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$PrMo_8O_{14}$, a Fourth Crystalline Form of the Series RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm)

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Abstract

The crystal structure of $PrMo_8O_{14}$ contains a mixture of *cis*-edge-sharing and *trans* bi-face-capped octahedral Mo_8 clusters in the ratio 2:1. The Mo_8 clusters and the O atoms, the arrangement of which derives from a close packing with the layer sequence *ABAC*..., form layers parallel to the *bc* plane of the orthorhombic unit cell. The Mo—Mo distances range from 2.587 (2) to 2.771 (2) Å and from 2.595 (1) to 2.871 (2) Å in the *trans* and *cis*-edge-sharing isomeric clusters, respectively. The shortest Mo—Mo distance between the Mo_8 clusters within the same layer is 3.053 (1) Å and that between the clusters of adjacent layers is 3.634 (2) Å. The Mo—O distances are between 2.036 (9) and 2.125 (11) Å in the *trans* isomer, and between 1.907 (13) and 2.189 (13) Å in the *cis*-edge-sharing isomer. The environment of each of the two crystallographically independent Pr^{3+} ions comprises twelve O atoms forming a distorted cuboctahedron. The Pr—O distances lie between 2.530 (10) and 2.913 (8) Å, and between 2.420 (7) and 3.198 (8) Å for the Pr(1) and Pr(2) sites, respectively.

Comment

This work constitutes part of our studies on the series of compounds RMo_8O_{14} (R = La, Ce, Pr, Nd, Sm) containing bi-face-capped octahedral Mo_8 clusters. These compounds have been obtained recently by fused-salt electrolysis in the case of $LaMo_{8-x}O_{14}$ (x = 0.0 and 0.3) (Leligny, Ledesert, Labbé, Raveau & McCarroll, 1990; Leligny, Labbé, Ledesert, Hervieu, Raveau & McCarroll 1993) and by solid-state reaction at high temperature for the members with R = La, Ce, Pr, Nd and Sm (Gougeon & McCarley, 1991; Kerihuel & Gougeon, 1995). Up to now, three different crystalline forms have been found for the RMo_8O_{14} compounds. In all of these forms, the R—O network is similar and they differ only by the arrangement of the capping Mo atoms of the Mo_8 clusters. The first crystalline form was observed for the compounds $LaMo_{7.7}O_{14}$ (Leligny *et al.*, 1990) and $NdMo_8O_{14}$ (Gougeon & McCarley, 1991), obtained by fused-salt electrolysis and by solid-state reaction, respectively. Both compounds crystallize in the non-centrosymmetric space group *Aba*2 with the following parameters: a_{La} = 9.196 (1), b_{La} = 9.985 (1), c_{La} = 11.171 (1) Å; a_{Nd} = 9.209 (3), b_{Nd} = 10.008 (2), c_{Nd} = 11.143 (4) Å. Their structures comprise only *cis*-edge-sharing bi-face-capped Mo_8 clusters. The second form, which was described by Leligny *et al.* (1993), corresponds to that shown by crystals of the stoichiometric compound $LaMo_8O_{14}$, synthesized by fused-salt electrolysis. The crystal structure of the latter compound is more complex due to a one-dimensional commensurate modulation of wavevector $q^* = b^*/3$ [a = 11.129 (1), b = 10.000 (1), c = 9.218 (1) Å]. The structure that was solved in superspace group $P^{C2ca}_{\bar{1}\bar{1}1}$ consists of *cis*-edge-sharing and *trans* bi-face-capped Mo_8 clusters, each occurring in two distinct configurations. More recently, a third form corresponding to the $CeMo_8O_{14}$ compound [space group *Pbcn*; a = 9.1937 (7), b = 11.121 (1), c = 20.014 (1) Å] (Kerihuel & Gougeon, 1995), obtained by solid-state reaction, was discovered. The Mo network of this compound is based on a well ordered mixture of *cis*-edge-sharing and *trans* bi-face-capped octahedral Mo_8 clusters in equal proportion. We present here the structure of $PrMo_8O_{14}$ which constitutes the fourth crystalline form in the RMo_8O_{14} series.

Like the structure of $CeMo_8O_{14}$, that of $PrMo_8O_{14}$ is characterized by the coexistence of *cis*-edge-sharing and *trans* bi-face-capped octahedral Mo_8 clusters. However, whereas the two isomeric forms are in equal proportions in the former compound, they are in the ratio 2:1 in the Pr compound. As a consequence of this, we observed a tripling, instead of doubling, of the *b* parameter of the unit cell of $NdMo_8O_{14}$ (*c* parameter in $CeMo_8O_{14}$ and $PrMo_8O_{14}$) in which only the *cis* isomer of the Mo_8 cluster occurs. The other parameters are close to those determined for $NdMo_8O_{14}$ and $CeMo_8O_{14}$. Both isomeric forms of the Mo_8 cluster occurring in $PrMo_8O_{14}$ are shown in Fig. 1 with their O-atom environments. Within the Mo_8O_{24} cluster units thus formed, the two capping Mo atoms have six O-atom neighbours forming a distorted octahedron and the remaining six Mo atoms have only five O atoms in an approximately square-pyramidal arrangement.

Fig. 2(*a*) is an *ORTEP*II (Johnson, 1976) drawing of the unit cell of $PrMo_8O_{14}$ as viewed parallel to the *b* axis. From this perspective view, the layer arrangement of the Mo_8 clusters and O atoms can be seen. The O-atom framework is similar to those in $LaMo_{7.7}O_{14}$, $NdMo_8O_{14}$ and $CeMo_8O_{14}$; it derives from a close packing with the layer sequence *ABAC*... where in

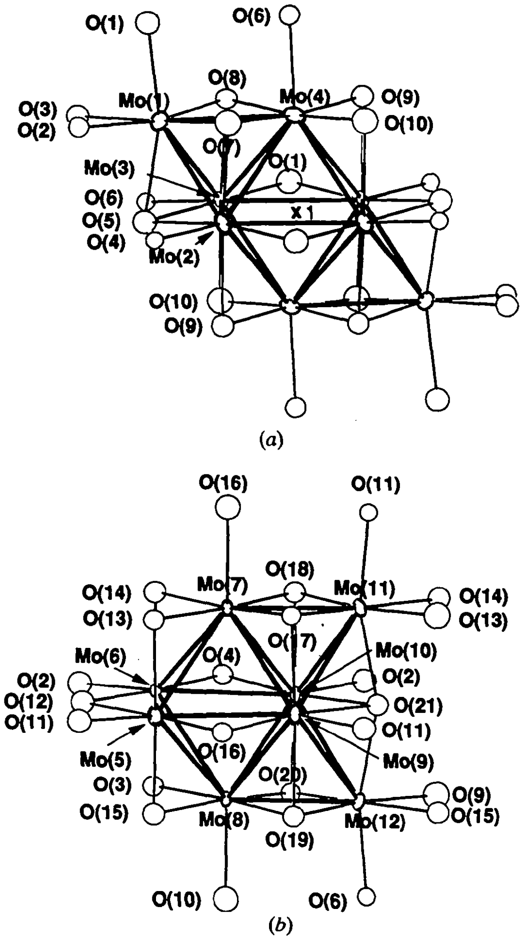

Fig. 1. (*a*) The *trans* and (*b*) the *cis*-edge-sharing bi-face-capped Mo_8 clusters with their O-atom environments.

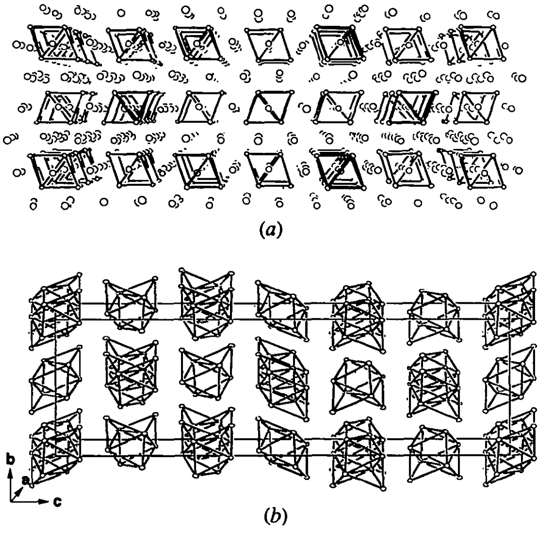

Fig. 2. (*a*) Perspective view of the structure along the *b* axis. The Mo_8 clusters are emphasized by bold lines. (*b*) The arrangement of the Mo_8 clusters within the unit cell.

the *A* layers some of the O atoms are missing in an ordered way or are substituted by the Pr ions, and the *B* and *C* layers are entirely occupied by O atoms. Fig. 2(*b*) depicts the Mo_8 clusters within the unit cell.

The Mo—Mo distances within the centrosymmetric *trans* bi-face-capped Mo_8 cluster show no large differences from those previously reported for $CeMo_8O_{14}$ and range from 2.587 (2) to 2.771 (2) Å [2.5825 (9) to 2.778 (1) Å in $CeMo_8O_{14}$]. The average value of 2.704 Å is slightly lower than that observed in the Mo_8 cluster occurring in $CeMo_8O_{14}$ (2.708 Å). The Mo—O distances lie between 2.036 (9) and 2.125 (11) Å [2.027 (6)–2.110 (7) Å in $CeMo_8O_{14}$] with an average distance of 2.069 Å [2.062 Å for the *trans* isomer in $CeMo_8O_{14}$]. The *cis* isomers present in $PrMo_8O_{14}$ have no imposed symmetry, whereas those previously observed in $NdMo_8O_{14}$ and $CeMo_8O_{14}$ possess C_2 symmetry. The Mo—Mo distances cover a range from 2.595 (1) to 2.871 (2) Å, slightly narrower than for the *cis* isomer occurring in $CeMo_8O_{14}$ [2.5958 (8)–2.886 (2) Å] but wider than in $NdMo_8O_{14}$ [2.590 (1)–2.848 (1) Å]. The mean Mo—Mo distance is 2.735 Å and is between the average distance of 2.731 Å in $NdMo_8O_{14}$, and that of 2.738 Å in $CeMo_8O_{14}$. As already observed for $CeMo_8O_{14}$, the range of Mo—O distances in the *cis* isomer [1.907 (13)–2.189 (13) Å] is much broader than in the *trans* form. The average Mo—O distance is 2.042 Å and corresponds to that in $CeMo_8O_{14}$ (2.042 Å). For $NdMo_8O_{14}$, the average Mo—O distance is slightly longer (2.050 Å). The shortest Mo—Mo intercluster distances within a given layer are 3.053 (1) Å between the two different isomers and 3.086 (2) Å between adjacent *cis*-edge-sharing Mo_8 clusters, compared to 3.078 (1) Å in $LaMo_{7.7}O_{14}$, 3.068 (1) Å in $NdMo_8O_{14}$ and 3.0790 (9) Å in $CeMo_8O_{14}$. On the other hand, the shortest Mo—Mo distance between adjacent cluster layers is as long as 3.634 (1) Å, excluding any direct Mo—Mo interactions. Consequently, although the structure is three dimensional overall, it can be considered to be two dimensional with respect to the Mo network. The Pr^{3+} ions occupy two crystallographically independent sites. The Pr(1) ions are located at the origin of the unit cell. They are surrounded by 12 O atoms forming a distorted cuboctahedron. The Pr(1)—O distances range from 2.53 (1) to 2.913 (8) Å. The Pr(2) ions occupy a general position. Their environment also consists of 12 O atoms forming a highly distorted cuboctahedron, as reflected in the Pr(2)—O distances, which lie between 2.420 (7) and 3.198 (8) Å.

Experimental

Single crystals were obtained by heating a mixture of overall composition $Pr_3Mo_{35}O_{62}$ (starting materials: Pr_6O_{11}, MoO_3 and Mo) in a sealed molybdenum crucible at about 2200 K for 5 min. The crucible was then cooled at a rate of $100\,K\,h^{-1}$ to 1373 K and finally furnace-cooled to room temperature.

Crystal data

$PrMo_8O_{14}$
$M_r = 1132.42$
Orthorhombic
Pbca
$a = 9.2037\ (6)$ Å
$b = 11.114\ (2)$ Å
$c = 30.012\ (5)$ Å
$V = 3069.9\ (8)$ Å^3
$Z = 12$
$D_x = 7.350$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7–15.4°$
$\mu = 13.995$ mm^{-1}
$T = 295$ K
Irregular
$0.12 \times 0.10 \times 0.10$ mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
$T_{\min} = 0.21,\ T_{\max} = 0.25$
7445 measured reflections
7445 independent reflections

3150 observed reflections $[I > 2.5\sigma(I)]$
$\theta_{\max} = 35°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 48$
3 standard reflections
frequency: 90 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.042$
$wR = 0.044$
$S = 1.649$
3150 reflections
209 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{\max} < 0.01$

$\Delta\rho_{\max} = 3.34$ e Å^{-3}
$\Delta\rho_{\min} = -1.21$ e Å^{-3}
Extinction correction: Stout & Jensen (1968)
Extinction coefficient: $6.84\ (2) \times 10^{-8}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{\rm iso}$ for O atoms; $B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$B_{\rm iso}/B_{\rm eq}$
Pr(1)	1	0	1/2	0.65 (1)
Pr(2)	1.0008 (1)	0.02713 (5)	0.16395 (2)	0.474 (8)
Mo(1)	0.8766 (1)	0.22522 (8)	0.05281 (3)	0.23 (1)
Mo(2)	0.8783 (1)	−0.00928 (8)	0.05283 (3)	0.23 (1)
Mo(3)	1.1211 (1)	0.12316 (8)	0.02879 (3)	0.23 (1)
Mo(4)	0.6237 (1)	0.62350 (8)	0.97526 (3)	0.24 (1)
Mo(5)	0.8799 (1)	−0.12861 (8)	0.30879 (3)	0.26 (1)
Mo(6)	1.1193 (1)	−0.12910 (8)	0.35857 (3)	0.24 (1)
Mo(7)	1.1209 (1)	−0.00674 (7)	0.27996 (3)	0.20 (1)
Mo(8)	0.8795 (1)	−0.00171 (8)	0.38690 (3)	0.23 (1)
Mo(9)	0.8774 (1)	0.11496 (8)	0.30403 (3)	0.26 (1)
Mo(10)	1.1260 (1)	0.11661 (8)	0.36182 (3)	0.27 (1)
Mo(11)	0.8773 (1)	−0.27331 (8)	0.22102 (3)	0.24 (1)
Mo(12)	0.8786 (1)	0.23197 (8)	0.38876 (3)	0.24 (1)
O(1)	0.761 (1)	0.3689 (7)	0.0246 (3)	0.6 (1)
O(2)	0.7586 (9)	0.2384 (7)	0.1108 (3)	0.4 (1)
O(3)	0.513 (1)	0.6310 (7)	0.5840 (2)	0.5 (1)
O(4)	0.739 (1)	0.4899 (7)	0.1139 (3)	0.6 (1)
O(5)	0.991 (1)	0.8927 (7)	0.9121 (3)	0.6 (1)
O(6)	0.7576 (9)	0.2447 (7)	0.4411 (3)	0.4 (1)
O(7)	0.728 (1)	0.3934 (7)	0.5253 (3)	0.4 (1)
O(8)	0.993 (1)	−0.2597 (7)	0.0005 (2)	0.4 (1)
O(9)	0.508 (1)	0.8675 (6)	0.4158 (2)	0.4 (1)
O(10)	0.769 (1)	0.5019 (7)	0.9469 (3)	0.5 (1)
O(11)	0.7398 (9)	0.2372 (7)	0.2761 (3)	0.5 (1)
O(12)	0.994 (1)	−0.2553 (6)	0.3335 (3)	0.4 (1)
O(13)	0.987 (1)	0.8639 (6)	0.2516 (3)	0.4 (1)
O(14)	0.754 (1)	0.8641 (7)	0.1930 (3)	0.5 (1)
O(15)	0.758 (1)	0.3714 (7)	0.3602 (3)	0.5 (1)
O(16)	0.736 (1)	0.5094 (6)	0.7807 (3)	0.3 (1)
O(17)	1.010 (1)	0.8927 (6)	0.7551 (2)	0.4 (1)
O(18)	0.765 (1)	0.3893 (7)	0.6918 (3)	0.4 (1)
O(19)	0.764 (1)	0.6154 (7)	0.3583 (3)	0.5 (1)
O(20)	0.986 (1)	0.8894 (7)	0.5786 (2)	0.4 (1)
O(21)	0.995 (1)	0.2617 (6)	0.3332 (3)	0.37 (9)

Table 2. *Selected bond distances* (Å)

trans-Mo_8 cluster			
Mo(1)—Mo(4)	2.587 (2)	Mo(1)—O(3)	2.113 (9)
Mo(1)—Mo(2)	2.606 (1)		
Mo(1)—Mo(3)	2.621 (2)	Mo(2)—O(9)	2.045 (10)
		Mo(2)—O(1)	2.050 (11)
Mo(2)—Mo(3)	2.725 (2)	Mo(2)—O(5)	2.061 (10)
Mo(2)—Mo(3)	2.757 (2)	Mo(2)—O(7)	2.061 (10)
Mo(2)—Mo(4)	2.757 (2)	Mo(2)—O(4)	2.125 (11)
Mo(2)—Mo(4)	2.771 (2)		
		Mo(3)—O(8)	2.042 (8)
Mo(3)—Mo(4)	2.744 (2)	Mo(3)—O(6)	2.054 (8)
Mo(3)—Mo(4)	2.767 (2)	Mo(3)—O(5)	2.058 (10)
Mo(4)—Mo(12)*	3.053 (1)	Mo(3)—O(1)	2.062 (11)
		Mo(3)—O(10)	2.077 (1)
Mo(1)—O(8)	2.039 (8)		
Mo(1)—O(2)	2.056 (9)	Mo(4)—O(7)	2.036 (9)
Mo(1)—O(7)	2.069 (10)	Mo(4)—O(8)	2.068 (9)
Mo(1)—O(5)	2.079 (11)	Mo(4)—O(9)	2.080 (10)
Mo(1)—O(1)	2.094 (10)	Mo(4)—O(10)	2.081 (11)
		Mo(4)—O(6)	2.095 (9)
cis-Mo_8 cluster			
Mo(5)—Mo(6)	2.662 (2)	Mo(8)—Mo(12)	2.598 (1)
Mo(5)—Mo(9)	2.711 (2)	Mo(8)—Mo(10)	2.728 (2)
Mo(5)—Mo(8)	2.736 (2)	Mo(8)—Mo(9)	2.805 (2)
Mo(5)—Mo(7)	2.740 (2)		
Mo(5)—Mo(11)†	3.086 (2)	Mo(9)—Mo(11)	2.684 (2)
		Mo(9)—Mo(12)	2.856 (2)
Mo(6)—Mo(7)	2.723 (2)	Mo(9)—Mo(10)	2.871 (2)
Mo(6)—Mo(10)	2.733 (2)		
Mo(6)—Mo(8)	2.756 (2)	Mo(10)—Mo(12)	2.735 (2)
		Mo(10)—Mo(11)	2.771 (2)
Mo(7)—Mo(11)	2.595 (1)		
Mo(7)—Mo(9)	2.715 (2)		
Mo(7)—Mo(10)	2.814 (2)	Mo(9)—O(16)	2.022 (10)
		Mo(9)—O(11)	2.038 (9)
Mo(5)—O(12)	1.907 (13)	Mo(9)—O(17)	2.060 (10)
Mo(5)—O(13)	1.983 (10)	Mo(9)—O(19)	2.087 (10)
Mo(5)—O(15)	1.999 (10)	Mo(9)—O(21)	2.144 (13)
Mo(5)—O(16)	2.052 (10)		
Mo(5)—O(11)	2.097 (9)	Mo(10)—O(2)	1.999 (8)
		Mo(10)—O(4)	2.016 (11)
Mo(6)—O(12)	1.965 (14)	Mo(10)—O(18)	2.056 (10)
Mo(6)—O(3)	1.984 (10)	Mo(10)—O(20)	2.064 (9)
Mo(6)—O(14)	1.986 (10)	Mo(10)—O(21)	2.189 (13)
Mo(6)—O(4)	2.035 (11)		
Mo(6)—O(2)	2.068 (8)	Mo(11)—O(11)	1.977 (10)
		Mo(11)—O(18)	2.036 (10)
Mo(7)—O(17)	2.039 (11)	Mo(11)—O(21)	2.044 (14)
Mo(7)—O(18)	2.045 (10)	Mo(11)—O(13)	2.049 (10)
Mo(7)—O(14)	2.054 (10)	Mo(11)—O(17)	2.071 (11)
Mo(7)—O(13)	2.073 (11)	Mo(11)—O(14)	2.079 (10)
Mo(7)—O(16)	2.107 (11)		
		Mo(12)—O(6)	1.931 (9)
Mo(8)—O(20)	2.039 (10)	Mo(12)—O(9)	2.006 (10)
Mo(8)—O(19)	2.044 (10)	Mo(12)—O(21)	2.010 (4)
Mo(8)—O(15)	2.061 (10)	Mo(12)—O(19)	2.059 (10)
Mo(8)—O(10)	2.070 (11)	Mo(12)—O(20)	2.081 (10)
Mo(8)—O(3)	2.082 (10)	Mo(12)—O(15)	2.088 (10)

* Between *trans* and *cis*-edge-sharing Mo_8 clusters belonging to the same layer.

† Between *cis*-edge-sharing Mo_8 clusters belonging to the same layer.

Pr environment			
Pr(1)—O(7) × 2	2.530 (10)		
Pr(1)—O(10) × 2	2.659 (12)		
Pr(1)—O(20) × 2	2.664 (8)		
Pr(1)—O(8) × 2	2.671 (8)		
Pr(1)—O(1) × 2	2.737 (11)		
Pr(1)—O(3) × 2	2.913 (8)		
Pr(2)—O(12)	2.420 (7)	Pr(2)—O(16)	2.763 (12)
Pr(2)—O(5)	2.452 (8)	Pr(2)—O(15)	2.903 (10)
Pr(2)—O(19)	2.468 (11)	Pr(2)—O(21)	2.951 (7)
Pr(2)—O(18)	2.504 (11)	Pr(2)—O(9)	2.981 (8)
Pr(2)—O(17)	2.589 (8)	Pr(2)—O(14)	3.033 (10)
Pr(2)—O(4)	2.701 (13)	Pr(2)—O(13)	3.198 (8)

Data were corrected for Lorentz–polarization and an empirical absorption correction following the *DIFABS* procedure (Walker & Stuart, 1983) was applied to isotropically refined data. Refinements of the occupancy factors for the Pr and Mo sites confirmed that they are fully occupied.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Structure solution and subsequent difference Fourier syntheses: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Molecular graphics: *ORTEP*II (Johnson, 1976). Other calculations: *MolEN* (Fair, 1990). Computer: Digital MicroVAX 3100.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: DU1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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σ-Dibarium Pyrophosphate

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Abstract

σ-Dibarium diphosphate, $Ba_2P_2O_7$, crystallizes in space group $P\bar{6}2m$ with the Ba atoms, separated by 4.703 Å, arranged in columns. Ba atoms are in sites of eleven- and tenfold coordination with Ba(1)—O and Ba(2)—O distances in the ranges 2.776 (8)–2.869 (6) and 2.878 (9)–3.080 (9) Å, respectively. One Ba atom has three interactions with bridging O atoms. P_2O_7 groups have threefold axes passing through the P atoms. The bridging O atom is disordered about these axes, with P—O—P angles of 130 (1) and 134 (4)°.

Comment

Historically, diphosphates of the $A_2P_2O_7$ type, in which A is a divalent cation, have been considered to exist as two types of structure predicated by the ionic radius of A, *i.e.* when the radius of A is less than 0.97 Å, the structure is of the thortveitite type, in which P_2O_7 groups display a staggered conformation (A = Mg, Mn, Fe, Co, Ni, Cu, Zn), and when the radius of A is greater than 0.97 Å (A = Ca, Sr, Ba, Pb), the diphosphate is seen to be in an eclipsed conformation (Brown & Calvo, 1970) and is categorized as the dichromate type.

Compounds of both types have been found to exist in allotropic forms. Thortveitite structures typically show a transition at temperatures below 873 K from a low-temperature or α form to a high-temperature or β form. Heating leads to a cell volume one quarter that of the ambient temperature form (one half in the case of Cu) and a more symmetrical structure. Typically, α forms show A atoms in layers, with AO_5 and AO_6 polyhedra sharing edges to form an irregular or 'broken-sided' two-dimensional array of hexagons. High-temperature forms are observed in space group $C2/m$ and show a regularization of the hexagon with the introduction of axial distortions in bonds to A. Cu (Robertson & Calvo, 1967, 1968), Co (Krishnamachari

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