

## Ammonium Selenate

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**Abstract.**  $(\text{NH}_4)_2\text{SeO}_4$ , monoclinic,  $C2/m$ ,  $a = 12.152(6)$ ,  $b = 6.418(3)$ ,  $c = 7.711(4)$  Å,  $\beta = 115.50(12)^\circ$ ,  $Z = 4$ ,  $D_o = 2.194$ ,  $D_c = 2.190$  g cm $^{-3}$ . The compound is isomorphous with  $(\text{NH}_4)_2\text{CrO}_4$ , and displays similar hydrogen bonding. The  $\text{SeO}_4^{2-}$  ion is a nearly regular tetrahedron with mean Se–O lengths of 1.644(8) Å (uncorrected). H positions were located from the difference map, but were not included in the refinement. The  $\text{NH}_4^+$  ions are not freely rotating on the time scale of X-ray determination.

**Introduction.** Single crystals of  $(\text{NH}_4)_2\text{SeO}_4$  were grown by slow evaporation of an aqueous solution of the commercially available salt (Alfa Division of Ventron Corporation). A small crystal (approx.  $0.10 \times 0.18 \times 0.30$  mm) was used to collect data on a Syntex P2 $_1$  fully automated diffractometer with Cu  $K\alpha$  radiation and a graphite monochromator. Unit-cell parameters were determined by least squares from 15 reflections. The axial lengths found in this work show only fair agreement with those reported by Hasegawa, Fujishige & Ogawa (1963) (hereafter HF&O) [ $a = 12.30(4)$ ,  $b = 6.37(2)$ ,  $c = 7.74(2)$  Å,  $\beta = 115.5(5)^\circ$ ], but they agree very well with the axial ratios listed by Groth (1908). Integrated intensities of 518 independent reflections were measured ( $2\theta_{\text{max.}} = 132^\circ$ ), of which seven were taken to have zero intensity. One reflection appeared to be significantly affected by extinction and was not used in the final refinement. Structure factors for the 511 non-zero reflections were calculated with the scattering factors for neutral H, N,

O and Se in *International Tables for X-ray Crystallography* (1962). Anomalous scattering was ignored, which might have a slight effect on thermal parameters for Se. No absorption correction was made ( $\mu = 100$  cm $^{-1}$ ). The heavy-atom positional parameters of HF&O were used in the initial least-squares refinements, neglecting H atoms. Weights were assigned as  $1/\sigma^2$ , where  $\sigma$  is the standard deviation of  $F$ . With anisotropic thermal parameters the structure refined to a conventional residual of  $R = 0.052$ . A difference map was computed, from which the positions of the H atoms were readily identified. However, inclusion of H positions in a full-matrix least-squares refinement led to chemically unreasonable values for N–H distances and H–N–H angles. The final refinement, holding H positions fixed with their values obtained from the difference map, gave  $R = 0.045$ . The refined heavy-atom parameters and unrefined H-atom parameters are listed in Table 1. The positional parameters for H atoms agree with those of Stephens & Cruickshank (1970) within  $\pm 0.01$  in  $x$ ,  $\pm 0.00$  in  $y$ , and  $\pm 0.02$  in  $z$ .\*

**Discussion.** The crystal structure of  $(\text{NH}_4)_2\text{SeO}_4$  has been obtained in conjunction with a continuing Raman investigation of ammonium salts of oxyanions (Carter & O'Hare, 1976a; Carter, 1976). Specifically, it was

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32195 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Refined heavy-atom and unrefined H-atom parameters for  $(\text{NH}_4)_2\text{SeO}_4$ The thermal parameters are in the form  $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$ .

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$		
Se	0.1752 (1)	0	0.2181 (1)	0.0013 (1)	0.0128 (3)	0.0060 (2)	0	0.0030 (2)	0		
O(1)	0.3221 (6)	0	0.3609 (11)	0.0010 (6)	0.025 (3)	0.009 (2)	0	0.001 (2)	0		
O(2)	0.0959 (7)	0	0.3453 (11)	0.0027 (6)	0.033 (3)	0.008 (2)	0	0.009 (2)	0		
O(3)	0.1439 (5)	0.2106 (9)	0.0842 (7)	0.0040 (5)	0.010 (1)	0.011 (1)	0.001 (1)	0.004 (1)	0.005 (2)		
N(1)	0.5151 (9)	0	0.2471 (13)	0.0038 (8)	0.014 (3)	0.011 (2)	0	0.007 (2)	0		
N(2)	0.8424 (8)	0	0.2612 (12)	0.0028 (7)	0.016 (3)	0.008 (2)	0	0.006 (2)	0		
	$x$	$y$	$z$	$x$	$y$	$z$		$x$	$y$	$z$	
H(1)	0.44	0	0.24	H(3)	0.58	0	0.37	H(5)	0.52	0.12	0.20
H(2)	0.92	0	0.26	H(4)	0.86	0	0.39	H(6)	0.80	0.12	0.20

hoped to determine whether the hydrogen bonding in  $(\text{NH}_4)_2\text{SeO}_4$  is in any way significantly different from its isomorph,  $(\text{NH}_4)_2\text{CrO}_4$  (Stephens & Cruickshank, 1970; Gatehouse & Leverett, 1969), and to test the conclusion of a previous Raman study that both  $\text{NH}_4^+$  and  $\text{SeO}_4^{2-}$  ions are highly distorted in this compound (Sankaranarayanan & Krishnan, 1972). This information could not be obtained from the partial structure determination of HF&O.

The hydrogen bonds in  $(\text{NH}_4)_2\text{SeO}_4$  and  $(\text{NH}_4)_2\text{CrO}_4$  are compared in Table 2. Since the H positions have not been refined in our work, only N—O distances have been listed. With only two exceptions, the hydrogen-bonded N—O distances are longer in  $(\text{NH}_4)_2\text{SeO}_4$  by an average of 0.02 Å. The difference may be significant and indicative of slightly weaker hydrogen bonds in  $(\text{NH}_4)_2\text{SeO}_4$ . This is consistent with Raman data, indicating  $\text{NH}_4^+$  translational frequencies of 200  $\text{cm}^{-1}$  for  $(\text{NH}_4)_2\text{CrO}_4$  (Carter & O'Hare, 1976a) and 193  $\text{cm}^{-1}$  for  $(\text{NH}_4)_2\text{SeO}_4$  (Carter & O'Hare, 1976b). Nonethe-

less, the hydrogen bonding in these two isomorphs is essentially the same.

Bond distances and angles for  $\text{SeO}_4^{2-}$  and  $\text{NH}_4^+$  ions are listed in Table 3. The Se—O distances have been corrected for thermal motion with the riding model (Busing & Levy, 1964). The data are not consistent with the assumption of a distorted  $\text{SeO}_4^{2-}$  ion. The mean vibrationally corrected Se—O length is 1.657 (8) Å, which compares favorably with 1.648 (10) in  $\text{K}_2\text{SeO}_4$  (Kálmán, Stephens & Cruickshank, 1970), 1.643 in  $\text{Cu}(\text{NH}_3)_2\text{SeO}_4$  (Morosin, 1969), and 1.654 (21) Å in  $\text{Na}_2\text{SeO}_4$  (Kálmán & Cruickshank, 1970). A mean value of 1.634 (12) Å (uncorrected) results from the reported Se—O distances in  $\text{K}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Peytavin, Philippot & Lindqvist, 1974).

While the data for the  $\text{NH}_4^+$  ion might indicate distortion, it must be remembered that the H positions were not refined. Thus, distances and angles listed for the ammonium ions in Table 3 are more indicative of the reliability of the H-atom positional parameters. The  $\text{NH}_4^+$  ions are not significantly distorted in  $(\text{NH}_4)_2\text{CrO}_4$  (Stephens & Cruickshank, 1970). In view of the isomorphism and similar hydrogen bonding, it does not seem likely that the  $\text{NH}_4^+$  ions are greatly distorted in  $(\text{NH}_4)_2\text{SeO}_4$ .

Table 2. N—O distances for hydrogen bonds in  $(\text{NH}_4)_2\text{SeO}_4$  and  $(\text{NH}_4)_2\text{CrO}_4$

	$(\text{NH}_4)_2\text{SeO}_4$	$(\text{NH}_4)_2\text{CrO}_4^a$
O(1) ... H(1)—N(1)	2.84 (1) Å	2.871 (4) Å
O(1) ... H(3)—N(1)	2.81 (1)	2.797 (8)
O(3) ... H(5)—N(1) <sup>b</sup>	3.03 (1)	2.992 (3)
O(3) ... H(5)—N(1) <sup>b</sup>	3.08 (1)	3.009 (6)
O(2) ... H(2)—N(2)	2.86 (1)	2.861 (4)
O(2) ... H(4)—N(2)	3.80 (1)	2.781 (4)
O(3) ... H(6)—N(2)	2.88 (1)	2.865 (5)

(a) Calculated from the data of Stephens & Cruickshank (1970).  
 (b) Non-equidistant bifurcated hydrogen bond to two O(3) atoms on different  $\text{XO}_4^{2-}$  ions.

Table 3. Bond distances (Å) and angles (°)

	Uncor- rected	Corrected		
Se—O(1)	1.645 (8)	1.657	O(1)—Se—O(2)	110.3 (10)
Se—O(2)	1.644 (8)	1.661	O(1)—Se—O(3)	108.2 (10)
Se—O(3)	1.643 (5)	1.653	O(2)—Se—O(3)	109.8 (10)
			O(3)—Se—O(3)	110.7 (10)
N(1)—H(1)	0.89		H(1)—N(1)—H(3)	117.2
N(1)—H(3)	0.94		H(1)—N(1)—H(5)	103.1
N(1)—H(5)	0.86		H(3)—N(1)—H(5)	104.2
N(2)—H(2)	0.95		H(5)—N(1)—H(5)	126.0
N(2)—H(4)	0.92		H(2)—N(2)—H(4)	103.9
N(2)—H(6)	0.94		H(2)—N(2)—H(6)	109.3
			H(4)—N(2)—H(6)	111.5
			H(6)—N(2)—H(6)	111.1

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