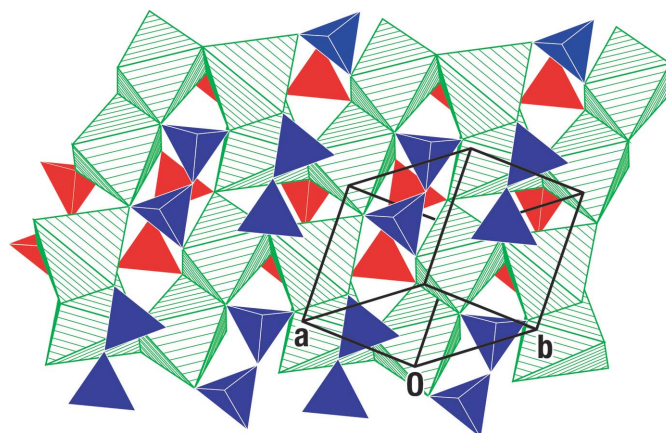
0.062 (3) Å, respectively, from the centres of gravity of their tetrahedra (Baur *et al.*, 1986). An eclipsed configuration and a P—O—P bridging angle of 132.56 (17)° are observed for the $[P_2O_7]$ unit.

Each Cd^{2+} is coordinated by six O atoms, and neighbouring octahedra share either an edge or a corner (Figs. 3 and 4). The coordination around Cd^{2+} can be described as a quite regular octahedron, with six Cd—O distances in the range 2.217 (3)–2.364 (3) Å for Cd2, or as a rather distorted octahedral environment, with five O atoms at distances of 2.260 (2)–2.410 (3) Å and a sixth at 2.648 (3) Å for Cd1. These values are in the ranges found for CdO_6 octahedra in $CdV_2(P_2O_7)_2$ (Boudin *et al.*, 1994), $Cd_2V_2O_7$ (Au & Calvo, 1967) and $CdMP_2O_7$ (*M* = Sr or Ba) (Alaoui El Belghiti *et al.*, 1991). The structure of (I) belongs to the α-CaP_2O_7 pyrophosphate (Calvo, 1968) series which are of the dichromate type, in which the $[P_2O_7]$ groups present an eclipsed conformation. The structure of (I) forms the lower limit of the alkaline earth series.

Bond-valence sums (Brown, 2002) were computed at the end of the refinement using the *softBV* applet (Adams, 2004): Cd1 (six neighbours) 1.80 v.u., Cd2 (six) 2.12 v.u., P1 (four) 4.91 v.u. and P2 (four) 4.95 v.u., and a global instability index of 0.103 v.u. While this last value, although a little large, is still within the field of stable structures, the valences of the Cd^{2+} ions (expected value 2 v.u.) clearly indicate some sort of shortcoming of the model. None of the possible reasons given by Brown (2002) for unusual bond valences seems to apply to (I). Firstly, vacancies are unlikely, since the microprobe analysis corroborated the empirical formula quite precisely. Secondly, a different oxidation state is very unlikely, since no oxidation states higher than +2 are known for cadmium and since Cd^{1+} is unstable (Cotton & Wilkinson, 1972). Finally, an alternative space group *i.e.* a subgroup of $P\bar{1}$ is explored. A refinement in $P1$ did not yield a more reasonable structure, but there was still the possibility of a superstructure for relaxation. Indeed, although the literature regarding the structure of (I) is scarce, that about other pyrophosphates is quite abundant. It turned out that in other pyrophosphates not only up to four thermotropic polymorphs (Assaaoudi *et al.*, 2005) have been observed, but also barotropic ones (Carlson & Krogh Andersen, 2001; Lipinska-Kalita *et al.*, 2003) and, most importantly, diffuse phase transitions (Dojčilović *et al.*, 1994). The low-temperature polymorphs are mainly superstructures of the high-temperature phase. With this in mind, we scrutinized reconstructed layers of reciprocal space. There is no trace of diffuse scattering (indicative of frustrated correlated nanodomains), but there are satellite reflections, according to the modulation vector $\mathbf{q}^* = (-0.35, 0, 0.30)$. The satellites are rather weak since our data collection, unfortunately, had not been set up for a determination of a modulated phase. Since, moreover, the manner of preparing the sample – in the light of the diffuse phase transition – did not appear to be ideal (quenching), we limit ourselves to presenting the average structure of cadmium diphosphate in this communication. However, we shall report, in due course, on our ongoing efforts to elucidate the phase transition sequence of cadmium pyrophosphate and, in particular, the modulated room-temperature phase.

Since the satellites are very weak, we must not expect dramatic displacements of the atoms, but, nevertheless, we may hope that the bond valences may be rectified to some more satisfactory values. Finally, it is noteworthy that the Cd bond valences in monteponite (Cimino & Marezio, 1960) and in cadmium peroxide (Hoffman *et al.*, 1959) are also quite far from the expected values, *viz.* 1.76 v.u. and 2.17 v.u. Even if there is a reason for this deviation in monteponite, *i.e.* excess cadmium, this might also mean that cadmium compounds simply require a more elaborate treatment than the approximate first-neighbour valence-bond theory.

Experimental

Colourless crystals of (I) were obtained as a minor product from a synthesis aimed at the preparation of $Cd_{0.5}TiP_2O_7$. The synthesis proceeded according to: $0.5CdO + 0.75TiO_2 + 2(NH_4)_2HPO_4 + 0.25Ti$ $= Cd_{0.5}TiP_2O_7 + 4NH_3 + 3H_2O$. First the mixture $CdO + 0.75\ TiO_2 + 2(NH_4)_2HPO_4$ was heated in air to 773 K for 4 h in order to obtain the intermediate compound $Cd_{0.5}TiP_2O_7$. Then 0.25Ti was added and the system heated to 1373 K in a sealed tube for 7 d. The sample was then quenched. The composition of (I) was confirmed by microprobe analysis.

Crystal data

$Cd_2(P_2O_7)$	$D_x = 4.964\ (2)$ Mg m^{-3}
$M_r = 398.74$	$D_m = 4.90$ Mg m^{-3}
Triclinic, $P\bar{1}$	D_m measured by Calvo & Au (1969)
$a = 6.6075\ (13)$ Å	Mo $K\alpha$ radiation
$b = 6.6371\ (13)$ Å	Cell parameters from 4542
$c = 6.7887\ (14)$ Å	reflections
$\alpha = 95.82\ (3)°$	$\theta = 3.1–29.4°$
$\beta = 115.13\ (3)°$	$\mu = 8.57$ mm^{-1}
$\gamma = 82.24\ (3)°$	$T = 292\ (2)$ K
$V = 266.75\ (11)$ Å^3	Platelet, colourless
$Z = 2$	$0.50 \times 0.40 \times 0.15$ mm

Data collection

Stoe IPDS-2 diffractometer	1162 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.052$
Absorption correction: integration	$\theta_{max} = 29.1°$
(X-RED; Stoe & Cie, 2005)	$h = -8 \rightarrow 8$
$T_{min} = 0.162$, $T_{max} = 0.314$	$k = -9 \rightarrow 8$
2251 measured reflections	$l = -9 \rightarrow 9$
1189 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{max} = 0.54$ e Å^{-3}
$wR(F^2) = 0.055$	$\Delta\rho_{min} = -0.88$ e Å^{-3}
$S = 1.25$	Extinction correction: *SHELXL97*
1189 reflections	(Sheldrick, 1997)
101 parameters	Extinction coefficient: 0.292 (7)
$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2$	
$+ 0.5407P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cd1—O5	2.260 (2)	Cd2—O5^{iv}	2.334 (3)
Cd1—O4^{i}	2.283 (3)	Cd2—O2^{ii}	2.364 (3)
Cd1—O4	2.296 (3)	P1—O7	1.505 (3)
Cd1—O6^{ii}	2.338 (3)	P1—O3	1.521 (3)
Cd1—O3^{i}	2.410 (3)	P1—O5^{v}	1.537 (3)
Cd1—O7	2.648 (3)	P1—O1^{vi}	1.626 (3)
Cd2—O7^{ii}	2.217 (3)	P2—O4	1.516 (3)
Cd2—O2^{iii}	2.245 (2)	P2—O2	1.520 (3)
Cd2—O6	2.263 (2)	P2—O6	1.532 (3)
Cd2—O3^{i}	2.294 (3)	P2—O1	1.597 (3)
O7—P1—O3	114.94 (16)	O4—P2—O2	114.55 (16)
O7—P1—O5^{v}	114.27 (16)	O4—P2—O6	113.72 (14)
O3—P1—O5^{v}	112.48 (15)	O2—P2—O6	106.92 (16)
O7—P1—O1^{vi}	106.77 (14)	O4—P2—O1	103.60 (14)
O3—P1—O1^{vi}	102.09 (14)	O2—P2—O1	107.62 (14)
O5^{v}—P1—O1^{vi}	104.78 (15)	O6—P2—O1	110.26 (16)

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

Since CA had taken the trouble to calibrate their films with rutile powder, we had cause to doubt our lattice constants without a similar calibration. Therefore, we determined the lattice constants of a red–brown rutile crystal from the Gotthard Pass (Switzerland) and found $a = 4.600\ (2)$ Å and $c = 2.964\ (2)$ Å. These values are within 0.2% of

those obtained from polycrystalline material (Cromer & Herrington, 1955), cited by CA. In this context, it might be noteworthy to communicate the cell constants of a second crystal of (I) we have studied, *viz.* $a = 6.599\,(4)$, $b = 6.634\,(4)$ and $c = 6.787\,(4)$ Å, $\alpha = 95.80\,(2)$, $\beta = 115.07\,(6)$ and $\gamma = 82.34\,(2)^{\circ}$, and $V = 266.4$ Å^3. Hence, we ascertain that our diffraction system furnishes trustworthy lattice constants, that CA's *a* and *c* constants are biased in some way and that our cell is better able to describe this compound, especially since it yields a calculated density much closer to the observed one, the error of which is commonly assumed to be 0.02 Mg m^{-3}. The cell in which we describe (I) is not reduced, but has the merit of allowing easy comparison with the original cell setting of CA.

Data collection: *X-AREA* (Stoe & Cie, 2005); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1996) and *CRYSTALMAKER* (Palmer, 2004); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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