Disodium nickel bis(sulfate) tetrahydrate: a nickel astrakanite

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The title compound, $[Na_2Ni(SO_4)_2(H_2O)_4]$ or Ni astrakanite, is part of an isostructural family containing the Mg (the original astrakanite mineral), Zn and Co species. The very regular $NiO(H_2O)_4O(SO_4)_2$ octahedra lie at centers of symmetry, while the rather distorted $NaO(H_2O)_2O(SO_4)_4$ octahedra are at general positions, linked into a three-dimensional network by the bridging water molecules and fully coordinated sulfate groups.

Comment

The original mineral astrakanite $[Na_2M(SO_4)_2(H_2O)_4]$, M = Mg, structurally characterized almost 50 years ago (Rumanova, 1958), gave its name to a whole isostructural family: M = Zn (Giglio, 1958; Bukin & Nozik, 1974); M = Co (Bukin and Nozik, 1975). We present here the crystal structure of a new member of the group, an Ni astrakanite, (I).
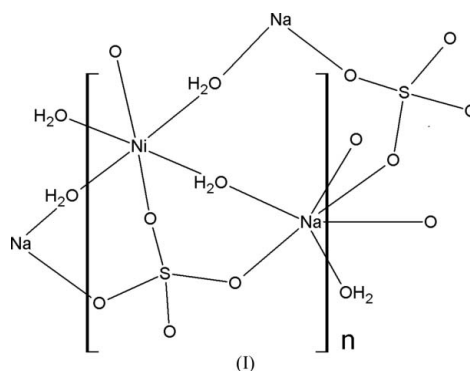

(I)

Fig. 1 shows the asymmetric unit of (I) as well as part of its close environment, and Table 1 presents selected bond distances and angles. The structure consists of $NiO(aqua)_4O(sulfate)_2$ and $NaO(aqua)_2O(sulfate)_4$ octahedra in a 1:2 ratio, linked through two bridging water molecules (O1W, O2W) and incorporating fully coordinated sulfate groups.

Ni cations lie on centers of symmetry and their coordination polyhedra defined by O3, O1W, O2W and their respective centrosymmetric counterparts are quite regular, possibly due to the large number of geometrically unconstrained aqua molecules [Ni—O = 2.0399 (14)–2.0848 (14) Å; (O—Ni—O)$_{cis}$ = 87.16 (6)–92.84 (6)°; (O—Ni—O)$_{trans}$ = 180°]. Na cations, instead, occupy general positions and, in contrast to the former, their O(sulf)-rich coordination octahedra appear quite irregular [Na—O = 2.3627 (16)–2.6120 (17) Å; (O—Na—O)$_{cis}$ = 73.64 (5)–113.12 (6)°; (O—Na—O)$_{trans}$ = 154.93 (6)–161.73 (6)°].

The geometry of the sulfate anion is fairly regular, with angles ranging from 108.05 (9) to 110.89 (9)° and S—O
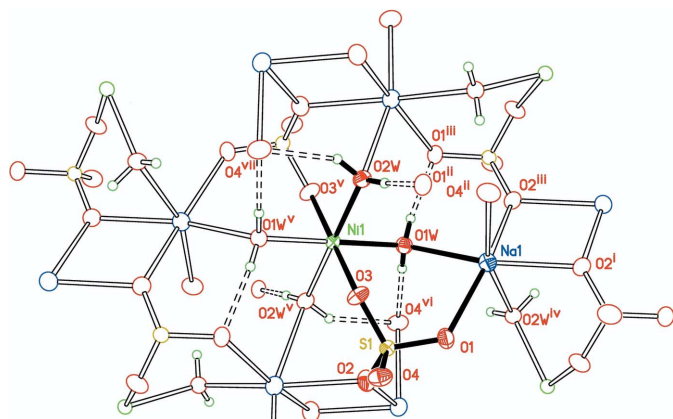
Figure 1
A (100) view of the structure with the labeled independent atoms drawn in full 50% displacement ellipsoids and full bonds. The symmetry-related part is shown in open ellipsoids and hollow bonds. Hydrogen interactions are drawn with broken lines, showing one bond in the plane and the remaining three providing for interplanar linkage (see text). Symmetry codes as in Tables 1 and 2.
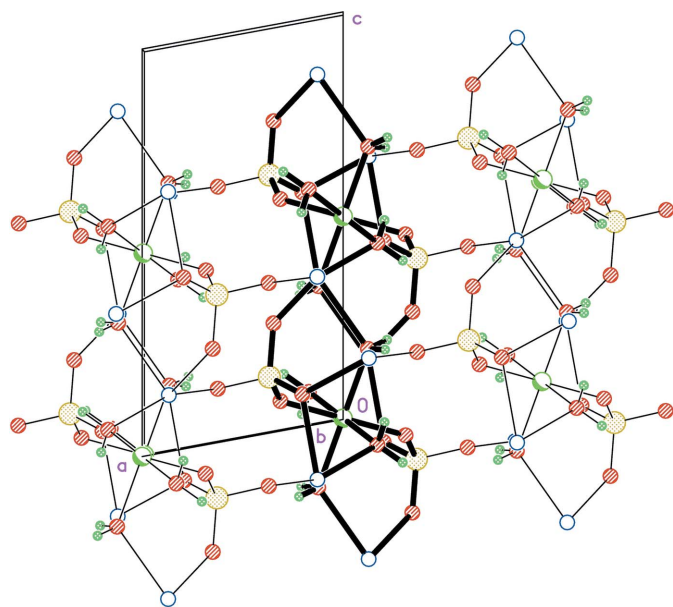

Figure 2
Packing view down the [010] direction showing a side view of the planar structures, and the way they interact through the O4—Na1 bonds along [100]. Hydrogen bonds have been omitted in this view, for clarity.

distances, from 1.4560 (15) to 1.4812 (15) Å. It exhibits a complex μ_5-κ^4-O:O':O'':O''' coordination, binding in a monocoordinated fashion to Ni through O3 and to Na through O1 and O4, while bridging two Na cations through O2. The result of this intricate interconnectivity is the formation of broad two-dimensional structures parallel to [100] containing both types of polyhedra (Fig. 1) and internally linked by the two bridging aqua and O atoms O1, O2 and O3 from the sulfate anion.

These 'planes', in turn, are interconnected along *a via* a single 'strong' interaction, the O4—Na1 bonds between sulfate O4 atoms from a given layer and Na1 cations from their neighbours (Fig. 2).

Also hydrogen-bonding interactions (Table 2) contribute to the intraplanar and interplanar cohesion.

It is worth noting that O1 and O4 act as the only (double) acceptors for hydrogen bonding. In analyzing the S—O bond lengths, it is apparent that S—O1/O4 distances are precisely the longest ones, perhaps suggesting a slight weakening effect on the S—O covalent link due to the oxygen involvement in H interactions.

Even though the gross structural features characterizing the astrakanite family are maintained in (I), the low precision with which the related members have been reported precludes any meaningful comparison of homologous structural parameters.

Experimental

The compound appeared as a by-product in a synthesis of Ni^{II} complexes, in a medium containing 1,10-phenanthroline and sodium pyrosulfite. 1,10-Phenanthroline and $NiCl_2 \cdot 6H_2O$ were dissolved together in ethanol at room temperature and were left to slowly diffuse into an aqueous solution of $Na_2S_2O_5$ (1:1:2 molar ratio). Four months later, light-blue prismatic crystals suitable for X-ray analysis were obtained.

Crystal data

$[Na_2Ni(SO_4)_2(H_2O)_4]$	$Z = 2$
$M_r = 368.87$	$D_x = 2.494$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 5.5284$ (6) Å	$\mu = 2.55$ mm^{-1}
$b = 8.1890$ (10) Å	$T = 294$ (2) K
$c = 11.0343$ (13) Å	Plate, light-blue
$\beta = 100.468$ (2)°	$0.22 \times 0.16 \times 0.08$ mm
$V = 491.23$ (10) Å^3	

Data collection

Bruker SMART CCD diffract-ometer	3942 measured reflections
	1094 independent reflections
φ and ω scans	1060 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)	$R_{int} = 0.016$
	$\theta_{max} = 27.8°$
$T_{min} = 0.604$, $T_{max} = 0.822$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$+ 0.2019P]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
1094 reflections	$\Delta\rho_{max} = 0.39$ e Å^{-3}
95 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Ni1—O3	2.0669 (14)	Na1—O2^{iii}	2.4237 (16)
Ni1—O2W	2.0848 (14)	Na1—O2W^{iv}	2.6120 (17)
Na1—O2^i	2.3627 (16)	S1—O2	1.4560 (15)
Na1—O4^{ii}	2.3848 (16)	S1—O3	1.4769 (14)
Na1—O1	2.3848 (17)	S1—O1	1.4787 (14)
Na1—O1W	2.4155 (16)	S1—O4	1.4812 (15)
O1W—Ni1—O3	90.66 (6)	O3—Ni1—O2W^v	91.57 (6)
O1W—Ni1—O2W^v	92.84 (6)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1$WB\cdots$O4[vi]	0.842 (10)	1.893 (10)	2.733 (2)	174 (3)
O1W—H1$WA\cdots$O1[iii]	0.841 (10)	1.894 (11)	2.709 (2)	163 (3)
O2W—H2$WA\cdots$O1[ii]	0.844 (10)	2.049 (13)	2.868 (2)	163 (2)
O2W—H2$WB\cdots$O4[vii]	0.846 (10)	2.16 (2)	2.921 (2)	150 (3)

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

H atoms of water molecules were found in difference Fourier maps and refined with restraints O—H = 0.85 (1) Å and H$\cdots$H = 1.32 (2) Å, but with free isotropic displacement parameters.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2005).

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