

hedron: O(1) (twice) and O(2) bridge to As(2) atoms but O(3) is terminal. The As(1)—O(3) bond is considerably shorter than the others and may be considered to possess some double-bond character; the large O—As(1)—O angles involving O(3) support this view. As(2) is coordinated by three O atoms at right angles, with As—O bonds substantially longer than for As(1). It is therefore reasonable to regard As(1) and As(2) as in oxidation states +5 and +3 respectively.

The extended structure forms layers parallel to the yz plane. There are two such layers (centrosymmetrically related) per cell. Short (<3.4 Å) As—O contacts between layers are As(2)···O(3) 2.94, 3.18; As(1)···O(3) 3.13 Å (O atoms at $0.5 + x$, $0.5 - y$, $-0.5 - z$; $-x, -y, -z$; $-x, 1 - y, -z$ respectively). Within layers the only such contact is As(2)···O(2) 3.19 Å [O(2) at $0.5 - x$, $0.5 + y$, $-0.5 + z$; all e.s.d.'s for non-bonded distances are 0.01 Å].

The system As_2O_{4-x} has been investigated by d'Yvoire, Prades & Guérin (1969). They obtained from powder photography the cell constants 8.566, 7.271, 5.236 Å (e.s.d.'s 0.002 Å) for $x = 0$; a increased with x , e.g. $x = 0.134$ when $a = 8.618$ Å, while b and c remained constant. Since the a axis of our material is 8.597 Å, this would imply that its x is not zero ($x = 0.08$ if x and a are linearly related). There is, however, no crystallographic evidence either for a small fraction of vacant O atom sites or for short O···O contacts caused by hydrogen bonding to OH groups derived from water.

Few crystal structure determinations have been performed in the arsenic/oxygen system, none of them of high accuracy. In lithium and sodium polyarsenates, the $(AsO_3)_n^{n-}$ ions (which contain tetrahedrally coor-

minated As^V) show mean As—O(bridging) and As—O(terminal) lengths of 1.76 and 1.64 Å respectively, but the terminal O atoms carry a formal 0.5- charge and their As—O bond orders are formally 1.5 (Hilmer & Dornberger-Schiff, 1956; Liebau, 1956). In claudetite II [a monoclinic form of arsenic(III) oxide], the pyramidal AsO_3 groups have As—O distances ranging from 1.77 to 1.82 Å (average 1.79 Å), in good agreement with the As^{III} —O distances in AsO_2 ; the angles at As are, however, somewhat larger (average 95.5° ; Pertlik, 1975).

The antimony oxide of empirical formula SbO_2 exists in two forms. Both may be regarded as containing Sb^{III} and Sb^V ; they consist of distorted Sb^VO_6 octahedra and Sb^{III} coordinated by four O atoms in a markedly one-sided manner (Rogers & Skapski, 1964; Skapski & Rogers, 1965). The structures of AsO_2 and SbO_2 are thus not closely related.

We thank the Verband der Chemischen Industrie for financial support and Dr M. Noltemeyer for technical assistance.

References

- HILMER, W. & DORNBERGER-SCHIFF, K. (1956). *Acta Cryst.* **8**, 87–88.
 LIEBAU, F. (1956). *Acta Cryst.* **8**, 811–817.
 PERTLIK, F. (1975). *Monatsh. Chem.* **106**, 755–762.
 ROGERS, D. & SKAPSKI, A. C. (1964). *Proc. Chem. Soc. London*, pp. 400–401.
 SKAPSKI, A. C. & ROGERS, D. (1965). *Chem. Commun.* pp. 611–613.
 D'YVOIRE, F., PRADES, F. & GUÉRIN, H. (1969). *C. R. Acad. Sci. Sér. C*, **268**, 1514–1517.

Acta Cryst. (1980). B36, 440–442

Diammonium Nickel Diselenate Hexahydrate*

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(Received 22 June 1979; accepted 25 October 1979)

Abstract. $(NH_4)_2Ni(SeO_4)_2 \cdot 6H_2O$, monoclinic $P2_1/a$, $a = 9.334$ (3), $b = 12.628$ (4), $c = 6.370$ (2) Å, $\beta = 106.31$ (3)°, $V = 720.61$ Å³, $D_o = 2.20$ (3), $D_c = 2.253$ Mg m⁻³, $Z = 2$. The structure, which is isomorphous with the corresponding sulfate, has been determined by the refinement of diffractometer data to a final R value of 0.028 for 813 observed reflexions.

* Tutton's Salts. X.

The metal–water distances are 2.068 (2), 2.055 (2) and 2.043 (2) Å.

Introduction. In the continuing study of the variation of hexaqua ions of the first transition group of elements (Montgomery, 1979) the structure of the title compound has been determined.

The compound $(NH_4)_2Ni(SeO_4)_2 \cdot 6H_2O$ was recrystallized by slow evaporation of an aqueous solution © 1980 International Union of Crystallography

at room temperature. Cell dimensions were first determined by means of rotation and zero-level Weissenberg photographs (*c* axis of rotation) calibrated with metallic Cu ($a = 6.428 \text{ \AA}$). The angle β was measured from the zero-level a^*c^* net of a precession photograph. The results were in good agreement with the diffractometer determination; $D_{\text{obs}} = 2.20 (3)$, D_{calc} (for $Z = 2$) = 2.253 Mg m^{-3} , $\mu(\text{Mo}) = 6.84 \text{ mm}^{-1}$, $\mu r = 0.51$.

Data were collected at 245 K on a PDP-11-controlled Picker four-circle goniometer from a rod-like crystal ($0.15 \times 0.15 \times 0.4 \text{ mm}$), mounted about the *c* axis, using Zr-filtered Mo radiation ($\lambda = 0.71069 \text{ \AA}$). Unit-cell dimensions were calculated by a least-squares refinement of 2θ values for fourteen pairs of centered reflexions ($hkl, \bar{h}\bar{k}\bar{l}$).

Reflexions were scanned in the $\theta/2\theta$ mode (scanning 60 steps of 0.04° in 2θ , counting for 1 s per step and for 30 s at each extremity). Three standard reflexions were recorded for every fifty observed reflexions, and from analysis of the values of the standards, a value for $\sigma(I)$ was obtained. In all, 813 reflexions were observed (out of 878) up to $2\theta = 44^\circ$ using the criterion that a reflexion was unobserved if the net count was less than $3\sigma(I)$. Lorentz and polarization corrections were applied and, at a later stage in the calculation, an absorption correction.

The refinement of the initial parameters, taken from the corresponding chromate (Montgomery, 1979), was by least squares, the function minimized being $\sum w(|F_o| - |F_c|)^2$. The programs used were those of Penfold (1969). Scattering factors for the Ni ion, Se, O and N were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Table 2

Table 1. Final coordinates ($\times 10^3$ for H; $\times 10^4$ for the others) and isotropic thermal parameters, with the least-squares standard errors in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}/B (\text{\AA}^2)$
Ni	0	0	0	1.4
Se	4130 (1)	1333 (1)	7412 (1)	1.6
O(3)	4224 (4)	2332 (3)	5806 (6)	2.6
O(4)	5664 (4)	655 (3)	7897 (7)	3.5
O(5)	2724 (4)	580 (3)	6127 (6)	2.1
O(6)	3846 (4)	1794 (3)	9673 (6)	2.5
O(7)	1659 (4)	1037 (3)	1617 (6)	2.1
O(8)	-1556 (4)	1081 (3)	371 (6)	2.0
O(9)	-4 (4)	-649 (3)	2936 (6)	2.0
N(10)	1413 (5)	3409 (4)	3555 (7)	2.6
H(11)	91 (9)	331 (6)	211 (12)	10.0 (3)
H(12)	209 (9)	308 (6)	395 (12)	5.6 (3)
H(13)	86 (9)	320 (6)	440 (12)	4.3 (3)
H(14)	160 (9)	405 (6)	384 (12)	7.0 (3)
H(15)	195 (9)	90 (6)	259 (12)	2.5 (3)
H(16)	236 (9)	115 (6)	95 (12)	5.6 (3)
H(17)	-236 (9)	90 (6)	-34 (12)	3.6 (3)
H(18)	-143 (9)	158 (6)	39 (12)	2.5 (3)
H(19)	-77 (9)	-65 (6)	343 (12)	3.3 (3)
H(20)	17 (9)	-127 (6)	304 (12)	4.8 (3)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Ni—O(7)	2.068 (2)	O(7)—Ni—O(8)	88.7 (1)
Ni—O(8)	2.055 (2)	O(7)—Ni—O(9)	89.5 (1)
Ni—O(9)	2.043 (2)	O(8)—Ni—O(9)	88.7 (1)
Se—O(3)	1.641 (3)	O(3)—Se—O(4)	109.0 (2)
Se—O(4)	1.622 (3)	O(3)—Se—O(5)	108.0 (2)
Se—O(5)	1.641 (3)	O(3)—Se—O(6)	108.9 (2)
Se—O(6)	1.643 (3)	O(4)—Se—O(5)	109.2 (2)
		O(4)—Se—O(6)	111.8 (2)
		O(5)—Se—O(6)	109.8 (2)

Table 3. Interatomic distances (\AA) and angles ($^\circ$) in double salts of nickel

	Ammonium sulfate	Ammonium chromate	Ammonium selenate	Guanidinium sulfate
Ni—O(7)	2.072	2.073	2.068 (2)	2.053
Ni—O(8)	2.069	2.054	2.055 (2)	2.052
Ni—O(9)	2.033	2.022	2.043 (2)	2.064
Mean	2.058	2.050		2.056
O(7)—Ni—O(8)	88.34	88.44	88.7 (1)	89.09
O(7)—Ni—O(9)	90.13	90.80	89.5 (1)	91.93
O(8)—Ni—O(9)	89.22	87.88	88.7 (1)	86.95
				Relative position of second atom*
Hydrogen bonds				
O(7)—O(5)	2.785	2.787	2.823 (6)	x, y, z
O(7)—O(6)	2.841	2.827	2.835 (5)	$x, y, z - 1$
O(8)—O(4)	2.708	2.720	2.685 (6)	$x - 1, y, z - 1$
O(8)—O(6)	2.759	2.741	2.763 (5)	$x - \frac{1}{2}, \frac{1}{2} - y, z - 1$
O(9)—O(5)	2.765	2.744	2.710 (5)	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$
O(9)—O(3)	2.719	2.731	2.768 (6)	$-x, -y, 1 - z$
N(10)—O(3)	2.951	2.935	2.945 (6)	x, y, z
N(10)—O(3)	2.978	2.940	2.959 (6)	$x - \frac{1}{2}, \frac{1}{2} - y, z$
N(10)—O(5)	2.867	2.816	2.848 (6)	$\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$
N(10)—O(6)	2.905	2.887	2.932 (6)	$x - \frac{1}{2}, \frac{1}{2} - y, z - 1$

* Transformation relating each second atom of ammonium nickel selenate to the corresponding atom in the original asymmetric unit.

of Stewart, Davidson & Simpson (1965). Anomalous-dispersion factors, both real and imaginary, were applied in the final stages to both the Ni and the Se scattering factors (*International Tables for X-ray Crystallography*, 1962). When *R* had fallen to 4.4%, an absorption correction was applied to the original data by the method of Coppens, Leiserowitz & Rabinovich (1965). At the same time a new weighting was applied of the form $w = 1/\sigma^2(F_o)$ where $\sigma = A + B \times |F_o| + C|F_o|^2 + D|F_o|^3$. When *R* reached a value of 0.030, two cycles of refinement were run on H positional parameters with isotropic temperature values. The final *R* value was 0.028 and R_w was 0.030.*

Discussion. The structure is isomorphous with the corresponding chromate (Tables 1, 2). The metal-water distances are 2.068, 2.055 and 2.043 \AA , which

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34871 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are very close to the corresponding values in the chromate and sulfate, the average values being the same for all three. Similarly, the hydrogen-bonding system is closely related to those of the analogues. Table 3 shows a comparison of ammonium nickel sulfate, chromate, selenate and guanidinium nickel sulfate (Morimoto, 1970).

The selenate ion is regular as judged by the bond-angle average of 109.5° . The Se—O bonds, however, show the same pattern as in the corresponding chromate (Montgomery, 1979), that is one Se—O(4) is shorter (1.622 \AA) than the other three (1.642 \AA). This is presumably due to hydrogen bonding since each atom in the SeO_4 ion, except for O(4), is hydrogen bonded to two or more atoms (Table 3). The similarity between the chromate and selenate ion is marked also in the structures of $(\text{NH}_4)_2\text{SeO}_4$ (Carter, Koerntgen & Margulis, 1977) and of $(\text{NH}_4)_2\text{CrO}_4$ (Stephens & Cruickshank, 1970). The average Se—O distance in the present determination is 1.637 \AA compared to 1.638 \AA in the isomorphous copper potassium selenate hexahydrate (Whitnall, Kennard, Nimmo & Moore, 1975). Other distances recorded in hydrated selenate salts are 1.634 \AA in $\text{CdK}_2(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Peytavin, Philippot & Lindqvist, 1974), and 1.65 \AA in $\text{Ni}_2\text{SeO}_4 \cdot 6\text{H}_2\text{O}$ (Fuess, 1970).

This research was supported by Defence Research Board Grant 9510-31. The use of facilities at the University of Victoria is gratefully acknowledged.

References

- CARTER, R. L., KOERNTGEN, C. & MARGULIS, T. N. (1977). *Acta Cryst.* **B33**, 592–593.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- FUESS, H. (1970). *Z. Anorg. Allg. Chem.* **379**, 204–212.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- MONTGOMERY, H. (1979). *Acta Cryst.* **B35**, 155–156.
- MORIMOTO, C. (1970). PhD thesis. Univ. of Washington, Seattle, Washington.
- PENFOLD, B. R. (1969). Univ. of Canterbury crystallographic programs, Christchurch, New Zealand (versions of *ORFLS* and *ORFFE*).
- PEYTAVIN, S., PHILIPPOT, E. & LINDQVIST, O. (1974). *Rev. Chim. Minér.* **11**, 37–47.
- STEPHENS, J. S. & CRUICKSHANK, D. W. J. (1970). *Acta Cryst.* **B26**, 437–439.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WHITNALL, J., KENNARD, C. H. L., NIMMO, J. K. & MOORE, F. H. (1975). *Cryst. Struct. Commun.* **4**, 709–712.