

$(B_{12})_4B_2C_2$ (Will & Kossobutzki, 1975) und $(B_{12})_4B_2Ti_{1,87}$ (Amberger & Polborn, 1975).

Die Punktlage 2(a) im Zentrum des aus Ikosaedern gebildeten Tetraeders ist mit Metall besetzt, wobei der $M-B(30)$ -Abstand (Notation siehe Amberger & Polborn, 1975, Fig. 2) in den ternären Verbindungen im Vergleich zu den binären Metallboriden verkürzt ist (Å): 2,462 (10) $(B_{12})_4C_2Ti_{1,86}$; 2,463 (11) $(B_{12})_4C_2V_{1,29}$; 2,502 (13) $(B_{12})_4B_2Ti_{1,87}$; 2,499 (13) $(B_{12})_4B_2V_{1,53}$. Dagegen ist der Abstand (Å) des Kohlenstoffatoms auf 2(b) zum Ikosaederboratom $C-B(30)$ in den ternären Verbindungen deutlich länger als im *I*-tetragonalen Borcarbid: 1,712 (9) $(B_{12})_4C_2Ti_{1,86}$; 1,705 (11) $(B_{12})_4C_2V_{1,29}$; 1,638 (4) $(B_{12})_4B_2C_2$. Beide Abstandsänderungen deuten auf die gerüststabilisierende Wirkung der Metallatome hin. Sie besetzen demgemäss nicht nur interstitielle Lücken im Gitter (Ploog, 1976), sondern gehen zu benachbarten Atomen Bindungen ein (Pauling, 1976; Amberger & Polborn, 1976a,b). Auf Grund der Bindungsbeziehungen der Metallatome muss bei ternären *I*-tetragonalen Boriden vom MO-Modell für das *I*-tetragonale Bor von Longuett-Higgins & de Roberts (1955) abgerückt werden, da die Autoren nur 12 bindende *sp*-Hybridorbitale in Richtung der Fünfzähligen Achsen ausserhalb des Borikosaeders zulassen. Durch Einbau von Metall verkürzt sich die *c*-Achse (Å): 5,062 $(B_{12})_4C_2Ti_{1,86}$ und 5,07 $(B_{12})_4C_2V_{1,29}$ gegenüber 5,08 $(B_{12})_4B_2C_2$ (Ploog, Schmidt, Amberger, Will & Kossobutzki, 1972).

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Ammonium Diselenite

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Abstract. $(NH_4)_2Se_2O_5$, orthorhombic, $P2_12_12_1$, $a = 6.9971$ (5), $b = 7.4879$ (7), $c = 13.4318$ (6) Å, $V = 703.74$ Å³, $Z = 4$, $d_x = 2.586$ Mg m⁻³, $\mu(Mo K\alpha) = 10.360$ mm⁻¹. The structure consists of $Se_2O_5^{2-}$ and NH_4^+ ions, hydrogen bonded in a three-dimensional network.

Introduction. A study of the crystal structures of a series of alkali-metal hydrogenselenites, $MHSeO_3$, has recently been started at this Institute. The aim is to determine whether any members of this series possess interesting physical properties similar to those found in

the corresponding group of alkali-metal trihydrogenselenites, $MH_3(SeO_3)_2$. Hydrogenselenites, $MHSeO_3$, have been reported to exist for $M = Li^+$, Na^+ , K^+ and NH_4^+ (Nilsson, 1875; *Gmelin's Handbuch der Anorganische Chemie*, 1936). Janickis (1934) reported that NH_4HSeO_3 does not exist, and that attempts to prepare this compound always resulted in the diselenite, $(NH_4)_2Se_2O_5$. We decided to determine the structure of the compound obtained when stoichiometric amounts of SeO_2 and NH_3 were mixed. The product turned out to be the diselenite as reported by Janickis (1934). The crystal structure of $LiHSeO_3$ has been reported (Chomnilpan & Liminga, 1979).

Colorless crystals of $(NH_4)_2Se_2O_5$ were grown at room temperature from an aqueous solution of SeO_2

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and NH_3 in stoichiometric ratio by slow evaporation. The crystals are deliquescent on exposure to moist air. An approximately spherical crystal of mean radius 0.073 mm ($\mu R_{\text{MoK}\alpha} = 0.756$) was selected for data collection. The space group and preliminary cell dimensions were determined from Weissenberg photographs which indicated $P2_12_12_1$. The crystals of $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ are thus piezoelectric.

Intensities were collected at room temperature on a PDP8/A-controlled Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The diffractometer was placed in an air-conditioned room with a constant relative humidity of about 30%. The crystal was stable in this atmosphere. The cell dimensions were determined by least-squares refinement from the θ values of 25 reflexions. An $\omega/2\theta$ step-scan technique was used. Background corrections were made by the profile-analysis method (Lehmann & Larsen, 1974). All 2025 reflexions within one hemisphere were collected out to $\sin \theta/\lambda = 0.595 \text{ \AA}^{-1}$. Seven standard reflexions, measured at regular intervals, showed an average decrease in intensity of about 4% by the end of the experiment. All intensities were corrected by a scaling function, taken as the average of the scaling functions for the different test reflexions. The intensities of equivalent reflexions within the two subsets h,k,l and h,k,\bar{l} (different due to anomalous-dispersion effects) were averaged, resulting in 918 independent reflexions. Of these, 51 had $I < 3\sigma_{\text{count}}$ and were later given zero weight in the refinement, which was thus based on 867 reflexions. E.s.d.'s of the intensities were estimated from Poisson counting statistics, the scatter observed in the test reflexions, and the uncertainty in scaling function (McCandlish, Stout & Andrews, 1975). The intensities were corrected for Lorentz, polarization and absorption effects. The crystal was described as a sphere for the absorption correction. The transmission factors were in the range 2.979–2.877.

All calculations were made on IBM 1800 and IBM 370/155 computers with programs described by Lundgren (1976).

The structure was solved by the heavy-atom technique, and refined with the least-squares program UPALS, minimizing $\sum w(|F_o| - |F_c|)^2$. Each reflexion was assigned a weight $w^{-1} = \sigma^2(F_o) = \sigma_{\text{count}}^2(F_o)/4F_o + k^2$, and k was chosen as $0.030F_o$. After refinement of a scale factor, and positions and anisotropic parameters for all atoms, a difference synthesis was calculated, but no H atoms could be located.

In the final cycles, 83 parameters were varied, comprising one scale factor, one isotropic extinction parameter, and coordinates and anisotropic thermal parameters for all nine independent atoms. The shifts in the last cycle were all $< 0.1\sigma$. The agreement factors were: $R(F_o) = \sum |F_o - |F_c|| / \sum |F_o| = 0.022$ and $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0.040$. The

Table 1. Atomic coordinates ($\times 10^5$) and B_{eq} (\AA^2)

	x	y	z	B_{eq}^*
Se(1)	35324 (12)	-17257 (8)	53568 (5)	1.89
Se(2)	54314 (11)	691 (8)	72456 (4)	1.66
O(1)	17819 (95)	-6881 (74)	59337 (38)	2.91
O(2)	43706 (100)	-2825 (65)	45586 (36)	3.30
O(3)	53916 (78)	-17113 (62)	62981 (30)	2.39
O(4)	70286 (82)	-8619 (65)	79757 (35)	2.33
O(5)	66499 (88)	16318 (58)	66486 (33)	2.56
N(1)	39942 (100)	33716 (75)	50213 (39)	2.63
N(2)	95031 (106)	-36213 (79)	74444 (39)	2.52

$$* B_{\text{eq}} = \frac{1}{3}(\beta_{11} a^2 + \beta_{22} b^2 + \beta_{33} c^2).$$

e.s.d. of an observation of unit weight $S = [\sum w(|F_o| - |F_c|)^2 / (m - n)]^{1/2} = 1.29$, where m is the number of observations and n the number of parameters varied. The final value of the isotropic extinction coefficient g was $0.344 (61) \times 10^4$ (Coppens & Hamilton, 1970), giving a maximum correction of 11% in $F(004)$. Scattering factors for Se, O, and N with their anomalous-dispersion effects were taken from *International Tables for X-ray Crystallography* (1974).

The anomalous scattering of Se makes it possible to determine the absolute configuration by reversing the signs of the Miller indices and repeating the refinement with the final set of parameters. The resulting R values were: $R(F_o) = 0.034$, $R_w(F_o) = 0.053$ and $S = 1.45$. Hamilton's (1965) R -factor ratio test indicates that the original combination of Miller indices* and coordinates listed in Table 1 corresponds to the correct absolute configuration.

The final fit between F_o and F_c was checked by computing the δR normal probability plot (Abrahams

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34956 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

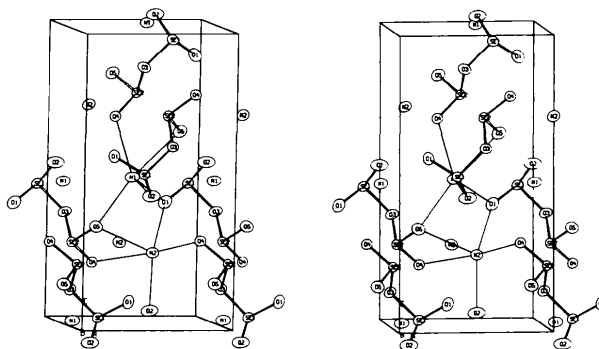


Fig. 1. Stereoscopic illustration of the $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ crystal structure. The covalent bonds within the diselenite ions are drawn as double lines and possible N-O hydrogen bonds as single lines.

Table 2. *Interatomic distances (Å) and bond angles (°)*

(A) $\text{Se}_2\text{O}_5^{2-}$ ion			
Se(1)—O(1)	1.645 (6)	O(2)—Se(1)—O(1)	105.3 (3)
—O(2)	1.631 (5)	O(2)—Se(1)—O(3)	101.3 (3)
—O(3)	1.814 (5)	O(1)—Se(1)—O(3)	101.7 (2)
		Se(1)—O(3)—Se(2)	119.8 (3)
Se(2)—O(3)	1.843 (4)	O(3)—Se(2)—O(4)	96.6 (2)
—O(4)	1.642 (5)	O(4)—Se(2)—O(5)	103.8 (3)
—O(5)	1.655 (5)	O(5)—Se(2)—O(3)	100.6 (2)
(B) NH_4^+ ion			
N(1)—O(1)	2.909 (8)	N(2)—O(1)	2.819 (8)
—O(2)	2.818 (8)	—O(2)	2.814 (7)
—O(4)	2.843 (7)	—O(4)	2.789 (9)
—O(5)	2.779 (7)	—O(4)	3.004 (9)
—O(5)	3.151 (8)	—O(5)	2.961 (10)

& Keve, 1971). The plot was slightly S-shaped, with a slope of 1.03 of the least-squares line and an intercept of 0.03.

Discussion. The structure of $(\text{NH}_4)_2\text{Se}_2\text{O}_5$ is illustrated in Fig. 1. Some selected bond distances and angles are listed in Table 2. The asymmetric unit consists of two NH_4^+ ions and one $\text{Se}_2\text{O}_5^{2-}$ ion. These ions are hydrogen bonded *via* $\text{N—H}\cdots\text{O}$ bonds to form a three-dimensional network.

The diselenite ion, $\text{Se}_2\text{O}_5^{2-}$, consists of two pyramidal SeO_3 groups sharing one corner. The geometry of the ion is in agreement with earlier reports on diselenite compounds (Koskenlinna & Valkonen, 1977*a,b*, and references therein).

The Se—O bonds to the bridging O atom are 1.814 and 1.843 Å, respectively, whereas the other Se—O bonds are about 1.65 Å. The latter type of bond is in agreement with similar bonds in other selenites (Chomnilpan, Tellgren & Liminga, 1978, and references therein). The Se—O—Se angle is 119.8° and the O—Se—O angles are about 100°.

The NH_4^+ ions both have five O atoms within possible hydrogen-bond distances (2.779–3.151 Å, Table 2). Tetrahedral coordination would be the ideal for an NH_4^+ ion in the present case. Larger coordination numbers, five to nine, are, however, frequently found for NH_4^+ ions in this type of compound, indicating the

presence of bifurcated (or polyfurcated) H bonds, disorder of the NH_4^+ ions or that some of the contacts do not represent H bonds (Khan & Baur, 1972). As was mentioned earlier, the H atoms could not be located, which might be due to large thermal motion or disorder of the NH_4^+ ions. The bridging O atom in the diselenite ion is not engaged in hydrogen bonding.

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