

O1	0.7861 (4)	1/4	0.7584 (3)	0.0362 (8)
O2	0.5942 (3)	0.3614 (3)	0.7124 (2)	0.0359 (6)
K1	0.08386 (11)	3/4	0.03730 (8)	0.0280 (2)
K2	0.12267 (9)	0.49576 (8)	0.31771 (6)	0.03523 (18)

Table 2. Selected geometric parameters (Å, °) for (1)

Zn—Cl3	2.2509 (10)	N—O2	1.246 (3)
Zn—Cl1	2.2676 (14)	N—O1	1.247 (5)
Zn—Cl2	2.2784 (14)		
Cl3—Zn—Cl3 ¹	110.63 (6)	Cl1—Zn—Cl2	106.79 (6)
Cl3—Zn—Cl1	110.41 (4)	O2 ¹ —N—O2	120.9 (4)
Cl3—Zn—Cl2	109.26 (3)	O2—N—O1	119.50 (18)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.**Compound (2)***Crystal data*(NH₄)₃[ZnCl₄]NO₃ $M_r = 323.31$

Orthorhombic

Pnma $a = 9.268 (3) \text{ \AA}$ $b = 10.042 (3) \text{ \AA}$ $c = 12.482 (3) \text{ \AA}$ $V = 1161.7 (6) \text{ \AA}^3$ $Z = 4$ $D_x = 1.849 \text{ Mg m}^{-3}$ $D_m = 1.8 (1) \text{ Mg m}^{-3}$ D_m measured by flotationMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 24 reflections

 $\theta = 16.3\text{--}21.6^\circ$ $\mu = 3.015 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Hexagonal prism

 $0.5 \times 0.5 \times 0.5 \text{ mm}$

Colorless

*Data collection*Syntex P2₁ diffractometer θ - 2θ scans

Absorption correction:

 ψ scan (Sheldrick, 1990) $T_{\min} = 0.523, T_{\max} = 0.645$

1962 measured reflections

1962 independent reflections

1962 reflections with

 $I > 0$ $\theta_{\max} = 31.06^\circ$ $h = 0 \rightarrow 13$ $k = 0 \rightarrow 14$ $l = 0 \rightarrow 18$

3 standard reflections

every 75 reflections

intensity decay: none

*Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.043$ $wR(F^2) = 0.105$ $S = 1.090$

1962 reflections

83 parameters

Only coordinates of H atoms refined

 $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.5098P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.093$ $\Delta\rho_{\max} = 0.509 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.808 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for**Crystallography* (Vol. C)Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)

	x	y	z	U_{eq}
Zn	0.82143 (5)	1/4	0.40896 (3)	0.02825 (13)
Cl1	1.03141 (11)	1/4	0.50387 (9)	0.0444 (3)
Cl2	0.88055 (13)	1/4	0.23134 (7)	0.0426 (2)
Cl3	0.69644 (9)	0.06329 (7)	0.44482 (6)	0.04310 (19)
N	0.6591 (3)	1/4	0.7273 (2)	0.0265 (6)
O1	0.7858 (3)	1/4	0.7601 (3)	0.0521 (8)
O2	0.5980 (2)	0.3574 (2)	0.7072 (2)	0.0502 (6)
N1	0.0879 (4)	3/4	0.0313 (3)	0.0357 (7)
N2	0.1194 (4)	0.4942 (3)	0.3220 (2)	0.0441 (6)

Table 4. Selected geometric parameters (Å, °) for (2)

Zn—Cl3	2.2489 (9)	N—O2	1.243 (3)
Zn—Cl1	2.2783 (12)	N—O1	1.243 (4)
Zn—Cl2	2.2837 (11)		
Cl3—Zn—Cl3 ¹	112.96 (5)	Cl1—Zn—Cl2	107.45 (5)
Cl3—Zn—Cl1	109.66 (3)	O2 ¹ —N—O2	120.3 (3)
Cl3—Zn—Cl2	108.47 (3)	O2—N—O1	119.76 (16)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

For both compounds, data collection: *P3/PC* (Siemens, 1993); cell refinement: *P3/PC*; data reduction: *XDISK* in *P3/PC*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1211). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 8–11**Na₂Mg(SO₄)₂·4H₂O, the Mg end-member of the bloedite-type of mineral**

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Abstract

The crystal structure of a natural sample of disodium magnesium bis(sulfate) tetrahydrate, Na₂Mg(SO₄)₂·4H₂O, the Mg end-member of the bloedite-type of min-

eral, is reported. The structure can be described in terms of parallel layers built up of $\text{MgO}_2(\text{H}_2\text{O})_4$ and $\text{NaO}_4(\text{H}_2\text{O})_2$ octahedra. Octahedral layers are interconnected through SO_4 tetrahedra. The two crystallographically independent water molecules give rise to a three-dimensional network of hydrogen bonds.

Comment

The structure of bloedite (astrakhanite) was reported by Rumanova & Malitskaja (1959) in terms of a two-dimensional structure determination. It corresponds to the Mg end-member of the bloedite-type of mineral, which are known to be isotypic for Mg, Zn, Fe, Ni and Co end-members; see also Giglio (1958), Bukin & Nozik (1974) and Nozik & Fykin (1980) for the Zn end-member, and Bukin & Nozik (1975) for the Co end-member.

The final X-ray model and the atomic labelling of the asymmetric unit are shown in Fig. 1 (ORTEP; Johnson, 1965). The structure can be described in terms of layers built up by $\text{MgO}_2(\text{H}_2\text{O})_4$ and $\text{NaO}_4(\text{H}_2\text{O})_2$ octahedra lying on the (001) planes (Fig. 2). These layers contain infinite chains of alternating $\text{MgO}_2(\text{H}_2\text{O})_4$ and $\text{NaO}_4(\text{H}_2\text{O})_2$ octahedra sharing corners, and pairs of $\text{NaO}_4(\text{H}_2\text{O})_2$ octahedra sharing one edge. Adjacent octahedral layers are interconnected by SO_4 tetrahedra.

The water molecules also play an important role in the crystal packing. They form a three-dimensional network of hydrogen bonds, some of them bifurcated, involving all O atoms of the sulfate group (Fig. 3). Atoms O1 and O4 are involved in strong hydrogen

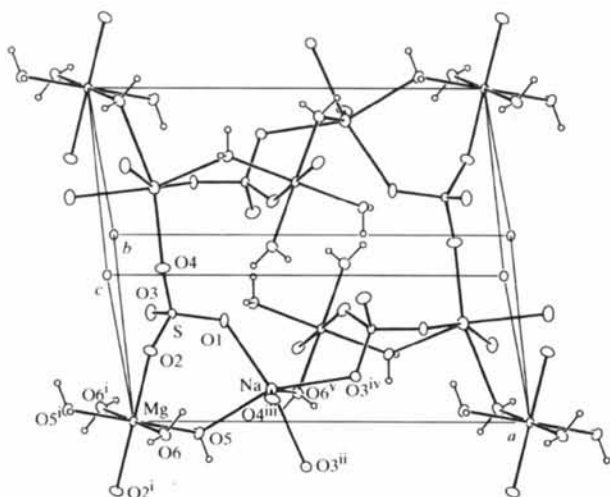


Fig. 1. Projection of the title structure showing the atom labels. Displacement ellipsoids are drawn at the 50% probability level. The atoms bonded to Mg at the cell corners (0,1,0), (0,0,1), (1,0,1) and (1,1,0) are not drawn for clarity. Symmetry codes: (i) $-x, y, -z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, -z$.

bonds and therefore have the largest S—O distances, whereas atoms O2 and O3 are only weakly bonded to H52 and H61, respectively, through bifurcated contacts (details are given in Table 3).

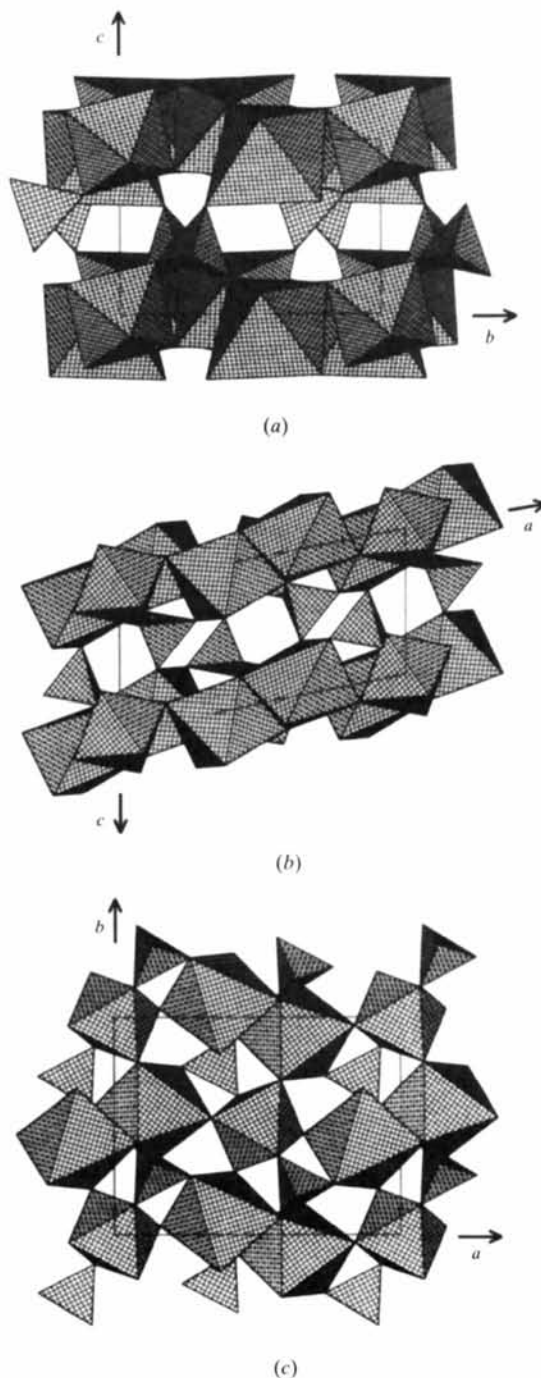


Fig. 2. Projections of the title structure showing the layers of $\text{MgO}_2(\text{H}_2\text{O})_4$ and $\text{NaO}_4(\text{H}_2\text{O})_2$ octahedra and the SO_4 tetrahedra linking two adjacent octahedral layers (a) down the *a* axis, (b) down the *b* axis and (c) down the *c* axis.

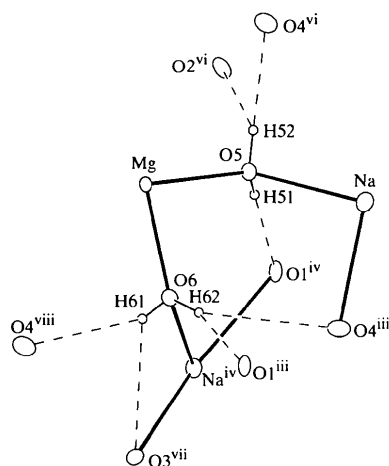


Fig. 3. Network of hydrogen bonds (symmetry codes as in Table 3).

Experimental

Mg–bloedite is a soluble saline mineral frequently identified in soil-salt efflorescences in many parts of the world. Vizcayno *et al.* (1995) found this mineral in the Ebro Valley Basin, north-eastern Spain, in surface evaporitic accumulations. Two types of these accumulations were distinguished, one type consists of microcrystalline efflorescences formed through capillary evaporation, and the other type consists of saline crusts formed through surface-water evaporation. Although Mg–bloedite is present in both types of accumulations, we have only succeeded in isolating a single crystal from a saline crust.

Crystal data

Na₂Mg(SO₄)₂·4H₂O

$M_r = 334.47$

Monoclinic

$P2_1/a$

$a = 11.129 (1) \text{ \AA}$

$b = 8.247 (1) \text{ \AA}$

$c = 5.5395 (3) \text{ \AA}$

$\beta = 100.88 (1)^\circ$

$V = 499.28 (8) \text{ \AA}^3$

$Z = 2$

$D_x = 2.225 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71070 \text{ \AA}$

Cell parameters from 42

reflections

$\theta = 10\text{--}18^\circ$

$\mu = 0.743 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism

$0.3 \times 0.3 \times 0.3 \text{ mm}$

Colourless

Data collection

Four-circle PW1100 diffractometer

$\omega/2\theta$ scans

Absorption correction: none

1024 measured reflections

883 independent reflections

871 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.010$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 9$

$l = -6 \rightarrow 6$

2 standard reflections

frequency: 90 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0289$

$wR(F^2) = 0.0790$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.353 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.589 \text{ e \AA}^{-3}$

$S = 1.207$

883 reflections

95 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2$

$+ 0.5203P]$

where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U^{ij} a^i a^j \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
S	0.13642 (4)	0.29066 (6)	0.36936 (9)	0.0116 (2)
Mg	0	0	0	0.0117 (3)
Na	0.36171 (8)	0.07038 (11)	0.1308 (2)	0.0212 (3)
O1	0.26635 (13)	0.2713 (2)	0.3476 (3)	0.0205 (4)
O2	0.07049 (15)	0.1370 (2)	0.3057 (3)	0.0204 (4)
O3	0.08003 (14)	0.4211 (2)	0.2091 (3)	0.0217 (4)
O4	0.13223 (15)	0.3284 (2)	0.6292 (3)	0.0217 (4)
O5	0.16021 (14)	0.0376 (2)	-0.1271 (3)	0.0165 (4)
O6	0.0810 (2)	-0.2085 (2)	0.1771 (3)	0.0185 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

S—O3	1.459 (2)	Na—O3 ⁱⁱⁱ	2.387 (2)
S—O2	1.473 (2)	Na—O4 ⁱⁱⁱ	2.392 (2)
S—O4	1.482 (2)	Na—O1	2.408 (2)
S—O1	1.4821 (15)	Na—O5	2.436 (2)
Mg—O5 ($\times 2$)	2.0602 (15)	Na—O3 ^{iv}	2.438 (2)
Mg—O2 ($\times 2$)	2.0636 (15)	Na—O6 ⁱ	2.655 (2)
Mg—O6 ($\times 2$)	2.098 (2)		

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

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H51...O1 ^{iv}	0.81 (4)	1.93 (4)	2.713 (2)	163 (4)
O5—H52...O4 ^{vi}	0.78 (4)	1.97 (4)	2.741 (2)	171 (4)
O5—H52...O2 ^{vi}	0.78 (4)	2.67 (4)	3.218 (2)	129 (3)
O6—H61...O3 ^{vii}	0.63 (4)	2.63 (4)	3.059 (2)	128 (4)
O6—H61...O4 ^{viii}	0.63 (4)	2.41 (5)	2.954 (3)	146 (5)
O6—H62...O1 ⁱⁱⁱ	0.90 (3)	1.98 (4)	2.856 (2)	165 (3)
O6—H62...O4 ⁱⁱⁱ	0.90 (3)	2.56 (4)	3.183 (2)	128 (3)

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

The coordinates published by Rumanova & Malitskaja (1959) were taken as a starting model which was subsequently refined by full-matrix least-squares techniques.

Data collection: PW1100 control program. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *XRAY80* (Stewart *et al.*, 1980). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1219). Services for accessing these data are described at the back of the journal.

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Cobalt(II) trisodium hexamolybdoperiodate tetradecahydrate

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Abstract

In the title salt, $\text{CoNa}_3[\text{IMo}_6\text{O}_{24}] \cdot 14\text{H}_2\text{O}$, the anion has the Anderson structure with crystallographic $\bar{3}m$ symmetry. The unique cation site is occupied by disordered Na^+ and Co^{2+} ions. The I—O bond length is 1.890 (4) Å. There are three types of Mo—O distances at 1.711 (4), 1.933 (2) and 2.352 (3) Å, corresponding to terminal O atoms, O atoms bridging to other Mo^{6+} ions and those bridging to I^{7+} ions, respectively. The anions form layers perpendicular to the *c* axis which are separated by double layers of cations.

Comment

The present study was undertaken as part of an investigation of the interaction of transition metals with polyoxometalate anions. Elemental analysis indicated one Co atom per six Mo atoms and the structure determination was performed to elucidate the role of cobalt in the salt.

The resulting structure (Fig. 1) reveals $[\text{IMo}_6\text{O}_{24}]^{5-}$ anions with crystallographic $3m$ symmetry. The anion has the well known Anderson structure (Pope, 1983), consisting of a central octahedron surrounded in a planar fashion by six additional octahedra. The anion is surrounded by cations above and below the plane of the anion. The anion structure was originally proposed for $[\text{IMo}_6\text{O}_{24}]^{5-}$ and similar hexametalates (Anderson, 1937) and later confirmed for $[\text{TeMo}_6\text{O}_{24}]^{6-}$ (Evans,

1948). For a review of the history of these and other polyoxometalates, see Baker & Glick (1998). Recent structural determinations of similar salts include $[\text{NH}_4]_4\text{-}[\text{Zn}(\text{OH})_6\text{Mo}_6\text{O}_{18}] \cdot 6\text{H}_2\text{O}$ (Allen *et al.*, 1997) and $[\text{Ga}(\text{H}_2\text{O})_6][\text{Co}(\text{OH})_6\text{Mo}_6\text{O}_{18}]$ (Panneerselvam *et al.*, 1996). These salts contain protons on the triply bridging O atoms, which is typical for Anderson ions with central atoms having a charge of +3 or +2.

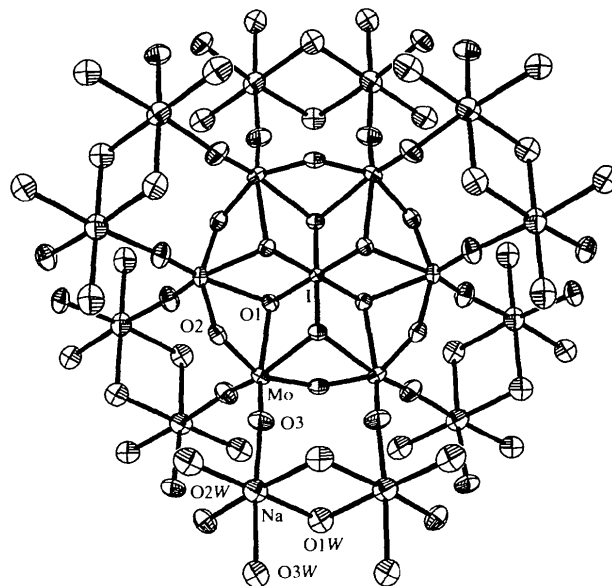


Fig. 1. View of the title compound, perpendicular to the *c* axis, showing the numbering scheme. Anisotropic displacement ellipsoids are shown at the 50% probability level.

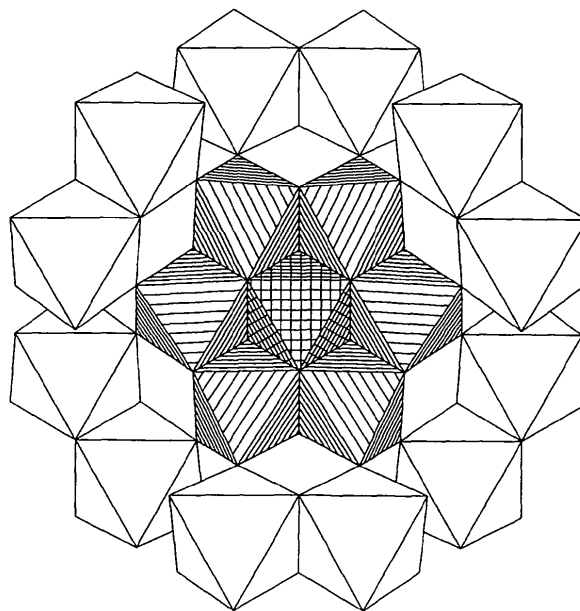


Fig. 2. Polyhedral representation of the title compound; vertices represent O atoms.