Data collection

AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: empirical ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.717$, $T_{\max} = 0.981$
496 measured reflections
481 independent reflections
352 reflections with $F > 3\sigma(F)$
$R_{\rm int} = 0.047$
$\theta_{\max} = 34.97°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 18$
3 standard reflections every 150 reflections intensity decay: 9.14%

Refinement

Refinement on *F*
$R = 0.042$
$wR = 0.049$
$S = 3.282$
338 reflections
20 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 5.55$ e Å^{-3}
$\Delta\rho_{\min} = -4.85$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: 10.48
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å)*

Pt—O	2.8039 (6)	Ca2—O$^{\rm ii}$	2.8415 (6)
Ca1—O	2.8320 (6)	Ca2—O$^{\rm iii}$	2.8511 (6)
Ca1—O$^{\rm i}$	2.8319 (6)	Ca2—O$^{\rm iv}$	2.8714 (7)
Ca2—O	2.8475 (6)		

Symmetry codes: (i) $\frac{1}{3} + y, x - \frac{1}{3}, \frac{1}{6} - z$; (ii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iii) $\frac{1}{3} + x - y, x - \frac{1}{3}, \frac{2}{3} - z$; (iv) $1 - y, x - y, z$.

The remaining residual electron density is concentrated around the Pt ion at a distance of 0.65 Å. Structure solution and refinement were performed on a Silicon Graphics INDIGO^2 computer using the *TEXSAN* (Molecular Structure Corporation, 1993) structure solution program library.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1172). Services for accessing these data are described at the back of the journal.

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Dibarium Magnesium Phosphate

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Abstract

$Ba_2Mg(PO_4)_2$ is found to be isostructural with $Ba_2Ni(PO_4)_2$. The structure can be described as a three-dimensional framework of MgO_6 octahedra and PO_4 tetrahedra generating tunnels which accommodate Ba atoms.

Comment

Compounds with the general formula $A_2Ni(PO_4)_2$, A = Sr, Ba, have been investigated recently because of their potential magnetic properties (Elbali, Boukhari, Holt & Aride, 1993; Elbali *et al.*, 1994). Most of the structural features of analogous diamagnetic compounds where Ni is replaced by Zn or Mg are still unknown, although the existence of such compounds was reported some time ago (Hoffman, 1965).

A powder pattern of $Ba_2Mg(PO_4)_2$, indexed from the approximate parameters measured from single-crystal diffraction photographs, showed it to be isostructural with $Ba_2Ni(PO_4)_2$. The systematic absences are consistent with space group $P2_1/n$. As in the case of $Ba_2Ni(PO_4)_2$, $Ba_2Mg(PO_4)_2$ has as a non-compact structure (23.6 Å^3 per O atom). The framework is based on bipolyhedral $MgP(1)O_8$ entities: the MgO_6 octahedron shares an edge with the $P(1)O_4$ tetrahedron (Fig. 1).

$P(1)O_4$ appears to be a fairly regular tetrahedron. The MgO_6 octahedron is slightly distorted because one of the two O atoms, O(12), forming the common edge is only weakly bound to the Mg atom: 0.19 valence units (v.u.) for O(12), compared to 0.36±0.02 v.u. for the other five. Inclusion of the sixth O atom in the coordination polyhedron of Mg is the result of a choice between two possible descriptions: distorted octahedron or square-based pyramid. The short distance

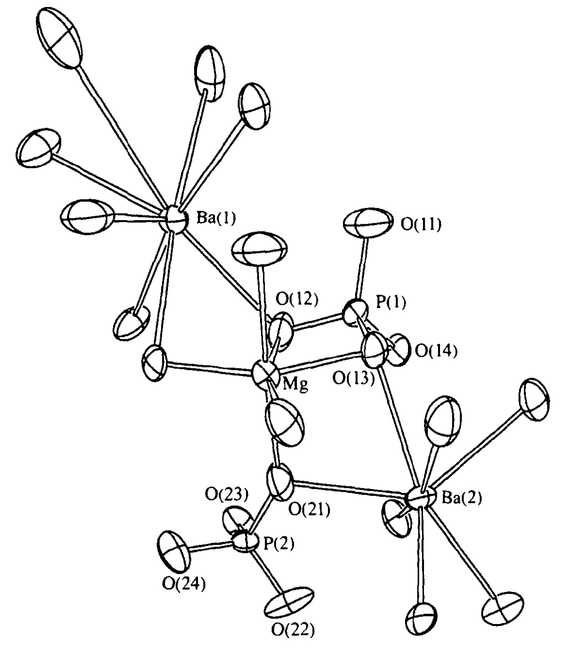

Fig. 1. A molecular representation of $Ba_2Mg(PO_4)_2$. Displacement ellipsoids are shown at the 90% probability level.

O(12)···O(13) [2.444 (7) Å] justifies the first choice and most likely represents an effective 'screening' of intercationic repulsions between edge-sharing PO_4 and MgO_6 polyhedra.

The $MgP(1)O_8$ units are corner connected, forming rings of four polyhedra organized in *a*-oriented chains. The regular $P(2)O_4$ tetrahedra connect neighbouring chains (Fig. 2).

The larger Ba atoms occupy sites in the *a*-oriented tunnels of the O-atom framework. The coordination polyhedra are irregular and the number of neighbours was determined by applying the empirical model of Brown & Wu (1976) (Fig. 3). Computation of bond strengths shows that Ba(2) is surrounded by seven O atoms forming a monocapped trigonal prism. For Ba(1), an eighth neighbour contributes 0.12 v.u. and has to be taken into account, giving a bicapped trigonal prism.

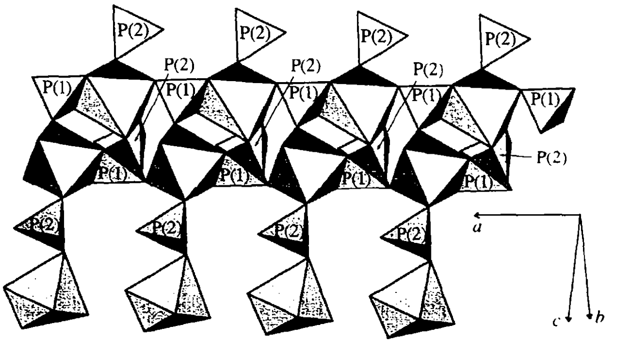

Fig. 2. The connections between the (MgO_6) octahedra and (PO_4) tetrahedra.

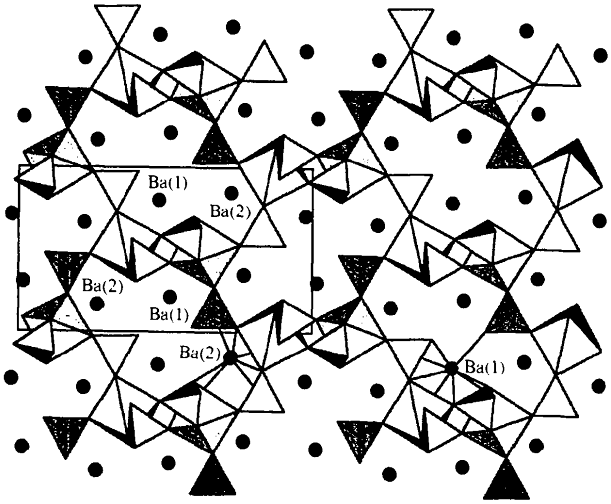

Fig. 3. A projection onto the (100) plane. The grey circles represent Ba atoms. The O-atom environments are shown for two Ba atoms.

Experimental

$Ba_2Mg(PO_4)_2$ powder was synthesized by solid-state reaction of stoichiometric amounts of $BaCO_3$, MgO and NH_4HPO_4. The mixture was heated at 1173 K in a platinum crucible for 24 h, then cooled to room temperature. Single crystals were grown from a melt of previously prepared $Ba_2Mg(PO_4)_2$ with barium fluoride (30% mol). The charge was heated above the melting point (1373 K), then slowly cooled (5 K h^{-1}) to room temperature.

Crystal data

$Ba_2Mg(PO_4)_2$
$M_r = 488.92$
Monoclinic
$P2_1/n$
$a = 5.294$ (4) Å
$b = 8.837$ (4) Å
$c = 16.143$ (8) Å
$\beta = 90.60$ (5)°
$V = 755.2$ (7) Å^3
$Z = 4$
$D_x = 4.30$ Mg m^{-3}
$D_m = 4.25$ (8) Mg m^{-3}
D_m measured by pycnometry

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 4.0$–10.1°
$\mu = 10.88$ mm^{-1}
$T = 293$ K
Parallelepiped
0.38 × 0.015 × 0.014 mm
Colorless

Data collection

Syntex Nicolet *P*3*F* diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.199$, $T_{\max} = 0.290$
1789 measured reflections

1789 independent reflections
$\theta_{\max} = 27.6$°
$h = -6 \rightarrow 6$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 20$
3 standard reflections every 60 reflections intensity decay: 2.1%

Refinement

Refinement on *F*
$R = 0.033$

Extinction correction: Becker & Coppens (1975)

$wR = 0.038$
$S = 1.95$
1789 reflections
119 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.0053$
$\Delta\rho_{\max} = 0.9$ e Å^{-3}
$\Delta\rho_{\min} = -0.7$ e Å^{-3}

Extinction coefficient: $1.17(4) \times 10^{-6}$
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Ba(1)—O(13^{i})	2.641 (2)	Mg—O(11^{ix})	2.046 (3)
Ba(1)—O(12^{ii})	2.702 (2)	Mg—O(21)	2.048 (2)
Ba(1)—O(22^{iii})	2.703 (2)	Mg—O(23^{ii})	2.059 (2)
Ba(1)—O(22)	2.732 (2)	Mg—O(14^{x})	2.061 (2)
Ba(1)—O(24^{iv})	2.823 (3)	Mg—O(13)	2.084 (3)
Ba(1)—O(11^{v})	2.917 (3)	Mg—O(12)	2.390 (3)
Ba(1)—O(14^{v})	2.952 (2)	P(1)—O(12)	1.512 (2)
Ba(1)—O(23^{iii})	3.114 (3)	P(1)—O(11)	1.513 (2)
Ba(2)—O(12)	2.731 (3)	P(1)—O(13)	1.534 (2)
Ba(2)—O(21^{vi})	2.732 (2)	P(1)—O(14)	1.552 (2)
Ba(2)—O(23)	2.733 (3)	P(2)—O(21)	1.515 (2)
Ba(2)—O(13^{vi})	2.747 (2)	P(2)—O(22)	1.517 (2)
Ba(2)—O(14)	2.776 (2)	P(2)—O(23)	1.545 (2)
Ba(2)—O(24^{vii})	2.789 (2)	P(2)—O(24)	1.549 (2)
Ba(2)—O(24^{viii})	2.898 (2)		
O(11^{ix})—Mg—O(21)	173.88 (9)	O(21)—Mg—O(12)	88.01 (8)
O(11^{ix})—Mg—O(23^{ii})	85.98 (8)	O(23^{ii})—Mg—O(14^{x})	112.27 (8)
O(11^{ix})—Mg—O(14^{x})	89.44 (8)	O(23^{ii})—Mg—O(13)	99.03 (8)
O(11^{ix})—Mg—O(13)	86.27 (8)	O(23^{ii})—Mg—O(12)	164.35 (7)
O(11^{ix})—Mg—O(12)	95.34 (8)	O(14^{x})—Mg—O(13)	148.02 (8)
O(21)—Mg—O(23^{ii})	89.42 (8)	O(14^{x})—Mg—O(12)	83.35 (8)
O(21)—Mg—O(14^{x})	96.04 (8)	O(13)—Mg—O(12)	65.56 (7)
O(21)—Mg—O(13)	90.48 (8)		

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

Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *ORXFLS* (Busing, 1971, locally modified by P. Laruelle). Molecular graphics: *ORTEP*III (Burkett & Johnson, 1996); *MOLVIEW* (Cense, 1990). Geometric calculations: *ORFFE* (Busing, Martin & Levy, 1964).

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A New Structural Variation of Nb_3YX_7 Compounds: Monoclinic Nb_3SI_7

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Abstract

Monoclinic triniobium sulfide heptaiodide, *m*-Nb_3SI_7, was obtained by reaction of the elements in evacuated sealed fused silica tubes at 1105 K. The structure comprises $[Nb_3SI_{10}]^{3-}$ clusters containing Nb triangles bicapped by μ_3-I and μ_3-S atoms. The clusters are linked by terminal I atoms to form dimeric units with a crystallographic center of symmetry. These dimeric units are cross-linked by the remaining terminal I atoms to form a novel two-dimensional structure.

Comment

Triangular Nb_3 cluster compounds Nb_3X_8 and Nb_3YX_7 (X = Cl, Br, I; Y = S, Se, Te) are well known (Simon & von Schnering, 1966; Furuseth, Hönle, Miller & von Schnering, 1988; Miller, 1995). Compounds with composition Nb_3SI_7 show a remarkable structural diversity with different cluster units (Miller & Lin, 1994; Miller, 1995). The bicapped 42 electron cluster $[Nb_3SI_{10}]^{3-}$, in contrast to the 42 electron clusters in $[Nb_3SI_{12}]^{5-}$ and $[Nb_3S_2I_{11}]^{6-}$, could only be stabilized in the solid state by co-condensation with NbI_5 monomers to form a further two-dimensional network of composition Nb_3SI_7.

The title compound, monoclinic Nb_3SI_7, which was discovered during our search for suitable layered materials to investigate electronic surface structures, is built up exclusively from bicapped $[Nb_3SI_{10}]^{3-}$ clusters with 42 electrons. The double capping by S and I atoms leads to marked shortening of the Nb—Nb distances within the clusters [2.767 (1)–2.780 (1) Å] in comparison with the single-capped clusters in hexagonal Nb_3SI_7

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