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The *cyclo*-tetraphosphate $Cd_2P_4O_{12}$, a member of the isotypic series $M_2P_4O_{12}$ (M = Mg, Mn, Fe, Co, Ni, Cu)

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Key indicators: single-crystal X-ray study; T = 296 K; mean σ(P–O) = 0.001 Å; R factor = 0.023; wR factor = 0.054; data-to-parameter ratio = 35.3.

The title compound, $Cd_2P_4O_{12}$, dicadmium *cyclo*-tetraphosphate, crystallizes isotypically with the members of the series $M^{II}{}_2P_4O_{12}$, where M = Mg, Mn, Fe, Co, Ni or Cu. Two CdO_6 octahedra, one with 2 and one with $\overline{1}$ symmetry, share corners with the centrosymmetric $P_4O_{12}{}^{4-}$ ring anion that is built up from four corner-sharing PO_4 tetrahedra. The isolated ring anions are arranged in layers parallel to $(10\overline{1})$ with the CdO_6 octahedra situated between these layers. The main difference between the individual $M^{II}{}_2P_4O_{12}$ structures pertains to the different sizes of the MO_6 octahedra whereas the geometric parameters of all *cyclo*-$P_4O_{12}{}^{4-}$ anions are very similar.

Related literature

For a previous powder X-ray study of $Cd_2P_4O_{12}$, see: Laügt *et al.* (1973). The structure of the low-temperature α-modification of the *catena*-polyphosphate $Cd(PO_3)_2$ was refined by Bagieu-Beucher *et al.* (1974). For isotypic $M^{II}{}_2P_4O_{12}$ structures, see: Nord & Lindberg (1975) for M = Mg; Glaum *et al.* (2002) for Mn; Nord *et al.* (1990) and Genkina *et al.* (1985) for Fe; Nord (1982) and Olbertz *et al.* (1998) for Co; Nord (1983) and Olbertz *et al.* (1998) for Ni; Laügt *et al.* (1972) for Cu. A review on the crystal chemistry of phosphates was published by Durif (1995). Ionic radii were compiled by Shannon (1976).

Experimental

Crystal data

$Cd_2P_4O_{12}$
M_r = 540.68
Monoclinic, $C2/c$
a = 12.3342 (2) Å
b = 8.6373 (2) Å
c = 10.4037 (2) Å
β = 119.402 (1)°
V = 965.59 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 5.13 mm^{-1}
T = 296 K
0.36 × 0.24 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008) T_{min} = 0.260, T_{max} = 0.578
11480 measured reflections
3001 independent reflections
2936 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.054
S = 1.23
3001 reflections
85 parameters
$\Delta\rho_{max}$ = 2.08 e Å^{-3}
$\Delta\rho_{min}$ = −1.04 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cd1—O1^{i}	2.1875 (12)	P1—O2	1.5052 (11)
Cd1—O6	2.3034 (10)	P1—O3^{iv}	1.5840 (12)
Cd1—O2^{ii}	2.3690 (11)	P1—O4	1.5983 (11)
Cd2—O5^{iii}	2.2037 (12)	P2—O5	1.4604 (12)
Cd2—O6	2.2563 (11)	P2—O6	1.5011 (11)
Cd2—O2	2.2809 (11)	P2—O3	1.5848 (12)
P1—O1	1.4624 (12)	P2—O4	1.5918 (12)

Symmetry codes: (i) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: MG2104).

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supplementary materials

Acta Cryst. (2010). E**66**, i75 [**doi:10.1107/S1600536810040195**]

The *cyclo*-tetraphosphate $Cd_2P_4O_{12}$, a member of the isotypic series $M_2P_4O_{12}$ (M = Mg, Mn, Fe, Co, Ni, Cu)

M. Weil

Comment

$M^{II}{}_2P_4O_{12}$ compounds containing the *cyclo*-tetraphosphate anion $P_4O_{12}{}^{4-}$ have been the subject of numerous crystallographic studies. Except for $Cd_2P_4O_{12}$ (X-ray powder data; Laügt *et al.*, 1973), detailed structure data are available for $Mg_2P_4O_{12}$ (Nord & Lindberg, 1975), $Mn_2P_4O_{12}$ (Glaum *et al.*, 2002), $Fe_2P_4O_{12}$ (Nord *et al.*, 1990; Genkina *et al.*, 1985), $Co_2P_4O_{12}$ (Nord, 1982; Olbertz *et al.*, 1998), $Ni_2P_4O_{12}$ (Nord, 1983; Olbertz *et al.*, 1998) and $Cu_2P_4O_{12}$ (Laügt *et al.*, 1972). During experiments intended for crystal growth of large single crystals of the low-temperature modification of cadmium *catena*-polyphosphate, α-$Cd(PO_3)_2$ (Bagieu-Beucher *et al.*, 1974), single crystals of the title compound were obtained instead.

The crystal structures of the isotypic $M^{II}{}_2P_4O_{12}$ family are built up from centrosymmetric $P_4O_{12}{}^{4-}$ ring anions. The isolated anions are arranged in layers parallel to $(10\overline{1})$. Two sets of slightly distorted MO_6 octahedra, one with $\overline{1}$ symmetry and one with 2 symmetry, share edges and are situated in the interlayer space. The three-dimensional framework is accomplished by corner-sharing of the MO_6 units and the $P_4O_{12}{}^{4-}$ anions. Figures 1 and 2 show the resulting arrangement for $Cd_2P_4O_{12}$.

The $P_4O_{12}{}^{4-}$ ring anion of $Cd_2P_4O_{12}$ (Fig. 3) consists of four corner-sharing PO_4 tetrahedra and shows the typical features with respect to bond lengths and angles, *i.e.* shorter terminal P—O bonds and longer P—O bonds to the bridging O atoms. A review on structures containing the *cyclo*-tetraphosphate anion has been given by Durif (1995) where characteristic distances and angles are compiled. The individual bond lengths and angles of the $P_4O_{12}{}^{4-}$ anions are very similar in all $M^{II}{}_2P_4O_{12}$ structures. The main difference between the structures is related to the varying ionic radii of the M^{II} cations. Correspondingly, the MO_6 octahedra show (slight) variations in the M—O bond lengths. In the $M^{II}{}_2P_4O_{12}$ family (M = Mg, Mn, Fe, Co, Ni, Cu, and Cd), Cd^{II} has the largest ionic radius (0.95 Å) for coordination number 6 (Shannon, 1976). This value seems to be the upper limit for the existence of the $M^{II}{}_2P_4O_{12}$ family of structures. For larger M^{II} cations like Hg^{II} or Pb^{II} (ionic radius 1.02 Å and 1.19 Å, respectively) solely long-chain *catena*-polyphosphate structures $M(PO_3)_2$ are realised.

In the review on condensed phosphates given by Durif it was stated that *cyclo*-$Cd_2P_4O_{12}$ transforms irreversibly into the low-temperature α-modification of the long-chain polyphosphate $Cd(PO_3)_2$ by prolonged heating at 573 K (Durif, 1995, and references therein), indicating that this transformation process is kinetically controlled. This assumption is confirmed by DSC (differential scanning calorimetry) measurements of the current sample (N_2 atmosphere, heating rate 10 $K\cdot min^{-1}$). Whereas no phase transition has been observed for this compound up to 873 K under these conditions, heating the sample at 873 K in a laboratory furnace under atmospheric conditions for 20 h resulted in a complete transformation into α-$Cd(PO_3)_2$.

Experimental

Single crystals suitable for X-ray structure analysis were grown using the phosphate flux method. CdO (0.7 g) was placed in a glassy carbon crucible and was covered carefully with 70%$_{wt}$ H_3PO_4 (5.4 g). The crucible was subjected to the following temperature programme: RT → 693 K [3 h] → 693 K [5 h] → 573 K [48 h]. Then the crucible was removed from the furnace. Prismatic colourless crystals with maximum edge lengths of 1.5 mm were obtained by leaching the phosphate flux with warm water.

Refinement

The highest peak in the final Fourier map is located 0.62 Å from Cd2 and the deepest hole is 0.96 Å from the same atom.

Figures

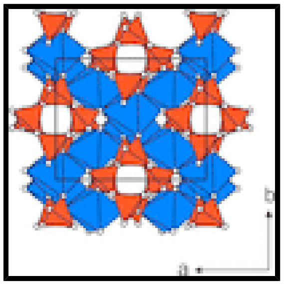

Fig. 1. The crystal structure of $Cd_2P_4O_{12}$ in a projection along [$00\bar{1}$]. PO_4 tetrahedra are red, CdO_6 octahedra are blue and O atoms are displayed as white spheres.

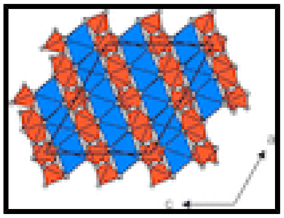

Fig. 2. The crystal structure of $Cd_2P_4O_{12}$ in a projection along [$0\bar{1}0$]. Colour code as in Fig. 1.

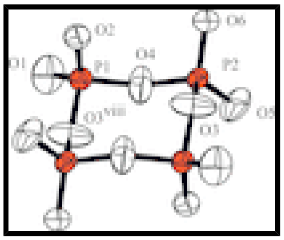

Fig. 3. The P_4O_{12} ring anion with displacement ellipsoids drawn at the 99% level. Non-labelled atoms are generated by inversion symmetry. [Symmetry code: (viii) -*x*, -*y* + 1, -*z*.]

dicadmium *cyclo*-tetraphosphate

Crystal data

Cd_2P_4O12	$F(000) = 1008$
$M_r = 540.68$	$D_x = 3.719$ Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -C 2yc	Cell parameters from 9733 reflections
a = 12.3342 (2) Å	θ = 3.0–40.1°
b = 8.6373 (2) Å	μ = 5.13 mm^{-1}

c = 10.4037 (2) Å
β = 119.402 (1)°
V = 965.59 (3) Å^3
Z = 4

T = 296 K
Fragment, colourless
0.36 × 0.24 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
graphite
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{\min}$ = 0.260, $T_{\max}$ = 0.578
11480 measured reflections

3001 independent reflections
2936 reflections with $I > 2\sigma(I)$
R_{int} = 0.036
$\theta_{\max}$ = 40.1°, $\theta_{\min}$ = 3.0°
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 15$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.054
S = 1.23
3001 reflections
85 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 0.873P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 2.08 e Å^{-3}
$\Delta\rho_{\min}$ = −1.04 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0306 (6)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cd1	0.5000	0.463931 (16)	0.2500	0.01089 (4)
Cd2	0.2500	0.2500	0.0000	0.00995 (4)

P1	−0.01063 (3)	0.27016 (4)	0.02086 (4)	0.00915 (6)
P2	0.18879 (3)	0.50069 (4)	0.19159 (3)	0.00957 (6)
O1	−0.04856 (12)	0.13811 (15)	0.07757 (14)	0.0192 (2)
O2	0.04150 (11)	0.24122 (13)	−0.08092 (13)	0.01274 (17)
O3	0.12504 (11)	0.61475 (16)	0.05498 (13)	0.0208 (2)
O4	0.08602 (11)	0.37174 (16)	0.15789 (13)	0.0188 (2)
O5	0.21814 (13)	0.57449 (17)	0.33127 (13)	0.0203 (2)
O6	0.29305 (9)	0.42682 (14)	0.17838 (12)	0.01323 (16)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd1	0.01110 (6)	0.00998 (7)	0.01157 (6)	0.000	0.00555 (4)	0.000
Cd2	0.01135 (6)	0.01049 (7)	0.00858 (6)	0.00011 (3)	0.00534 (4)	0.00030 (3)
P1	0.01011 (12)	0.00779 (13)	0.01007 (12)	0.00002 (9)	0.00536 (9)	0.00080 (9)
P2	0.00955 (12)	0.00927 (14)	0.00907 (11)	0.00068 (10)	0.00393 (9)	−0.00214 (9)
O1	0.0242 (5)	0.0138 (5)	0.0198 (4)	−0.0032 (4)	0.0111 (4)	0.0051 (4)
O2	0.0118 (4)	0.0150 (5)	0.0129 (4)	−0.0001 (3)	0.0072 (3)	−0.0029 (3)
O3	0.0209 (5)	0.0247 (6)	0.0205 (5)	0.0139 (4)	0.0132 (4)	0.0109 (4)
O4	0.0198 (4)	0.0225 (5)	0.0176 (4)	−0.0106 (4)	0.0120 (4)	−0.0095 (4)
O5	0.0245 (5)	0.0202 (6)	0.0146 (4)	−0.0011 (4)	0.0084 (4)	−0.0098 (4)
O6	0.0102 (3)	0.0129 (4)	0.0156 (4)	0.0016 (3)	0.0056 (3)	−0.0030 (3)

Geometric parameters (Å, °)

Cd1—O1^{i}	2.1875 (12)	Cd2—Cd1^{iv}	3.4370
Cd1—O1^{ii}	2.1875 (12)	P1—O1	1.4624 (12)
Cd1—O6^{iii}	2.3034 (10)	P1—O2	1.5052 (11)
Cd1—O6	2.3034 (10)	P1—O3^{viii}	1.5840 (12)
Cd1—O2^{iv}	2.3690 (11)	P1—O4	1.5983 (11)
Cd1—O2^{v}	2.3690 (11)	P2—O5	1.4604 (12)
Cd1—Cd2	3.4370	P2—O6	1.5011 (11)
Cd1—Cd2^{iii}	3.4370	P2—O3	1.5848 (12)
Cd2—O5^{vi}	2.2037 (12)	P2—O4	1.5918 (12)
Cd2—O5^{vii}	2.2037 (12)	O1—Cd1^{ix}	2.1875 (12)
Cd2—O6^{iv}	2.2563 (11)	O2—Cd1^{iv}	2.3690 (11)
Cd2—O6	2.2563 (11)	O3—P1^{viii}	1.5840 (12)
Cd2—O2^{iv}	2.2809 (11)	O5—Cd2^{i}	2.2037 (12)
Cd2—O2	2.2809 (11)		
O1^{i}—Cd1—O1^{ii}	93.10 (7)	O5^{vii}—Cd2—O2	90.06 (5)
O1^{i}—Cd1—O6^{iii}	90.95 (4)	O6^{iv}—Cd2—O2	84.63 (4)
O1^{ii}—Cd1—O6^{iii}	100.06 (4)	O6—Cd2—O2	95.37 (4)
O1^{i}—Cd1—O6	100.06 (4)	O2^{iv}—Cd2—O2	180.00 (6)
O1^{ii}—Cd1—O6	90.95 (4)	O1—P1—O2	119.08 (8)
O6^{iii}—Cd1—O6	164.00 (6)	O1—P1—O3^{viii}	107.89 (8)

O1^{i}—Cd1—O2^{iv}	174.69 (4)	O2—P1—O3^{viii}	109.73 (6)
O1^{ii}—Cd1—O2^{iv}	91.90 (5)	O1—P1—O4	108.33 (7)
O6^{iii}—Cd1—O2^{iv}	86.40 (4)	O2—P1—O4	109.24 (6)
O6—Cd1—O2^{iv}	81.64 (4)	O3^{viii}—P1—O4	101.05 (8)
O1^{i}—Cd1—O2^{v}	91.90 (5)	O5—P2—O6	118.14 (7)
O1^{ii}—Cd1—O2^{v}	174.69 (4)	O5—P2—O3	113.12 (8)
O6^{iii}—Cd1—O2^{v}	81.64 (4)	O6—P2—O3	104.61 (6)
O6—Cd1—O2^{v}	86.40 (4)	O5—P2—O4	107.83 (7)
O2^{iv}—Cd1—O2^{v}	83.17 (6)	O6—P2—O4	107.92 (7)
O5^{vi}—Cd2—O5^{vii}	180.0	O3—P2—O4	104.28 (8)
O5^{vi}—Cd2—O6^{iv}	93.87 (5)	P1—O1—Cd1^{ix}	148.67 (8)
O5^{vii}—Cd2—O6^{iv}	86.13 (5)	P1—O2—Cd2	121.90 (7)
O5^{vi}—Cd2—O6	86.13 (5)	P1—O2—Cd1^{iv}	129.45 (7)
O5^{vii}—Cd2—O6	93.87 (5)	Cd2—O2—Cd1^{iv}	95.30 (4)
O6^{iv}—Cd2—O6	180.00 (5)	P1^{viii}—O3—P2	139.93 (8)
O5^{vi}—Cd2—O2^{iv}	90.06 (5)	P2—O4—P1	138.17 (8)
O5^{vii}—Cd2—O2^{iv}	89.94 (5)	P2—O5—Cd2^{i}	162.37 (10)
O6^{iv}—Cd2—O2^{iv}	95.37 (4)	P2—O6—Cd2	119.78 (6)
O6—Cd2—O2^{iv}	84.63 (4)	P2—O6—Cd1	140.75 (7)
O5^{vi}—Cd2—O2	89.94 (5)	Cd2—O6—Cd1	97.83 (4)

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1/2; (ii) *x*+1/2, *y*+1/2, *z*; (iii) −*x*+1, *y*, −*z*+1/2; (iv) −*x*+1/2, −*y*+1/2, −*z*; (v) *x*+1/2, −*y*+1/2, *z*+1/2; (vi) −*x*+1/2, *y*−1/2, −*z*+1/2; (vii) *x*, −*y*+1, *z*−1/2; (viii) −*x*, −*y*+1, −*z*; (ix) *x*−1/2, *y*−1/2, *z*.

Fig. 1

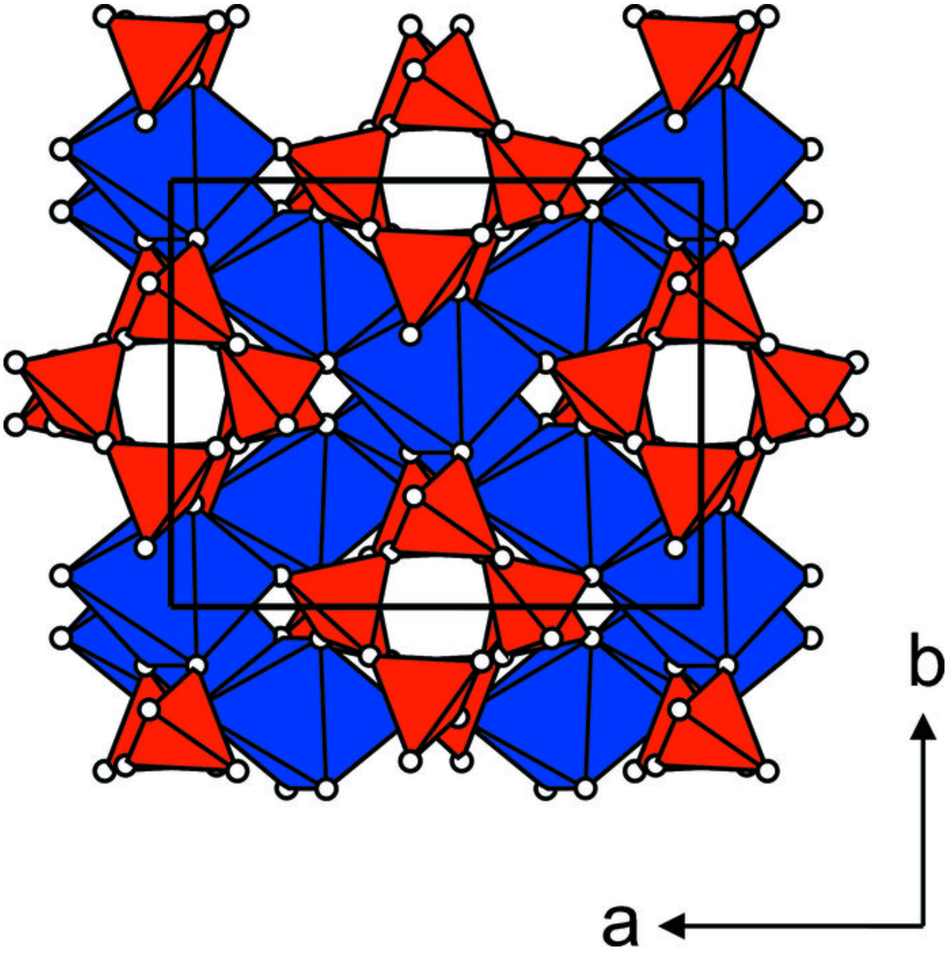

Fig. 2

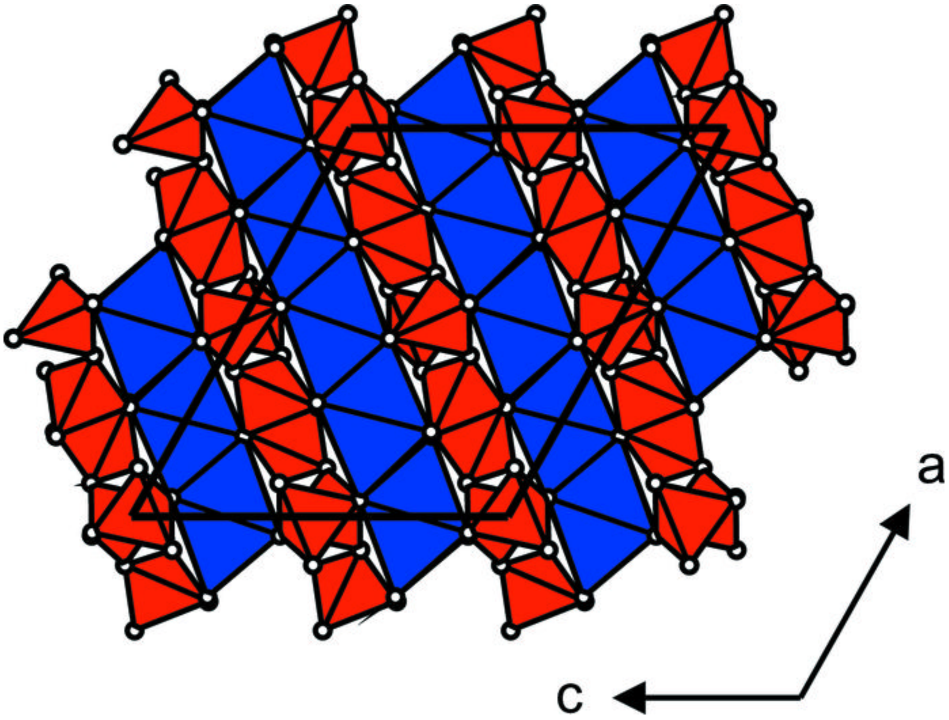

Fig. 3