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$KNi_3(AsO_4)(As_2O_7)$

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The structure of the title compound, potassium trinickel arsenate diarsenate, is built up from corner- and edge-sharing NiO_6 octahedra, AsO_4 tetrahedra and As_2O_7 groups, giving rise to a polyhedral connectivity which produces large tunnels running along the crystallographic [010] direction. The K^+ cations are located within these tunnels.

Comment

Until now, in the system K_2O–NiO–As_2O_5, only the structure of $K_4Ni_7(AsO_4)_6$ (Ben Smail *et al.*, 1999) has been refined from single-crystal data. For $KNiAsO_4$ (Buckley *et al.*, 1988), the crystal structure has been determined by high-resolution neutron powder diffraction. In this paper, we present the synthesis and structural determination of the new potassium nickel arsenate $KNi_3(AsO_4)(As_2O_7)$ refined from single-crystal data. The structure of this compound, viewed along the *b* axis, is shown in Fig. 1. It contains parallel tunnels running along the [010] direction wherein the K^+ cations are located. The three-dimensional open anionic framework is made up of corner- and edge-sharing NiO_6 octahedra, AsO_4 tetrathedra and As_2O_7 groups. It can be described in terms of layers lying parallel to the (100) plane. These layers are connected to each other by corner sharing with the $As3O_4$ tetrahedron of the $As2As3O_7$ group and with the $Ni3O_6$ octahedron. In each layer, centrosymmetric pairs of $Ni1O_6$, $Ni2O_6$ and $Ni3O_6$ octahedra share six edges to constitute an Ni_6O_{24} unit. Each unit is connected to its four adjacent neighbours by eight corners (Fig. 2). The cohesion between these units is reinforced by $As1O_4$ tetrahedra and $As2As3O_7$ groups. Each $As1O_4$ tetrahedron shares two edges, O8–O11 and O10–O11, with two adjacent NiO_6 octahedra of one Ni_6O_{24} unit and two corners, O3 and O10, with two NiO_6 octahedra of another unit. The diarsenate group shares five corners, O1, O2, O4, O6 and O7, with three units of one layer and the sixth, O5, with one unit of another layer. The As_2O_7 group has no internal symmetry and a nearly eclipsed conformation, with O9 as the bridging oxygen. The As2—O9—As3 bridging angle is 120.4 (2)°. The average As—O bond distance is 1.649 (3) Å. Both values agree with those generally observed for As_2O_7 groups (Effenberger & Pertlik, 1993).

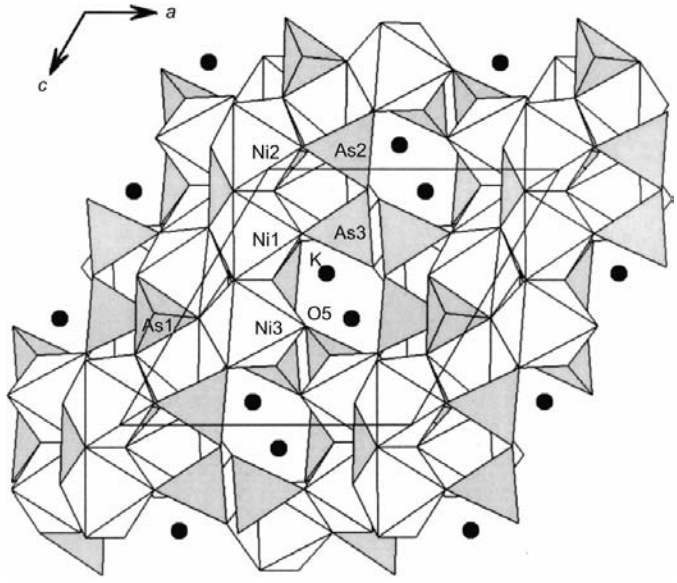

Figure 1
A projection of the $KNi_3(AsO_4)(As_2O_7)$ structure along the *b* axis.

The As—O bond lengths range from 1.640 (3) to 1.788 (3) Å. These values compare well with those obtained for the two arsenate diarsenates reported previously, *i.e.* $Ag_5Cu(AsO_4)(As_2O_7)$ (Effenberger & Pertlik, 1993) and $Na_5Bi_2(AsO_4)(As_2O_7)_2$ (Boughzala & Jouini, 1998).

The three Ni atoms in the asymmetric unit exhibit a normal octahedral coordination, with average Ni—O distances of 2.083 (3), 2.079 (3) and 2.086 (3) Å for Ni1, Ni2 and Ni3, respectively. These values are in the same range as those found in $K_4Ni_7(AsO_4)_6$ and $KNiAsO_4$.

The K^+ ion is 11-coordinated. The K···O distances range between 2.809 (4) and 3.105 (4) Å, with a mean distance of 2.960 (4) Å. We note here that the structure of the rubidium cadmium vanadate, $NaCd_3(VO_4)(V_2O_7)$ (Mertens & Müller-Buschbaum, 1997), although analogous in composition, is fundamentally different in structure from the arsenate studied in the present work.

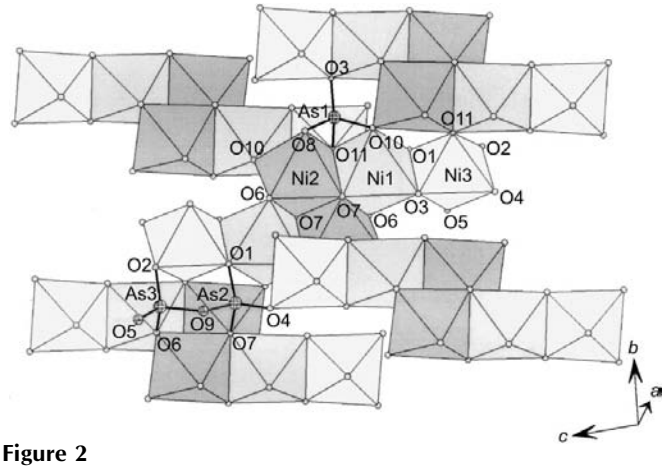

Figure 2
A perspective view of a portion of the structure of $KNi_3(AsO_4)(As_2O_7)$, showing the connections between the NiO_6 octahedra, AsO_4 tetrahedra and As_2O_7 groups.

Experimental

The title compound was prepared by the reaction of NiO, As_2O_5 and K_2CO_3 in the molar ratio 0.5:1:1. The mixture was ground in an agate mortar and heated at 673 K for 12 h. After grinding, the mixture was heated at 968 K for 6 h, followed by slow cooling at a rate of 10 K h^{-1} to 773 K and further cooling to room temperature at a rate of 100 K h^{-1}.

Crystal data

$KNi_3(AsO_4)(As_2O_7)$
M_r = 615.99
Monoclinic, $P2_1/c$
a = 10.066 (1) Å
b = 9.681 (2) Å
c = 10.234 (1) Å
β = 119.780 (1)°
V = 865.6 (2) Å^3
Z = 4
D_x = 4.727 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.49–16.96°
μ = 18.383 mm^{-1}
T = 293 (2) K
Parallelepiped, green
0.14 × 0.07 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.217, T_{max} = 0.371
2653 measured reflections
2526 independent reflections
R_{int} = 0.023
θ_{max} = 29.96°
$h = 0 \rightarrow 14$
$k = -13 \rightarrow 0$
$l = -14 \rightarrow 12$
2 standard reflections
frequency: 120 min
intensity decay: 0.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.059
S = 1.144
2526 reflections
164 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 1.2839P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$
$\Delta\rho_{max}$ = 1.078 e Å^{-3}
$\Delta\rho_{min}$ = −1.207 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.00219 (14)

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL*93.

Table 1
Selected geometric parameters (Å).

Ni1—O3	2.025 (3)	Ni3—O1^{i}	2.101 (3)
Ni1—O1^{i}	2.033 (3)	Ni3—O3	2.112 (3)
Ni1—O6	2.064 (3)	Ni3—O11	2.118 (3)
Ni1—O10^{ii}	2.104 (3)	As1—O8	1.663 (3)
Ni1—O11^{i}	2.122 (3)	As1—O3^{iv}	1.669 (3)
Ni1—O7^{iii}	2.152 (3)	As1—O10	1.707 (3)
Ni2—O6^{iv}	2.000 (3)	As1—O11^{ix}	1.737 (3)
Ni2—O8^{v}	2.026 (3)	As2—O4	1.640 (3)
Ni2—O10	2.028 (3)	As2—O1	1.680 (3)
Ni2—O7^{vi}	2.056 (3)	As2—O7^{iv}	1.713 (3)
Ni2—O11^{vii}	2.173 (3)	As2—O9^{viii}	1.741 (3)
Ni2—O7^{viii}	2.188 (3)	As3—O5^{iv}	1.643 (3)
Ni3—O4	2.045 (4)	As3—O2	1.654 (3)
Ni3—O2^{v}	2.054 (3)	As3—O6	1.694 (3)
Ni3—O5	2.085 (3)	As3—O9	1.788 (3)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1273). Services for accessing these data are described at the back of the journal.

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