catena-Poly[bis(ethane-1,2-diammonium) [manganese(II)-di-μ-phosphato-κ⁴O:O′]]: a one-dimensional manganese phosphate

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The title compound, $\{(C_2H_{10}N_2)_2[Mn(PO_4)_2]\}_n$, contains anionic square-twisted chains of formula $[Mn(PO_4)_2]^{4-}$ constructed from corner-sharing four-membered rings of alternating MnO_4 and PO_4 units. The Mn and P atoms have distorted tetrahedral coordination and the Mn atom lies on a twofold axis. The linear manganese–phosphate chains are held together by hydrogen-bonding interactions involving the framework O atoms and the H atoms of the ethane-1,2-diammonium cations, which lie in the interchain spaces.

Comment

Crystallization under solvothermal conditions has proved very successful for the synthesis of a wide range of metal–phosphate frameworks (Cheetham *et al.*, 1999; Maspoch *et al.*, 2007). Much of this work has focused on aluminium and gallium phosphates and their hetero-metal-substituted analogues, and many new materials with zeolite-like properties have been produced. The solvothermal method has also been used for the preparation of a range of transition-metal phosphates, including manganese(II) and manganese(III) compounds. Examples include $Mn_7(HPO_4)_4(PO_4)_2$ (Riou *et al.*, 1987; Rojo *et al.*, 2002), $Mn_6(PO_4)_4 \cdot H_2O$ (Stock, 2002) and $MnPO_4 \cdot H_2O$ (Lightfoot *et al.*, 1987), and synthetic minerals, such as hureaulite, $Mn_5(HPO_4)_2(PO_4)_2 \cdot 4H_2O$ (Gerault *et al.*, 1987; DeAmorim *et al.*, 1996), and gatehouseite, $Mn_5(PO_4)_2(OH)_4$ (Ruszala *et al.*, 1977), as well as open-framework materials in which inorganic or organic cations are accommodated in pores or interlayer spaces in the metal–phosphate frameworks. Of these materials, which are rather few in number compared with the phosphates of other transition metals, such as iron, cobalt or zinc, only one example, $NH_4Mn_4(PO_4)_3$ (Neeraj *et al.*, 2002), has a three-dimensional manganese–phosphate framework. The remainder, *viz.* $NH_4Mn_2O(PO_4)(HPO_4) \cdot H_2O$ (Lightfoot & Cheetham, 1989),

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$Na_2Mn_2O(PO_4)_2 \cdot H_2O$ (Tong *et al.*, 2002), $Ba(MnPO_4)_2 \cdot H_2O$ (Escobal *et al.*, 1999), $(pipH_2)[Mn_6(H_2O)_2(HPO_4)_4(PO_4)_2] \cdot H_2O$ (pip is piperazine; Kongshaug *et al.*, 2001), $[NH_3(CH_2)_2NH_3][Mn_2(PO_4)_2] \cdot 2H_2O$ (Song *et al.*, 2003), $[NH_3(CH_2)_2NH_3][Mn_2(PO_4)_3] \cdot xH_2O$ [$x = 1$ (Escobal *et al.*, 2000) and $x = \frac{1}{5}$ (Chippindale *et al.*, 2001)], $[NH_3(CH_2)_2NH_3]_{3/2}[Mn_2(PO_4)_3] \cdot H_2PO_4$ (Chippindale *et al.*, 2001) and $(trenH_3)_2[Mn_3(PO_4)_4] \cdot 6H_2O$ [tren is tris(2-aminoethyl)amine; Thoma *et al.*, 2004], all have two-dimensional manganese–phosphate frameworks. We describe here the synthesis and characterization of $[NH_3(CH_2)_2NH_3]_2[Mn(PO_4)_2]$, (I), the first example of an organically templated manganese phosphate with a one-dimensional chain-like structure.

(I)
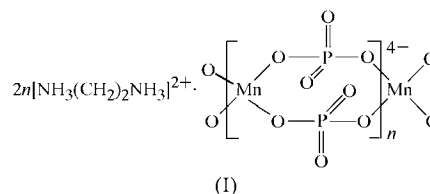
The structure of (I) consists of inorganic chains of formula $[Mn(PO_4)_2]^{4-}$ separated by ethane-1,2-diammonium cations. Atom Mn1 occupies a special position ($4c$) and is tetrahedrally coordinated to two O2 and two O3 atoms with an average Mn1—O distance of 2.024 Å (Table 1). The bond-valence sum around atom Mn1 is 2.14 (Brese & O'Keeffe, 1991), confirming that manganese is present in the compound in the +2 oxidation state. The Mn—O bond lengths are in close agreement with those found in other compounds in which Mn^{2+} is in a tetrahedral MnO_4 unit, for example, in $(trenH_3)_2[Mn_3(PO_4)_4] \cdot 6H_2O$ (Thoma *et al.*, 2004). Atom Mn1 is con-
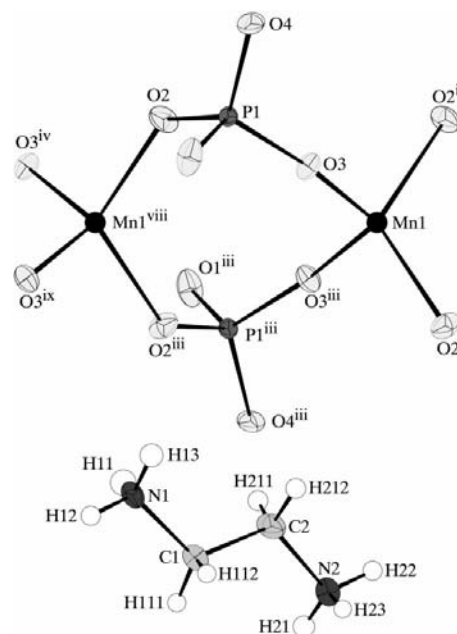
Figure 1
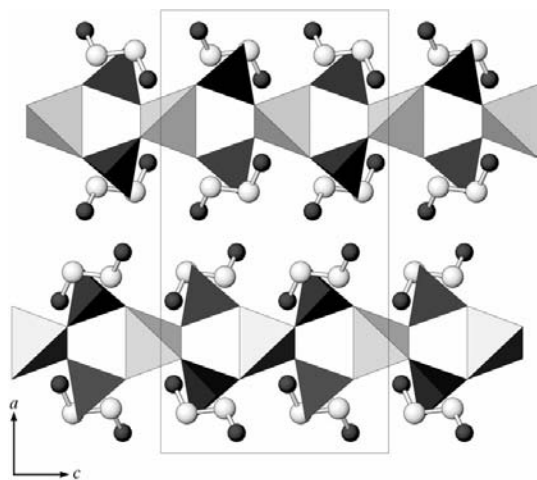The local coordination of atoms in $[NH_3(CH_2)_2NH_3]_2[Mn(PO_4)_2]$ (50% probability displacement ellipsoids). [Symmetry codes: (i) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (ii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iv) $-x + \frac{1}{2}, y, z - \frac{1}{2}$; (viii) $x, y, z - \frac{1}{2}$; (ix) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.]

nected *via* Mn—O—P linkages through atoms O2 and O3 to an independent P atom, P1, which lies on a general position. In addition to the P1—O2 and P1—O3 bonds involved in bridging to atom Mn1, two terminal P1—O bonds, to atoms O1 and O4, complete the tetrahedral coordination around atom P1 (Fig. 1). The O—P—O angles lie in the range 107.5 (1)–110.2 (1)°. The P1=O1 and P1=O4 distances, at 1.536 (1) and 1.534 (1) Å, are somewhat longer than expected for terminal P=O bonds. Their elongation arises as a result of strong hydrogen-bonding interactions with the ethane-1,2-diammonium cations (see below).

The $Mn1O_4$ and $P1O_4$ tetrahedra are linked in strict alternation through their vertices to generate infinite square-twisted chains of formula $[Mn(PO_4)_2]^{4-}$ containing four-membered Mn_2P_2 rings of alternating Mn- and P-based units [described as single 4-rings (*S4R*) in zeolite notation]. The Mn^{2+} cations are well separated from each other within the chains [Mn1···Mn1^{viii} = 4.434 (1) Å]. The chains run parallel to the *c* axis (Fig. 2) and lie in layers in the *bc* plane. These layers are then stacked in an *ABAB* fashion along the *a* axis (Fig. 3), with the chains in layer *A* lying antiparallel to those in layer *B*.
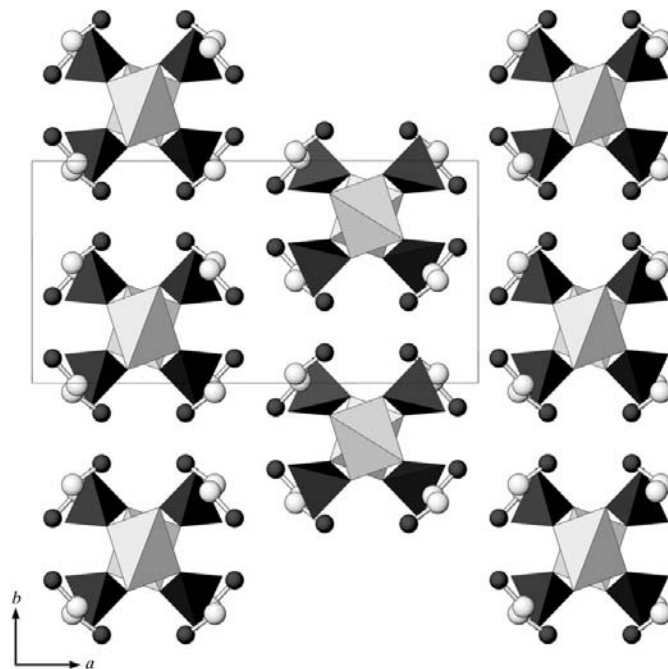
In order to balance the negative charge of the manganese-phosphate chains, the ethane-1,2-diammonium cations located in the interlayer space must be diprotonated, and this is confirmed by the location of all H atoms in a difference Fourier map. A network of hydrogen bonds between the two NH_3 groups of the ethane-1,2-diammonium cations and the O atoms of the phosphate groups serves to link the chains together to generate a three-dimensional assembly (Table 2). Hydrogen bonds involving atom N1 link the manganese–phosphate chains into layers in the *bc* plane. Atom N1 is within *ca* 3.1 Å of four O atoms, three of which are within the same chain [N1···O2^i = 2.816 (2) Å, N1···O3 = 3.064 (2) Å and N1···O4 = 2.811 (2) Å; all symmetry codes are as in

Table 2], with the fourth in a neighbouring chain [N1···O4^v = 2.737 (2) Å]. Adjacent layers are then linked together by hydrogen bonds *via* atom N2, which is within *ca* 3.1 Å of five O atoms. Three of these O atoms are within the same chain [N2···O1^{ii} = 2.877 (2) Å, N2···O1^{vi} = 2.729 (2) Å and N2···O3^{ii} = 2.951 (2) Å] and the remaining two are in a chain in an adjacent layer [N2···O1^{vii} = 2.924 (2) Å and N2···O4^{vii} = 3.116 (3) Å].

Curiously, to date, the title compound has only been synthesized by heating a mixture of pre-formed $[NH_3(CH_2)_2NH_3]_{3/2}[Mn_2(HPO_4)_3]\cdot H_2PO_4$ and ethane-1,2-diamine in an autoclave at 433 K. Attempts to prepare it directly from a manganese(II) salt, phosphoric acid and ethane-1,2-diamine in a conventional solvothermal reaction have not so far been successful. In $[NH_3(CH_2)_2NH_3]_{3/2}$-$[Mn_2(HPO_4)_3]\cdot H_2PO_4$, Mn^{II} is present in MnO_6 units with octahedral geometry and in MnO_5 units with a geometry intermediate between square pyramidal and trigonal bipyramidal. These units are linked through HPO_4 tetrahedra to generate a layered structure, with ethane-1,2-diammonium cations and hydrogen phosphate anions residing within the interlayer space. By contrast, the title compound contains Mn^{2+} in tetrahedral MnO_4 units. The change in the coordination geometry of manganese on heating $[NH_3(CH_2)_2$-$NH_3]_{3/2}[Mn_2(HPO_4)_3]\cdot H_2PO_4$ in ethane-1,2-diamine probably proceeds *via* a dissolution process, although the mechanism is not yet known. Tetrahedral MnO_4 coordination geometry is still rather rare in manganese(II) phosphates and is most commonly found in mixed-metal phosphates, such as MnAlPOs and MnGaPOs, which have zeolite-like frameworks. With the exception of $(trenH_3)_2[Mn_3(PO_4)_4]\cdot 6H_2O$ (Thoma *et al.*, 2004), all the compounds listed in the intro-

Figure 2
A view of the title compound along the *b* axis, showing corner sharing of alternating MnO_4 tetrahedra (white) and PO_4 tetrahedra (grey), generating $[Mn(PO_4)_2]^{4-}$ chains. Ethane-1,2-diammonium cations lie between the manganese–phosphate chains (key: C light-grey spheres; N dark-grey spheres; H atoms omitted).

Figure 3
A view along the *c* axis, showing the stacking of the manganese–phosphate chains. The key is as for Fig. 2.

duction contain manganese coordinated to five, six or seven O atoms.

A number of amine-templated metal phosphates with chain structures based on MO_4 and PO_4 units have been reported. Two chain structure types have been identified. The first, more common type, contains edge-sharing M_2P_2 four-membered rings forming ladder-like structures with additional pendant phosphate groups; examples include $[NH_3(CH_2)_2NH_3]$-$[Al(PO_4)(HPO_4)]$ (Wang *et al.*, 2003) and $[NH_3(CH_2)_2NH_3]$-$[M(HPO_4)_2]$ [M = Co (Cowley & Chippindale, 1999) and M = Zn (Chidambaram *et al.*, 1999)]. The second chain type contains corner-sharing M_2P_2 rings of the sort described here, for example $(NH_4)[NH_3CH_2CH(NH_3)CH_3][Al(PO_4)_2]$ (Ayi *et al.*, 2001), $[NH_3(CH_2)_4NH_3][Ga(PO_4)(HPO_4)]$ (Chippindale *et al.*, 1998), $(dmpH_2)[Co(HPO_4)_2]$ (dmp is *N,N'*-dimethyl-piperazine; Choudhury *et al.*, 2000) and $(pipH_2)[Zn(HPO_4)_2]$ (Natarajan, 2002).

In all cases, the packing together of the chains is driven by hydrogen-bonding interactions. Where the chains contain hydrogenphosphate groups, *e.g.* PO(OH) and $PO(OH)_2$ groups, the possibility exists for interchain hydrogen-bonding interactions in addition to chain–amine interactions, as is observed, for example, in $[NH_3(CH_2)_2NH_3][Co(HPO_4)_2]$ (Cowley & Chippindale, 1999). In the title compound {and $(NH_4)[NH_3CH_2CH(NH_3)CH_3][Al(PO_4)_2]$; Ayi *et al.*, 2001}, no interchain interactions are possible and the metal–phosphate chains are well separated. Hydrogen-bonding networks in these cases therefore involve only chain–amine interactions.

Experimental

Single crystals of (I) were prepared under solvothermal conditions. $[NH_3(CH_2)_2NH_3]_{3/2}[Mn_2(HPO_4)_3]\cdot H_2PO_4$ (0.15 g; Chippindale *et al.*, 2001) was stirred with ethane-1,2-diamine (6.00 ml) at room temperature until homogeneous, sealed in a Teflon-lined autoclave and heated at 433 K for 3 d. The solid product was collected by filtration, washed with methanol and dried in air at room temperature. It consisted of a cream–white powder containing colourless rectangular plates of the title compound suitable for single-crystal X-ray analysis. The powder X-ray diffraction pattern of the bulk product could be indexed on the basis of the orthorhombic unit cell determined from the single-crystal determination with refined lattice parameters a = 8.5667 (13) Å, b = 8.8633 (16) Å and c = 17.207 (3) Å, confirming that the sample is monophasic. An IR spectrum of the product showed features consistent with the presence of ethane-1,2-diammonium cations. A series of strong broad bands occurred in the region 3500–2400 cm⁻¹, corresponding to –NH and –CH₂– stretching modes. The two medium-intensity sharp bands observed at 1645 and 1540 cm⁻¹ are due to NH_3^+ bending modes (antisymmetric and symmetric, respectively). A number of strong sharp bands appearing below 1400 cm⁻¹ correspond to –CH₂– group bending modes with P—O and Mn—O stretching and bending modes. Unambiguous individual assignments of these bands are not possible. Thermogravimetric analysis under flowing N_2 showed a weight loss of *ca* 15.8% over the range 443–521 K and *ca* 17% over the range 521–823 K. These correspond to the loss of two moles of ethane-1,2-diamine from (I) (the calculated value for the loss of one mole of ethane-1,2-diamine is 16.27%). Collapse of the framework occurred above 823 K to give an amorphous residue.

Crystal data

$(C_2H_{10}N_2)_2[Mn(PO_4)_2]$	V = 1310.47 (6) Å³
M_r = 369.12	Z = 4
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
a = 17.2363 (5) Å	μ = 1.29 mm⁻¹
b = 8.5726 (2) Å	T = 293 (2) K
c = 8.8689 (2) Å	0.19 × 0.07 × 0.03 mm

Data collection

Enraf–Nonius KappaCCD diffractometer	1724 measured reflections
Absorption correction: multi-scan (*DENZO/SCALEPACK*; Otwinowski & Minor, 1997)	1477 independent reflections
	1167 reflections with $I > 3\sigma(I)$
	R_{int} = 0.051
T_{min} = 0.90, T_{max} = 0.96	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.026	
S = 1.09	
1167 reflections	$\Delta\rho_{max}$ = 0.33 e Å⁻³
111 parameters	$\Delta\rho_{min}$ = −0.35 e Å⁻³

Table 1
Selected geometric parameters (Å, °).

Mn1—O2ⁱ	2.0486 (13)	P1—O4	1.5339 (13)
Mn1—O3	1.9976 (13)	N1—C1	1.482 (3)
P1—O1	1.5363 (14)	N2—C2	1.474 (3)
P1—O2	1.5437 (13)	C1—C2	1.512 (3)
P1—O3	1.5275 (13)		
O2ⁱ—Mn1—O2ⁱⁱ	116.56 (8)	O1—P1—O4	109.66 (9)
O2ⁱ—Mn1—O3	98.52 (5)	O2—P1—O4	108.71 (8)
O2ⁱ—Mn1—O3ⁱⁱⁱ	114.89 (6)	O3—P1—O4	110.03 (8)
O3—Mn1—O3ⁱⁱⁱ	114.47 (8)	Mn1ⁱᵛ—O2—P1	126.65 (8)
O1—P1—O2	110.22 (8)	Mn1—O3—P1	147.24 (9)
O1—P1—O3	107.53 (8)	N1—C1—C2	110.02 (16)
O2—P1—O3	110.69 (8)	N2—C2—C1	110.41 (16)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H11⋯O2ⁱ	0.92 (3)	1.91 (4)	2.816 (2)	173 (3)
N1—H12⋯O4	0.84 (3)	1.99 (3)	2.811 (2)	168 (3)
N1—H13⋯O4ᵛ	0.89 (3)	1.88 (3)	2.737 (2)	163 (3)
N2—H21⋯O1ⁱⁱ	0.86 (3)	2.02 (3)	2.877 (2)	174 (3)
N2—H22⋯O1ᵛⁱ	0.93 (3)	1.81 (3)	2.729 (2)	170 (2)
N2—H23⋯O1ᵛⁱⁱ	0.80 (3)	2.21 (3)	2.924 (3)	147 (4)
N2—H23⋯O4ᵛⁱⁱ	0.80 (3)	2.41 (3)	3.116 (3)	147 (4)

Symmetry codes: (i) $-x+\frac{1}{2}, y, z+\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (vi) $x, y, z+1$; (vii) $-x, -y+1, -z+1$.

All H atoms were located in difference Fourier maps. The fractional coordinates and isotropic displacement parameters of H atoms bonded to N atoms were refined, whilst the remaining H atoms were placed geometrically and constrained to ride on their parent C atoms [C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

metal-organic compounds

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Ayi, A. Y., Choudhury, A. & Natarajan, S. (2001). *J. Solid State Chem.* **156**, 185–193.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.

Cheetham, A. K., Ferey, G. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3268–3292.

Chidambaram, D., Neeraj, S., Natarajan, S. & Rao, C. N. R. (1999). *J. Solid State Chem.* **147**, 154–169.

Chippindale, A. M., Bond, A. D., Law, A. D. & Cowley, A. R. (1998). *J. Solid State Chem.* **136**, 227–232.

Chippindale, A. M., Gaslain, F. O. M., Cowley, A. R. & Powell, A. V. (2001). *J. Mater. Chem.* **11**, 3172–3179.

Choudhury, A., Natarajan, S. & Rao, C. N. R. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2595–2598.

Cowley, A. R. & Chippindale, A. M. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2147–2149.

DeAmorim, H. S., DoAmaral, M. R., Moreira, L. F. & Mattievich, E. (1996). *J. Mater. Sci. Lett.* **15**, 1895–1897.

Escobal, J., Mesa, J. L., Pizarro, J. L., Lezama, L., Olazcuaga, R. & Rojo, T. (1999). *J. Mater. Chem.* **9**, 2691–2695.

Escobal, J., Pizarro, J. L., Mesa, J. L., Lezama, L., Olazcuaga, R., Arriortua, M. I. & Rojo, T. (2000). *Chem. Mater.* **12**, 376–382.

Gerault, Y., Riou, A. & Cudennec, Y. (1987). *Acta Cryst.* C**43**, 1829–1830.

Kongshaug, K. O., Fjellvag, H. & Lillerud, K. P. (2001). *J. Solid State Chem.* **156**, 32–36.

Lightfoot, P. & Cheetham, A. K. (1989). *J. Solid State Chem.* **78**, 17–22.

Lightfoot, P., Cheetham, A. K. & Sleight, A. W. (1987). *Inorg. Chem.* **26**, 3544–3547.

Maspoch, D., Ruiz-Molina, D. & Veciana, J. (2007). *Chem. Soc. Rev.* **36**, 770–818.

Natarajan, S. (2002). *Inorg. Chem.* **41**, 5530–5537.

Neeraj, S., Noy, M. L. & Cheetham, A. K. (2002). *Solid State Sci.* **4**, 397–404.

Nonius (2001). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Riou, A., Cudennec, Y. & Gerault, Y. (1987). *Acta Cryst.* C**43**, 821–823.

Rojo, J. M., Larranaga, A., Mesa, J. L., Urtiago, M. K., Pizarro, J. L., Arriortua, M. I. & Rojo, T. (2002). *J. Solid State Chem.* **165**, 171–177.

Ruszala, F. A., Anderson, J. B. & Kostiner, E. (1977). *Inorg. Chem.* **16**, 2417–2422.

Song, Y. N., Zavalij, P. Y., Chernova, N. A. & Whittingham, M. S. (2003). *Chem. Mater.* **15**, 4968–4973.

Stock, N. (2002). *Z. Naturforsch. Teil B*, **57**, 187–192.

Thoma, S. G., Bonhomme, F. & Cygan, R. T. (2004). *Chem. Mater.* **16**, 2068–2075.

Tong, W., Xia, G. G., Tian, Z. R., Liu, J., Cai, J., Suib, S. L. & Hanson, J. C. (2002). *Chem. Mater.* **14**, 615–620.

Wang, Y., Yu, J., Li, C. & Xu, R. R. (2003). *Inorg. Chem.* **42**, 4597–4602.

Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.