$wR = 0.081$
$S = 5.8$
449 reflections
25 parameters
$w = 1/[\sigma^2(F)+0.00063F^2]$
$(\Delta/\sigma)_{max} = 0.003$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2)

Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976).

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba1	0.0000	0.0000	0.2148 (1)	0.0131 (4)
Ba2	0.0000	0.0000	0.3165 (1)	0.0134 (4)
Ba3	0.0000	0.0000	0.5000	0.0220 (5)
Ga1	0.0000	0.0000	0.1218 (1)	0.0205 (6)
Ga2	0.0000	0.0000	0.0338 (3)	0.023 (3)
Al	0.0000	0.0000	0.0000	0.037 (5)
X	0.1960 (4)	0.8040 (4)	0.0721 (1)	0.045 (1)

Site occupancies: Ga2 = 0.31 (1); Al = 0.69 (1); X = 0.63 (1)Al + 0.37 (1)Ga.

Table 2. *Interatomic distances* (Å) *in the coordination polyhedra of the Ga and Al atoms up to* $d/\Sigma r = 1.18$

Ga1—X	2.75 (1)	×3	Al—X	3.35 (1)	×6
Ga1—Ga2	3.23 (1)		Al—Ba2	3.56 (1)	×6
Ga1—Ba1	3.41 (1)		X—Ga2	2.49 (1)	
Ga1—Ba1	3.51 (1)	×3	X—X	2.50 (1)	×2
Ga1—Ba3	3.87 (1)	×3	X—Ga1	2.75 (1)	
Ga2—Ga2	2.48 (2)		X—Al	3.35 (1)	
Ga2—X	2.49 (1)	×3	X—Ba1	3.50 (1)	×2
Ga2—Ga1	3.23 (1)		X—Ba2	3.57 (1)	
Ga2—Ba2	3.56 (1)	×3	X—Ba2	3.66 (1)	×2
Ga2—Ba2	3.97 (1)	×3	X—Ba3	3.76 (1)	

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55341 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1010]

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Structure of Phase III of (NH4)3H(SeO4)2

A. Pietraszko and K. Łukaszewicz

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 927, 50–950 Wrocław, Poland

M. A. Augustyniak

Institute of Molecular Physics, Polish Academy of Sciences, ul. Smoluchowskiego 17/19, 60–179 Poznań, Poland

Abstract

Contrary to previous results, phase III of triammonium hydrogen selenate $(NH_4)_3H(SeO_4)_2$ (which is stable in the temperature range 279–302 K) is found to be triclinic with a small deviation from the monoclinic C-centered lattice cell. The triclinic deformation and presence of two non-equivalent $H(SeO_4)_2$ groups is in good agreement with ESR measurements.

Comment

Triammonium hydrogen selenate (TAHSe) belongs to the family of compounds $M_3H(XO_4)_2$ (where $M = NH_4^+$, K^+, Rb^+ or Cs^+, and $X = S$ or Se) which undergo numerous phase transitions. The room-temperature crystal structures of $(NH_4)_2H(SO_4)_2$ (Leclaire, Ledésert, Monier, Daoud & Damak, 1985), $(ND_4)_3D(SO_4)_2$ (Tanaka & Shiozaki, 1981), $K_3H(SO_4)_2$ (Noda, Uchiyama, Kafuku, Kasatani & Terauchi, 1990), $K_3D(SO_4)_2$ (Noda, Kasatani, Watanbe, Terauchi & Gesi, 1990) and $Rb_3H(SO_4)_2$ (Makarova, Verin & Shchagina, 1986) have been determined as monoclinic, although Davis & Johnson (1984) have found a triclinic deformation of $(NH_4)_3H(SO_4)$. The lattice parameters of $(NH_4)_3H(SeO_4)_2$ with a monoclinic cell were measured by Kamoun, Halouani & Daoud (1987) and Furukava, Akahoshi, Fukami & Hukuda (1990). The triclinic deformation has probably been overlooked as a result of the insufficiently accurate photographic methods used by both research groups. The triclinic deformation follows both from the lattice-parameter measurements and from the comparison of R_{int} values (0.0265 and 0.0560 for space groups $C\bar{1}$ and $C2/c$ respectively).

The non-conventional setting $C\bar{1}$ and the pseudo-monoclinic C-centered lattice cell have been adopted

and used in the refinement and presentation of these data because, in phase III, TAHSe is nearly isomorphic with monoclinic phases of $(NH_4)_3H(SO_4)_2$, $K_3H(SO_4)_2$ and $Rb_3H(SeO_4)_2$. The initial refinement used atomic positions based on monoclinic $(NH_4)_3H(SO_4)$ (Leclaire, Lédésert, Monier, Daoud & Damak, 1985) and resulted in a triclinic structure with two non-equivalent $H(SeO_4)_2$ groups which is in good agreement with ESR measurements (Augustyniak, 1992). The relations between the triclinic primitive (t) and the pseudo-monoclinic C-centered (pm) lattice cells are $\bar{a}_{pm} = 2\bar{a}_t + \bar{b}_t$, $a_t = 1/2\bar{a}_{pm} - 1/2\bar{b}_{pm}$, $\bar{b}_{pm} = \bar{b}_t$ and $\bar{c}_{pm} = \bar{c}_t$.

Single crystals of $(NH_4)_3H(SeO_4)$ were grown by slow evaporation of an aqueous solution of NH_4OH and H_2SeO_4 in stoichiometric ratio 280 K. A small as-grown crystal was carefully selected and checked for twinning. The atomic parameters are listed in Table 1 and bond distances in Table 2. The standard deviations for the H-atom parameters produced by *SHELXTL-Plus* (Sheldrick, 1986) appeared to be unreasonably small and so were increased to realistic values. Hydrogen bonds shorter than 3 Å are given in Table 3. Fig. 1 shows a projection of the structure along the y axis. The selenium–oxygen tetrahedra are connected in pairs by the symmetric disordered (double-well) hydrogen bonds. Crystal structure investigations of the high- and low-temperature phases of TAHSe are in progress.
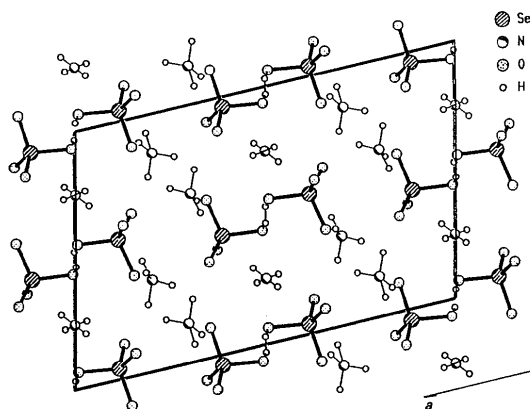

Fig. 1. Projection of phase III of $(NH_4)_3H(SeO_4)_4$ along [010] in the pseudo-monoclinic lattice cell.

Experimental

Crystal data

$(NH_4)_3H(SeO_4)_2$
$M_r = 341.1$
Triclinic

$D_x = 2.312$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

$C\bar{1}$ [$P\bar{1}$]
$a = 15.810$ (3) [8.421 (2)] Å
$b = 6.052$ (1) [6.052 (1)] Å
$c = 10.482$ (2) [10.482 (2)] Å
$\alpha = 90.79$ (3) [90.79 (3)]°
$\beta = 102.31$ (3) [101.25 (3)]°
$\gamma = 89.13$ (3) [110.19 (3)]°
$V = 979.7$ [489.9] Å^3
$Z = 4$ [2]

Cell parameters from 23 reflections
$\theta = 15.5$–31°
$\mu = 6.827$ mm^{-1}
$T = 296$ K
Irregular
$0.34 \times 0.22 \times 0.21$ mm
Colorless

Data collection

Kuma Diffraction KM-4 diffractometer
ω/θ scans
Absorption correction: empirical
$T_{min} = 0.1257$, $T_{max} = 0.2148$
8319 measured reflections
3168 independent reflections
2250 observed reflections
[$I > 4\sigma(I)$]

$R_{int} = 0.0265$
$\theta_{max} = 35$°
$h = -25 \rightarrow 25$
$k = -9 \rightarrow 9$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 50 reflections
intensity variation: $\leq 0.04\%$

Refinement

Refinement on F^2
Final $R = 0.0283$
$wR = 0.0343$
$S = 1.1617$
2250 reflections
178 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F)+0.00025F^2]$
$(\Delta/\sigma)_{max} = 0.453$

$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.74$ e Å^{-3}
Extinction correction: empirical, φ scans
Extinction coefficient: 0.00097 (6)
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1986)

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = 1/3$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Se(1)	0.11382 (2)	0.22378 (5)	0.45950 (3)	0.025
Se(2)	−0.11459 (2)	0.22804 (5)	0.04056 (3)	0.026
O(1)	0.0078 (2)	0.1778 (5)	0.4418 (3)	0.052
O(2)	0.1563 (2)	0.1914 (4)	0.6140 (3)	0.043
O(3)	0.1258 (2)	0.4727 (4)	0.4114 (3)	0.043
O(4)	0.1498 (2)	0.0404 (4)	0.3686 (3)	0.041
O(5)	−0.0080 (2)	0.1774 (5)	0.0629 (3)	0.054
O(6)	−0.1481 (2)	0.2793 (4)	−0.1138 (3)	0.041
O(7)	−0.1294 (2)	0.4380 (4)	0.1313 (3)	0.041
O(8)	−0.1564 (2)	0.0043 (4)	0.0829 (3)	0.044
N(1)	0.5000 (2)	0.2396 (5)	0.2500 (3)	0.032
N(2)	0.2024 (2)	0.2634 (5)	0.1531 (3)	0.037
N(3)	0.7998 (2)	0.2728 (5)	0.3492 (3)	0.040
H(1)	0.470 (3)	0.161 (7)	0.212 (4)	0.048
H(2)	0.468 (3)	0.346 (7)	0.256 (4)	0.066
H(3)	0.536 (3)	0.173 (7)	0.300 (4)	0.046
H(4)	0.525 (3)	0.350 (7)	0.245 (4)	0.051
H(5)	0.192 (3)	0.220 (7)	0.242 (4)	0.055
H(6)	0.187 (3)	0.150 (7)	0.069 (4)	0.046
H(7)	0.262 (3)	0.258 (7)	0.188 (4)	0.048
H(8)	0.169 (3)	0.384 (7)	0.101 (4)	0.062
H(9)	0.810 (3)	0.275 (7)	0.258 (4)	0.061
H(10)	0.817 (3)	0.122 (7)	0.383 (4)	0.048
H(11)	0.746 (3)	0.266 (7)	0.311 (4)	0.055
H(12)	0.826 (3)	0.368 (7)	0.432 (4)	0.041
H(13)	0.000 (3)	0.052 (7)	0.468 (4)	0.029
H(14)	0.000 (3)	0.026 (7)	0.030 (4)	0.037

Table 2. *Main interatomic distances* (Å) *and angles* (°)
with e.s.d.'s in parentheses

Se(1)—O(1)	1.674 (3)	Se(2)—O(5)	1.676 (3)
Se(1)—O(2)	1.629 (3)	Se(2)—O(6)	1.625 (3)
Se(1)—O(3)	1.622 (3)	Se(2)—O(7)	1.621 (3)
Se(1)—O(4)	1.626 (3)	Se(2)—O(8)	1.624 (3)
O(1)—O(2)	2.641 (4)	O(5)—O(6)	2.638 (4)
O(1)—O(3)	2.672 (4)	O(5)—O(7)	2.674 (4)
O(1)—O(4)	2.642 (5)	O(5)—O(8)	2.635 (4)
O(2)—O(3)	2.698 (4)	O(6)—O(7)	2.689 (4)
O(2)—O(4)	2.699 (4)	O(6)—O(8)	2.694 (4)
O(3)—O(4)	2.683 (3)	O(7)—O(8)	2.690 (4)
O(1)—Se(1)—O(2)	106.15 (16)	O(5)—Se(2)—O(6)	106.14 (17)
O(1)—Se(1)—O(3)	108.32 (16)	O(5)—Se(2)—O(7)	108.42 (16)
O(1)—Se(1)—O(4)	106.35 (15)	O(5)—Se(2)—O(8)	105.93 (15)
O(2)—Se(1)—O(3)	112.20 (14)	O(6)—Se(2)—O(7)	111.88 (14)
O(2)—Se(1)—O(4)	112.04 (14)	O(6)—Se(2)—O(8)	112.05 (14)
O(3)—Se(1)—O(4)	111.39 (16)	O(7)—Se(2)—O(8)	111.99 (16)
N(1)—H(1)	0.73 (4)	N(3)—H(9)	1.01 (4)
N(1)—H(1)	0.83 (4)	N(3)—H(10)	0.99 (2)
N(1)—H(3)	0.79 (4)	N(3)—H(11)	0.86 (4)
N(1)—H(4)	0.79 (3)	N(3)—H(12)	1.05 (3)
N(2)—H(5)	1.02 (4)		
N(2)—H(6)	1.10 (3)		
N(2)—H(7)	0.93 (4)		
N(2)—H(8)	1.00 (3)		

Table 3. *Hydrogen bonds* D—$H \cdots A$ *with distances*
D—$A < 3$ Å *and* $H \cdots A < 2.5$ Å

D—$H \cdots A$	D—A (Å)	D—H (Å)	$H \cdots A$ (Å)	D—$H \cdots A$ (°)
O(1)—H(13)···O(1^{ix})	2.529 (6)	0.83 (3)	1.72 (3)	166 (3)
O(5)—H(14)···O(5^{v})	2.541 (6)	1.00 (3)	1.57 (3)	163 (3)
N(1)—H(1)···O(7^{i})	2.833 (4)	0.73 (4)	2.11 (4)	169 (4)
N(1)—H(3)···O(3^{i})	2.824 (4)	0.79 (4)	2.03 (4)	173 (3)
N(2)—H(5)···O(4)	2.921 (5)	1.02 (4)	1.96 (4)	157 (2)
N(2)—H(6)···O(8^{ii})	2.903 (4)	1.10 (3)	1.81 (3)	172 (2)
N(2)—H(7)···O(2^{iii})	2.950 (4)	0.93 (4)	2.22 (4)	135 (3)
N(2)—H(7)···O(8^{ii})	2.911 (5)	0.93 (4)	2.41 (4)	113 (2)
N(2)—H(8)···O(6^{v})	2.893 (4)	1.00 (3)	2.07 (2)	139 (3)
N(3)—H(9)···O(7^{v})	2.942 (5)	1.01 (4)	2.06 (4)	145 (3)
N(3)—H(10)···O(2^{vii})	2.895 (4)	0.99 (2)	1.94 (2)	161 (3)
N(3)—H(11)···O(4^{ii})	2.893 (5)	0.86 (4)	2.40 (4)	117 (2)
N(3)—H(12)···O(3^{viii})	2.957 (4)	1.05 (3)	1.91 (3)	177 (3)

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

Lattice parameters and other data of the conventional primitive triclinic lattice cell are given in square brackets. The reflections were measured in 100 scan steps [$\Delta\omega = (1.75 + 0.35\tan\theta')°$; $\sin\theta' = 1.002\sin\theta$]; the 12 steps at each side of the reflection profile were taken as the background. All H atoms were observed in difference Fourier maps and refined with isotropic temperature factors.

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Metallointercalators: Structure of *rac*-Bis(ethylenediamine)(9,10-phenanthrenequinone diimine)rhodium(III) Tribromide Trihydrate

William P. Schaefer, Achim H. Krotz, Louis Y. Kuo, Thomas P. Shields and Jacqueline K. Barton

Division of Chemistry and Chemical Engineering† and The Beckman Institute, Mail Code 139-74, California Institute of Technology, Pasadena, California 91125, USA

Abstract

Bis(ethylenediamine)(phenanthrenequinone diimine)rhodium(III) tribromide trihydrate has a nearly planar phenanthrenequinone diimine ligand and two ordered ethylenediamine ligands, giving a distorted octahedral coordination to the compound. The N—Rh—N angles range from 77.1 (6) to 96.5°, with the largest deviations from 90° associated with the N atoms of the phenanthrenequinone diimine ligand. The two Rh—N distances involving these N atoms are 0.05 Å shorter than Rh—N distances to ethylenediamine ligands; other distances and angles are within normal ranges.