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A Reinvestigation of the Structure of Sodium Hydrogenselenite

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Abstract. NaHSeO₃, monoclinic, *C2/c*, *a* = 21.9799 (12), *b* = 5.7910 (2), *c* = 10.2796 (4) Å, β = 105.107 (4)°, *V* = 1263.23 Å³, *Z* = 16, *d*_x = 3.17 Mg m⁻³, $\mu(\text{Mo } K\alpha)$ = 11.6 mm⁻¹, *R*_w = 0.0355, *R* = 0.0259. The refinement was based on *F* for 1924 reflexions. The structure comprises Na⁺ ions and two independent hydrogen-bonded centrosymmetric [HSeO₃]₂²⁻ dimers, linked to form a three-dimensional network by Na⁺–O bonds. The structure can be considered as a superstructure having a pseudo-translation **e** = 1/2(**a** + **c**).

Introduction. This investigation is part of a series of studies, in progress in Uppsala, of the crystal structures of alkali-metal trihydrogenselenites, *MH*₃(SeO₃)₂, and hydrogenselenites, *MHSeO*₃, respectively (*M* = alkali metal or NH₄⁺) (Chomnilpan 1980*a*). In the hydrogenselenite series, the structures of LiHSeO₃ (Chomnilpan & Liminga, 1979) and (NH₄)₂Se₂O₅ (Chomnilpan,

1980*b*) have been reported. The hydrogenselenite does not exist for *M* = NH₄⁺. Attempts to prepare the NH₄⁺ hydrogenselenite result in the diselenite (Janickis, 1934). At Delft, interest in the study of NaHSeO₃ arose when it was found that intensities, derived from powder photographs, did not agree with calculated intensities based on the structure as reported by Chou, Hu & Yu (1963). A dimeric [Se₂O₄(OH)₂]²⁻ ion with an unexpected configuration was reported to exist in this structure. Disagreement between the reported structure and results based on an NMR study have also been reported (Roslyakov & Vinogradova, 1979). There were therefore reasons to reinvestigate the structure of NaHSeO₃. According to the above-mentioned NMR study no phase transitions occur in the temperature range 133–333 K.

The cell dimensions were determined from a powder photograph recorded with a Guinier–Hägg XDC-700 focusing camera with Cr *K*_α radiation (λ = 2.289753 Å) and CoP₃ (*a* = 7.707780 Å at 298 K) as an internal standard. A least-squares refinement based on the θ values of 45 reflexions provided the cell

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parameters. These values are in full agreement with the corresponding parameters as determined at Delft from Guinier–Johansson powder photographs.

Well developed crystals of NaHSeO_3 were grown from an aqueous solution of H_2SeO_3 and Na_2CO_3 in the stoichiometric ratio by slow evaporation at room temperature. Precession photographs showed that reflexions with $h + l$ odd are usually much weaker than those with $h + l$ even, which can be explained by assuming a superstructure with a pseudotranslation $\mathbf{e} = 1/2(\mathbf{a} + \mathbf{c})$. The space group derived from these photographs is either Cc or $C2/c$. Attempts to detect the piezoelectric d_{11} and d_{33} coefficients, using a technique described by Abrahams (1975), were not successful. The absence of a measurable piezoelectric effect indicates that the crystals are centrosymmetric, *i.e.* they crystallize in space group $C2/c$. The structure was refined successfully with this choice of space group.

The determination of the structure was based on a preliminary data set of 434 reflexions collected at Delft on a CAD-4 diffractometer using a crystal with dimensions $0.3 \times 0.3 \times 0.2$ mm. A Patterson synthesis, based on the corrected intensities (Lorentz, polarization and absorption effects), yielded approximate Se positions. These positions were consistent with the expected superstructure, since both independent Se atoms were close to the n -glide plane at $y = \frac{1}{4}$ (and $y = \frac{3}{4}$) generated by the space-group symmetry, thus making it a pseudo mirror plane. A pseudotranslation $\mathbf{e} = 1/2(\mathbf{a} + \mathbf{c})$ is hence generated. Because of this the Se atoms make only small contributions to the structure factors for reflexions with $h + l$ odd. The phases of these reflexions could thus not be determined. The subsequent Fourier synthesis was based on reflexions with $h + l$ even only. Consequently, the resulting electron density maps showed peaks at the 'true' atom positions and at their mirror images with respect to the n -glide plane. Na^+ and O peaks could be distinguished in these maps, together with their mirror images. The 'true' positions of these atoms as well as of the Se atoms were derived from geometrical considerations. A difference Fourier synthesis based on all atoms and data confirmed the model. A least-squares refinement, including correction for extinction, using all data converged to a conventional R of 0.042.

A complete data set was collected in Uppsala using a CAD-4 diffractometer with graphite-monochromatized $\text{Mo } K\alpha$ radiation and an $\omega/2\theta$ step-scan technique. The crystal used was ground to a sphere with radius 0.082 mm ($\mu R = 0.948$). Background corrections were made with the profile-analysis method (Lehmann & Larsen, 1974). All 5477 reflexions within one hemisphere were collected up to $\sin \theta/\lambda = 0.866 \text{ \AA}^{-1}$. Eight standard reflexions, monitored at regular intervals, all indicated an average increase in intensity of about 17% by the end of the experiment.

The stronger reflexions increased more than the weaker ones. All intensities were corrected with a scaling function, derived as the average of the individual scaling functions for the different test reflexions. The intensities were corrected for Lorentz, polarization, and absorption effects. The transmission factors varied between 0.260 and 0.291. Standard deviations of the intensities were estimated from Poisson counting statistics, the scatter observed in the test reflexions, and the uncertainty in the scaling function (McCandlish, Stout & Andrews, 1975). The intensities of equivalent reflexions were averaged, resulting in 3417 independent observations.

The structure was refined, starting with the parameters derived at Delft, by minimizing $\sum w(|F_o| - k|F_c|)^2$ using the full-matrix least-squares program *UPALS* (Lundgren, 1979). Each reflexion was assigned a weight $w^{-1} = \sigma^2(F)$, where $\sigma^2(F) = \sigma^2(F^2)/4F^2$. Of the 3417 independent reflexions, 1456 had $F_o < 2\sigma(F_o)$ and were given zero weight in the refinements. This large number of weak reflexions is due to the pseudotranslation as described above. The number of parameters refined in the final cycles was 92: one scale factor, one isotropic extinction coefficient, 30 positional parameters, and 60 anisotropic thermal parameters. Some reflexions seemed to be very severely affected by secondary extinction, resulting in a refined coefficient that caused an overcorrection of other reflexions. The 37 reflexions having corrections $>20\%$ were excluded from the final refinements. The refined value of the extinction coefficient g was $1.916(68) \times 10^4$ (Coppens & Hamilton, 1970), giving a maximum correction of 81% for $F(602)$. The shifts in the last cycle were all $<0.1\sigma$. The final agreement factors based on 1924 reflexions were $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.0259$, $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.0355$. The e.s.d. of an observation of unit weight was $S = 1.47$. The $R(F)$ value including all 3417 reflexions was 0.11.

The final fit between F_o and F_c was examined by computing the $\delta R = (F_o - F_c)/\sigma(F_o)$ normal prob-

Table 1. *Atomic coordinates* ($\times 10^5$, for Se $\times 10^6$) *and equivalent isotropic thermal parameters* in NaHSeO_3

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^* (\AA^2) [*]
Se(1)	343436 (12)	266013 (41)	466986 (27)	130 (1)
Se(2)	37824 (12)	234487 (42)	120511 (30)	140 (1)
Na(1)	19704 (6)	28196 (18)	21774 (14)	171 (1)
Na(2)	37528 (6)	24766 (15)	16808 (12)	153 (1)
O(1)	31455 (8)	7504 (31)	56055 (19)	157 (2)
O(2)	30444 (8)	52142 (28)	49295 (19)	150 (2)
O(3)	30322 (9)	19784 (31)	31131 (20)	155 (2)
O(4)	4462 (12)	24153 (31)	-4229 (23)	183 (2)
O(5)	10206 (9)	9314 (31)	19996 (21)	166 (2)
O(6)	5598 (9)	51448 (32)	16722 (22)	184 (2)

* U_{eq} is the arithmetic mean of the r.m.s. components of thermal displacement along the principal axes ($\times 10^3$).

ability plot (Abrahams & Keve, 1971). The plot was slightly S shaped; the least-squares line had a slope of 1.31 with a *y* intercept of 0.07. A difference Fourier synthesis based on the final parameters and 1924 reflexions did not reveal any systematic features. The H-atom positions could not be derived from these maps.

Scattering factors for O, Na⁺, and Se and their anomalous-dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). The XRAY system (1972) was used to carry out the calculations at Delft. The calculations in Uppsala were made on IBM 1800, NORD 100, and IBM 370/155 computers with programs described by Lundgren (1979). The final positional parameters are given in Table 1.*

Discussion. The structure of NaHSeO₃ is illustrated in Fig. 1. Some selected distances and angles are listed in Table 2. The asymmetric unit consists of two Na⁺ ions and two HSeO₃⁻ ions. The pyramidal HSeO₃⁻ ions are hydrogen bonded to form centrosymmetric dimers. The Na⁺ ions link these dimers to form a three-dimensional network by Na⁺-O interactions.

The Na⁺ coordinations: One of the Na⁺ ions is five-coordinated with Na-O distances in the range 2.321–2.633 Å (average 2.443 Å). The other Na⁺ ion is six-coordinated with Na-O distances in the range 2.375–2.448 Å (average 2.417 Å). The other Na-O distances are >3.20 Å. Different environments for these two Na⁺ ions were predicted in the NMR study by Roslyakov & Vinogradova (1979).

The HSeO₃⁻ ions: The Se(1)-O bond lengths are 1.662, 1.694, and 1.764 Å, respectively, with a hydrogen bond of length 2.589 Å within the [HSe(1)O₃]₂ dimer. The corresponding bonds for HSe(2)O₃⁻ are 1.652, 1.709, 1.719, and 2.656 Å, respectively (Table 2, Fig. 1).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36205 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

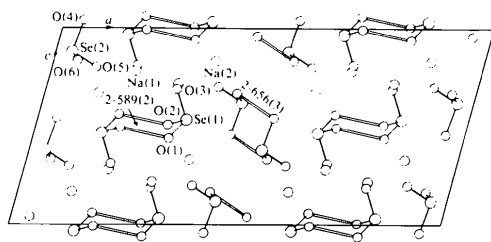


Fig. 1. Projection of the structure of NaHSeO₃ along the *b* direction.

Table 2. *Interatomic distances (Å) and bond angles (°) in NaHSeO₃*

Ionic bonds			
Na(1)-O(1)	2.500 (3)	Na(2)-O(1)	2.393 (2)
O(2)	2.633 (2)	O(2)	2.448 (2)
O(3)	2.332 (2)	O(3)	2.445 (3)
O(3)	2.427 (2)	O(4)	2.442 (3)
O(5)	2.321 (2)	O(5)	2.396 (2)
		O(6)	2.375 (2)
Covalent bonds			
Se(1)-O(1)	1.694 (2)	O(1)-Se(1)-O(2)	101.11 (9)
O(2)	1.764 (2)	O(2)-Se(1)-O(3)	100.80 (9)
O(3)	1.662 (2)	O(3)-Se(1)-O(1)	101.98 (9)
Se(2)-O(4)	1.719 (3)	O(4)-Se(2)-O(5)	102.30 (11)
O(5)	1.652 (2)	O(5)-Se(2)-O(6)	102.96 (9)
O(6)	1.709 (2)	O(6)-Se(2)-O(4)	100.25 (10)

In the alkali-metal trihydrogenselenites, the average Se-O bond is about 1.75 Å. In the case of disorder of the H atoms, a superposition of pure Se-O and Se-OH bonds, respectively, results in apparent Se-O bonds of about 1.70 Å (Chomnilpan, Tellgren & Liminga, 1978). In LiHSeO₃, the two shorter Se-O bonds were 1.654 and 1.664 Å, respectively, and the longer Se-OH bond was 1.792 Å (Chomnilpan & Liminga, 1979). Based on this previous evidence it is reasonable to assume that the H atoms are ordered in the Se(1) dimer, but disordered in the other. In the Se(1) dimer, Se-O(2) (1.764 Å) corresponds to the Se-OH bond, whereas in the Se(2) dimer H is distributed between O(4) and O(6) (Se-O 1.709, 1.719 Å), respectively. In the latter case the H atoms thus occupy two possible sites in each hydrogen bond. Similar types of disorder have been reported for some alkali-metal trihydrogenselenites where the HSeO₃⁻ ions are usually hydrogen bonded to form chains (Chomnilpan *et al.*, 1978). In some cases of disorder, the distribution of H atoms among the two possible sites has not been 1:1. Such a case has been reported for CsH₃(SeO₃)₂ (Chomnilpan *et al.*, 1978). Another interesting case for comparison is the structure of KHCO₃, in which the HCO₃⁻ ions are hydrogen bonded to form centrosymmetric dimers (Thomas, Tellgren & Olovsson, 1974). The distribution of H atoms among the two sites was about 4:1. In the present case it is not possible to draw any conclusions about the degree of disorder. A neutron diffraction study might clarify this matter. The observed hydrogen bonds (2.589, 2.656 Å) compare well with those reported for the trihydrogenselenites (2.52–2.65 Å) (Chomnilpan *et al.*, 1978), and for LiHSeO₃ (2.616 Å) (Chomnilpan & Liminga, 1979).

A comparison of our positional parameters with the parameters reported by Chou *et al.* (1963) revealed that the latter's *x* and *z* coordinates (after transformation to the *C2/c* coordinate system) agree with ours. However, there is a large discrepancy between the

y coordinates as presented in this study and those given by Chou *et al.* Consequently, the structure reported by the latter authors is incorrect.

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Structure of *trans*-Dichloro(ethylene)(pyrazole)platinum(II)

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Abstract. [*trans*-Pt(C₂H₄)(C₃H₄N₂)Cl₂], *P*2₁/*c*, *a* = 7.086 (1), *b* = 11.204 (2), *c* = 11.118 (1) Å, β = 103.08 (1)°, *Z* = 4, *D*_o = 2.74 (2), *D*_c = 2.79 Mg m⁻³; *R*_F = 0.051 for 1172 reflections collected with a manual diffractometer and Mo X-rays. A nearly coplanar conformation [dihedral angle = 3.5 (7)°] is observed for the ligation plane and molecular plane of the aromatic ligand, as a result of intramolecular hydrogen bonding between the pyrazole NH proton and a chloro ligand.

Introduction. In an investigation of the chemical properties of a series of pyrazole adducts of Zeise's anion, [Pt(C₂H₄)Cl₃]⁻, we have noted that deprotonation of the coordinated pyrazole (Hpz) ligand yields an anion which can react as a bridging metalochelator toward a number of class-*B* metal centers (Johnson & Deese, 1981). In a structural study of the symmetrical binuclear product (Deese, Johnson & Cordes, 1981) [(C₂H₄)(Cl)Pt(μ-pz)(μ-Cl)Pt(Cl)(C₂H₄)], it was found that, with the exception of the olefinic moieties, the complex was planar. The possibility of a metal interaction with the ring π system in maintaining the planarity of the central portion of this structure was

discussed; however, strong support for such an interaction could not be inferred from one crystallographic determination. In an attempt to obtain further data on the tendency of coplanar coordination by the pyrazole group, we have carried out a crystallographic investigation of the structure of the neutral adduct of Zeise's anion and a monodentate pyrazole, *trans*-Pt(C₂H₄)Cl₂(Hpz). Again, to our surprise, an essentially planar conformation is observed for all non-olefinic atoms. Al-Najjar, Green & Sarhan (1980) have suggested that enhanced platinum-to-aromatic-ligand π bonding may occur when such a coplanar conformation is forced by other molecular interactions. In the present case, an intramolecular hydrogen bond between the ring NH proton of the pyrazole and a coordinated chloride appears to be important in establishing the conformation of this complex; however, structural evidence for metal–ligand π bonding was not observed.

All reagents used were reagent-grade chemicals and were used without further purification. Synthesis of the title compound has been previously reported (Johnson, Deese & Howe, 1980). Yellow parallelepiped-shaped