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$BaNi_2(PO_4)_2$

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Abstract

The structure of the title compound, barium dinickel(II) bis(phosphate), at 173 K can be described as a three-dimensional network in which two sheets, consisting of NiO_6 octahedra [d_{av}(Ni—O) = 2.059 (3) Å] and PO_4 tetrahedra [d_{av}(P—O) = 1.55 (3) Å], are interconnected by BaO_{12} polyhedra [d_{av}(Ba—O) = 3.0 (2) Å]. The title compound is isostructural with $BaNi_2(AsO_4)_2$, $BaNi_2(VO_4)_2$ and $BaCo_2(PO_4)_2$.

Comment

Binary systems of the form $A_{3-x}(PO_4)_2M_x(PO_4)_2$, where A is an alkaline earth dication and M a bivalent transition metal or magnesium, have been extensively studied, and various compounds of this kind have been characterized. However, only a few crystallographic studies on these mixed phosphates have been reported. In our laboratory, we have focused on the systems $A_x(PO_4)_2M_y(PO_4)_2$ (A = Ca, Sr or Ba, and M = Cu, Co or Ni), resulting in the structure determinations of $SrNi_2(PO_4)_2$ (El-Bali *et al.*, 1993), $SrCo_2(PO_4)_2$ (El-Bali *et al.*, 1993*b*), $Sr_2Ni(PO_4)_2$ (El-Bali *et al.*, 1993*a*), $Ba_2Ni(PO_4)_2$ (El-Bali *et al.*, 1994), $Ca_{8.5}Ni_{9.5}(PO_4)_{12}$ (El-Bali *et al.*, 1995) and $BaCu_2(PO_4)_2$ (Moqine *et al.*, 1993). We report here the low-temperature structure of $BaNi_2(PO_4)_2$, which is isostructural with $BaNi_2(AsO_4)_2$ (Eymond *et al.*, 1969), $BaNi_2(VO_4)_2$ (Wichmann & Müller-Buschbaum, 1984) and $BaCo_2(PO_4)_2$ (Bircsak & Harrison, 1998).

The structure of $BaNi_2(PO_4)_2$ at 173 K can be described as a two-dimensional framework made up of NiO_6 octahedra (Ni site symmetry 3) and PO_4 tetrahedra (P site symmetry 3) linked by edges and/or vertices. Such sheets, lying parallel to the (001) plane, are connected to each other by barium ions (site symmetry $\bar{3}$). In the phosphometallic layer, two neighbouring NiO_6 octahedra are linked by two O—P—O bridges. The Ni atoms are exclusively bonded to O, with a mean distance of 2.059 (3) Å. Comparable Ni···O distances are in the range 2.007–2.462 Å in $SrNi_2(PO_4)_2$, 1.999–2.139 Å in $Sr_2Ni(PO_4)_2$, 2.041–2.306 Å in $Ba_2Ni(PO_4)_2$, and 1.999–2.190 Å in $Ni_3(PO_4)_2$ (Calvo & Faggiani, 1975).

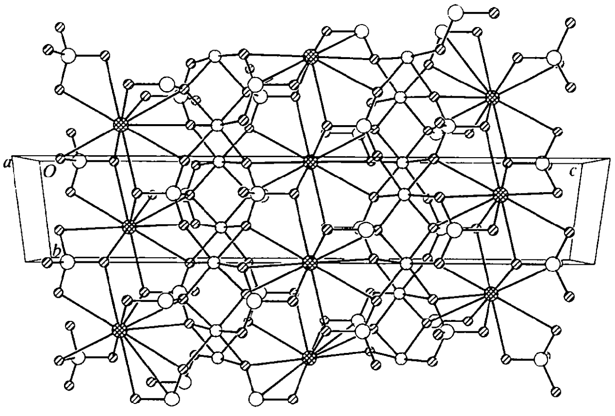

Fig. 1. Packing diagram of $BaNi_2(PO_4)_2$. Ba atoms are indicated by cross-hatched circles, Ni by dotted circles, P by open circles and O by shaded circles.

The Ni—Ni distance [2.7796 (4) Å] is in the same range as in the two isostructural compounds, $BaNi_2(AsO_4)_2$ (2.855 Å) and $BaNi_2(VO_4)_2$ (2.912 Å), but shorter than in $Ni_3(PO_4)_2$ (3.184 Å), $SrNi_2(PO_4)_2$ (3.320 Å), $Sr_2Ni(PO_4)_2$ (4.838 Å) or $Ba_2Ni(PO_4)_2$ (4.896 Å).

The P atom is tetrahedrally coordinated, with a mean P—O bond length of 1.55 (3) Å. However, the two symmetrically independent P—O bonds display a different length, which is due to the different coordinations of the

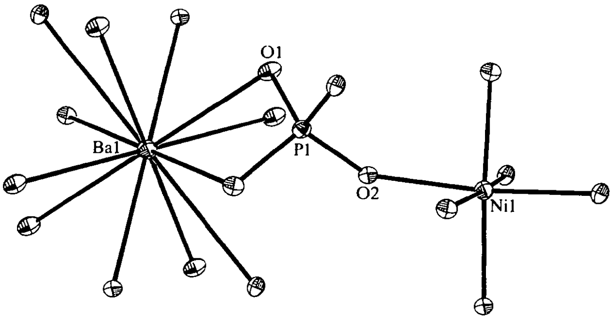

Fig. 2. Fragment of $BaNi_2(PO_4)_2$, showing the coordination of Ba, Ni and P by O atoms. Displacement ellipsoids are drawn at the 50% probability level.

two O atoms: O1, which bridges the barium ions, shows a shorter P—O bond than O2, which bridges the nickel ions.

The Ba atom is bonded to 12 O atoms with two different distances: there are six O atoms at 2.8567 (19) Å and six O atoms at 3.135 (4) Å from the Ba atom. The same coordination pattern is found for $BaCo_2(PO_4)_2$ (Ba—O 2.873 and 3.117 Å), $BaNi_2(AsO_4)_2$ (Ba—O 2.900 and 3.122 Å), $BaNi_2(VO_4)_2$ (Ba—O 2.934 and 3.024 Å) and for the dodecacoordinated Ba atom in $Ba_3(PO_4)_2$ (Ba—O 2.802–3.234 Å; Zachariasen, 1948).

Experimental

A mixture of $BaCO_3$, NiO and $(NH_4)_2HPO_4$ (Merck), in a molar ratio of 2:3:4, was first heated to 1222 K for 12 h to effect decarbonation, and then fired to fusion (1573 K) in a platinum crucible. Slow cooling ($10\ \mathrm{K\ h^{-1}}$) down to 1073 K followed by a faster cooling phase ($100\ \mathrm{K\ h^{-1}}$) produced a blend of crystals, not all of good quality. The best ones turned out to be $BaNi_2(PO_4)_2$. The orange–red crystals also obtained were identified as $BaNi(P_2O_7)$ (Riou *et al.*, 1991).

Crystal data

$BaNi_2(PO_4)_2$
$M_r = 444.70$
Trigonal
$R\bar{3}$
$a = 4.8112\ (7)$ Å
$c = 23.302\ (5)$ Å
$V = 467.12\ (14)$ Å^3
$Z = 3$
$D_x = 4.742$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 821 reflections
$\theta = 1–25°$
$\mu = 12.761$ mm^{-1}
$T = 173\ (2)$ K
Parallelepiped
0.2 × 0.1 × 0.1 mm
Green

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.142$, $T_{\max} = 0.279$
3343 measured reflections
215 independent reflections
214 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.079$
$\theta_{\max} = 26.40°$
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 6$
$l = -28 \rightarrow 28$
107 standard reflections
frequency: 600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.099$
$S = 1.167$
215 reflections
22 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 8.9136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.231$ e Å^{-3}
$\Delta\rho_{\min} = -1.188$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.028 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ba1	0	0	1/2	0.0120 (6)
Ni1	0	0	0.33117 (7)	0.0111 (7)
P1	0	0	0.07358 (14)	0.0104 (8)
O1	0	0	0.1380 (3)	0.0138 (17)
O2	0.0095 (10)	0.3135 (10)	0.05179 (17)	0.0112 (12)

Table 2. *Selected geometric parameters (Å, °)*

Ba1—O1$^{\rm i}$	2.8567 (19)	Ni1—O2$^{\rm iii}$	2.061 (4)
Ba1—O2$^{\rm i}$	3.135 (4)	P1—O1	1.502 (8)
Ni1—O2$^{\rm ii}$	2.056 (4)	P1—O2	1.570 (4)
O2$^{\rm iv}$—Ni1—O2$^{\rm v}$	91.44 (17)	O1—P1—O2	108.87 (19)
O2$^{\rm iv}$—Ni1—O2$^{\rm iii}$	95.06 (15)	O2$^{\rm viii}$—P1—O2	110.07 (18)
O2$^{\rm ii}$—Ni1—O2$^{\rm iii}$	87.0 (2)	P1—O2—Ni1$^{\rm v}$	126.0 (2)
O2$^{\rm iii}$—Ni1—O2$^{\rm vi}$	86.66 (17)	P1—O2—Ni1$^{\rm ix}$	129.5 (3)
O2$^{\rm iv}$—Ni1—O2$^{\rm vii}$	173.4 (2)	Ni1$^{\rm v}$—O2—Ni1$^{\rm ix}$	84.94 (15)

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

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1337). Services for accessing these data are described at the back of the journal.

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