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A Neutron Diffraction Study of Mercury(II) Selenate Monohydrate

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The structure of $HgSeO_4.H_2O$ has been determined by direct methods and refined to a final R of 0·026 for 904 single-crystal neutron diffraction intensities. The crystals are monoclinic, space group $P2_1/c$ with a = 7·7446 (13), b = 7·7174 (14), c = 8·2481 (15) Å, β = 119·96 (2)° and Z = 4. The structure is isotypic with $CdSeO_4.H_2O$ and $CdSO_4.H_2O$ but different from $HgSO_4.H_2O$. The Hg atom is coordinated to six O atoms forming a distorted octahedron with Hg—O distances varying between 2·260 and 2·499 Å. Out of these the shortest distances of 2·260 and 2·280 Å are to selenate groups, the bonds to Hg being nearly linear. Four of the O atoms in the coordination octahedron belong to four different selenate groups and two to water molecules. The $HgO_4(OH_2)_2$ octahedra and the SeO_4 tetrahedra build up the three-dimensional structure by sharing corners. Hydrogen bonds of 2·706 and 2·734 Å link the water molecule to selenate groups. In the water molecules the O—H distances are 0·983 (2) and 0·984 (2) Å with an angle H—O(W)—H of 104·8 (2)°.

Introduction

This investigation is part of a structural study of inorganic Hg^{II} hydrates. Recently, the structures of $HgCrO_4.\frac{1}{2}H_2O$, $Hg_3(OH)_2(SO_4)_2.H_2O$ and $HgCl_2.2KCl.H_2O$ (Aurivillius & Stålhandske, 1975, 1976*a*,*b*) have been refined from neutron diffraction data in order to reveal the hydrogen-bonding systems. The present article, which deals with the structure of $HgSeO_4.H_2O$, will be followed by a report on $HgSO_4.H_2O$.

Experimental

Colourless crystals were grown at room temperature from an aqueous solution obtained by dissolving yellow HgO in 2·0 M H_2SeO_4. The solution was slowly evaporated for one month in a desiccator with silica gel as drying agent.

Crystal data

Mercury(II) selenate monohydrate, $HgSeO_4.H_2O$, FW 361·56, monoclinic, $P2_1/c$, a = 7·7446 (13), b =7·7174 (14), c = 8·2481 (15) Å, β = 119·96 (2)°, V = 427·10 Å^3, Z = 4, D_x = 5·62 g cm^{-3}. Cell parameters were determined from powder photographs taken in a Guinier–Hägg focusing camera at 22 °C with Cu $K\alpha_1$ radiation (λ = 1·54051 Å) and KCl (a = 6·2928 Å) as an internal standard. The crystal data are in good agreement with values reported earlier by Aurivillius & Malmros (1961).

Intensity data were collected at room temperature on a prismatic crystal of volume 5·4 mm^3. The intensity measurements were carried out on a Hilger & Watts computer-controlled four-circle diffractometer located at the Swedish Atomic Energy reactor $R2$, Studsvik. The wavelength of the monochromatized neutron beam was 1·210 Å and the flux at the specimen about 10^6 n cm^{-2} s^{-1}. A quadrant in the reciprocal space out to $\sin\theta/\lambda$ = 0·693 Å^{-1} was examined using the ω–2θ step-scan method. The scan time for each reflexion was approximately 15 min. Three standard reflexions were measured at regular intervals to provide a check on the stability of crystal and electronics. No significant fluctuations in their intensities were observed. Background corrections were made (Lehmann & Larsen, 1974). The peak is separated from the background in such a way that $\sigma(I)/I$ is minimized, where I is the integrated intensity and $\sigma(I)$ its e.s.d. based on counting statistics. Out of the 1084 independent reflexions collected, 180 resulted in $I < 2\sigma(I)$ and were deleted. Squared structure amplitudes were obtained as $F_o^2 = I \sin 2\theta$ and were corrected for absorption by Gaussian numerical integration. The crystal shape was described by seven boundary planes. The linear absorption coefficient was measured as 3·38 cm^{-1}, corresponding to a value of 59 b for the incoherent scattering cross-section for H. The resulting transmission factors fall in the range 0·57–0·67.

Structure determination and refinement

The structure was solved by direct methods using the program *GAASA* (Lindgren, Lindqvist & Nyborg, 1970). An E map showed all the non-hydrogen atoms. Cycles of least-squares refinement followed by difference syntheses revealed the H atoms of the water molecule. All atoms were then refined with anisotropic

Table 1. *Positional parameters* ($\times 10^5$) *for* $HgSeO_4.H_2O$

The estimated standard deviations are in parentheses.

	x	*y*	*z*
Hg	20171 (6)	23144 (5)	25768 (6)
Se	26303 (9)	61406 (8)	51593 (8)
O(1)	11884 (14)	48804 (13)	33820 (14)
O(2)	34474 (14)	50545 (12)	71324 (13)
O(3)	45091 (14)	69520 (13)	50713 (14)
O(4)	11224 (14)	77050 (12)	50524 (14)
O(*W*)	27301 (14)	9351 (12)	54288 (13)
H(1)	20521 (29)	−1892 (24)	52118 (28)
H(2)	41584 (27)	6593 (25)	61734 (26)

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

(*a*) In the $HgO_4(OH_2)_2$ polyhedron			
Hg–O(1)	2·280 (1)	O(1)–Hg–O(2^{i})	168·99 (4)
Hg–O(2^{i})	2·260 (1)	O(3^{iii})–Hg–O(*W*)	72·70 (4)
Hg–O(3^{iii})	2·472 (1)	O(*W*)–Hg–O(4^{ii})	126·57 (4)
Hg–O(4^{ii})	2·332 (1)	O(4^{ii})–Hg–O(W^{i})	76·57 (4)
Hg–O(*W*)	2·382 (1)	O(W^{i})–Hg–O(3^{iii})	83·88 (4)
Hg–O(W^{i})	2·499 (1)		
(*b*) In the SeO_4 group			
Se–O(1)	1·645 (1)	O(1)–Se–O(2)	109·50 (6)
Se–O(2)	1·650 (1)	O(1)–Se–O(3)	114·46 (6)
Se–O(3)	1·619 (1)	O(1)–Se–O(4)	103·73 (6)
Se–O(4)	1·651 (1)	O(2)–Se–O(3)	109·28 (6)
		O(2)–Se–O(4)	109·68 (6)
		O(3)–Se–O(4)	110·02 (6)
(*c*) In the water molecule and hydrogen bonds			
O(*W*)–H(1)	0·983 (2)	H(1)–O(*W*)–H(2)	104·8 (2)
O(*W*)–H(2)	0·984 (2)	O(*W*)–H(1)–O(4^{v})	172·9 (2)
H(1)–H(2)	1·558 (3)	O(*W*)–H(2)–O(2^{iv})	167·3 (2)
H(1)–O(4^{v})	1·756 (2)	O(2^{iv})–O(*W*)–O(4^{v})	97·04 (4)
H(2)–O(2^{iv})	1·738 (2)		

Symmetry code
None x,y,z
(i) $x, \frac{1}{2}-y, z-\frac{1}{2}$
(ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$
(iii) $1-x, 1-y, 1-z$
(iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$
(v) $x, y-1, z$

thermal parameters together with a scale factor and a parameter to correct for isotropic secondary extinction (Zachariasen, 1967). The function minimized was $\Sigma w_i(|F_o| - |F_c|)^2$; weights were $w_i^{-1} = \sigma_c^2(|F_o|^2)/4|F_o|^2 + (0{\cdot}006|F_o|)^2$. The final $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0{\cdot}026$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2} = 0{\cdot}020$; the extinction parameter $g = 0{\cdot}21\ (1) \times 10^4$ and for only 11 of the 904 reflexions did the extinction factor fall below 90%. Attempts with anisotropic extinction corrections gave no further improvement. The value of $S = [\Sigma w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m is the total number of observations and n the number of parameters varied, was 1·38. The coherent scattering amplitudes used for O and H were 0·580 and $-0{\cdot}374 \times 10^{-12}$ cm (Bacon, 1972). The scattering amplitudes of Hg and Se were included as parameters in the final refinement. The values obtained for Hg and Se, 1·255 (3) and 0·791 (5) $\times 10^{-12}$ cm, are comparable to 1·27 and 0·80 $\times 10^{-12}$ cm given by Bacon (1972). Positional parameters are given in Table 1.[*] Selected interatomic distances and angles are listed in Table 2.

Description and discussion of the structure

In the structure a three-dimensional network is formed from distorted $HgO_4(OH_2)_2$ octahedra and SeO_4 tetrahedra sharing all corners (Fig. 1). One octahedron comprises four O atoms from four SeO_4 groups and two from water molecules (Fig. 2). The octahedra are linked by the water molecules to form endless chains running in the **c** direction.

Two-coordination is prevalent among Hg^{II} compounds. In the coordination to O, Hg is in most cases almost linearly bonded to two O atoms at the short distances 2·0–2·2 Å. There are often 3–5 more O neighbours at 2·4–2·7 Å, indicating weak Hg–O interactions. Three-coordination is found in, for example, $HgTiO_3$ (Sleight & Prewitt, 1973) [Hg–O 2·20 (4) Å] and four-coordination exists in $Hg(OHg)_4Br_2$ (Aurivil-

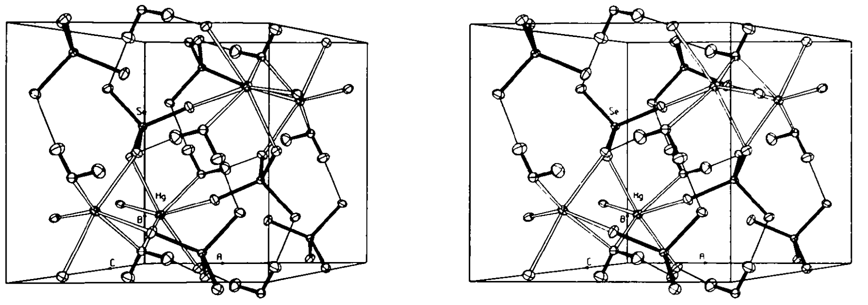

Fig. 1. A stereoscopic pair showing the contents of a unit cell. Bonds to Hg are drawn with double lines and hydrogen bonds with thin lines.

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[*] Lists of neutron structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33225 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

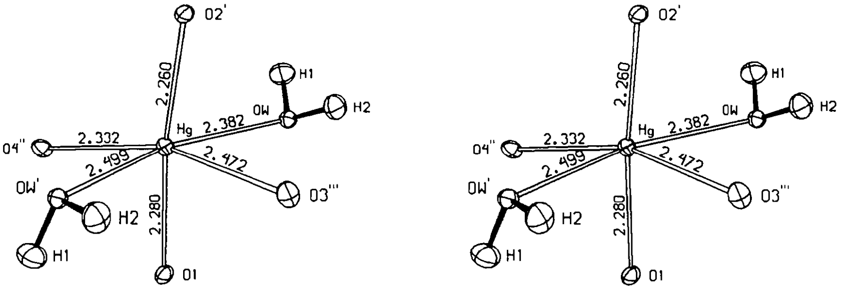

Fig. 2. A stereoview of the coordination about the Hg atom.

lius, 1968) [Hg—O 2·24 (3) Å]. Six-coordinated Hg is rare in the solid state, but Carlin, Roitman, Dankleff & Edwards (1962) have pointed out the existence of octahedral coordination about Hg for some compounds with the formula $[HgL_6](ClO_4)_2$, where L is, for example, pyridine 1-oxide and dimethyl sulphoxide. The structure of the former compound (Kepert, Taylor & White, 1973) is built up of $[Hg(C_5H_5NO)_6]^{2+}$ and ClO_4^- ions with a regular octahedral coordination about Hg, the Hg—O distances being 2·35 (2) Å. A recent X-ray investigation of $[Hg\{(CH_3)_2SO\}_6](ClO_4)_2$ by Sandström & Persson (1978) also confirms an almost octahedral coordination with Hg—O distances of 2·32–2·38 Å (mean value 2·34 Å). In the present structure four Hg—O distances fall in the range 2·26–2·38 Å and the other two are 2·47 and 2·50 Å (Fig. 2). The mean value is 2·37 Å. The only Hg—O distance, outside the coordination octahedron, shorter than 3·0 Å is a Hg—O(1) distance of 2·89 Å. There are thus two weak Hg—O bonds in the deformed $HgO_4(OH_2)_2$ octahedron and the coordination may be described as 4 + 2 rather than 6. Coordination octahedra with two water molecules as ligands are found in other selenate structures, *e.g.* $Na_2Cu(SeO_4)_2.2H_2O$ (Peytavin, Philippot & Maurin, 1974) in which the $CuO_4(OH_2)_2$ octahedron is tetragonally distorted consistent with the Jahn–Teller effect and in $K_2Cd(SeO_4)_2.2H_2O$ (Peytavin, Philippot & Lindqvist, 1974), built up of more regular $CdO_4(OH_2)_2$ octahedra.

The structures of $CdSO_4.H_2O$ and $CdSeO_4.H_2O$ are isotypic (Brégeault & Herpin, 1968), and both are isotypic with $HgSeO_4.H_2O$. This is unexpected since there are only a few examples known of inorganic compounds in which Cd can be substituted for Hg without changing the structure. In the structure of $CdSO_4.H_2O$ (Brégeault & Herpin, 1970) the Cd—O distances vary between 2·21 and 2·36 Å with a mean value of 2·29 Å. A close comparison between the two distorted octahedra $CdO_4(OH_2)_2$ and $HgO_4(OH_2)_2$ is, however, not worth while as the standard deviations in the Cd—O distances are about 0·05 Å.

According to Templeton, Templeton & Zalkin (1964) the Hg atom in $HgSO_4.H_2O$ is coordinated to one sulphate O atom at a distance of 2·17 (1) Å and one O atom of a water molecule at 2·24 (1) Å, but is also in contact with another four sulphate O atoms at distances of 2·50–2·51 Å, forming a distorted $HgO_5(OH_2)$ octahedron.

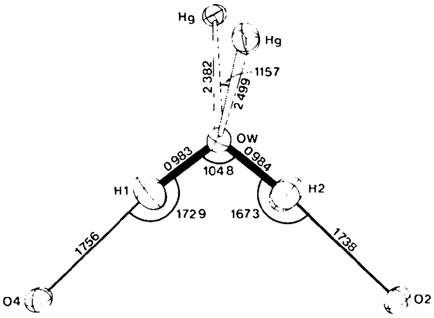

Fig. 3. A perspective drawing of the tetrahedral environment of the water molecule.

If in the present structure only the Hg—O contacts of 2·26–2·38 Å are considered as bond distances, the coordination polyhedron of Hg is a very distorted tetrahedron. The structure is then built up of layers formed from linked $HgO_3(OH_2)$ and SeO_4 tetrahedra in the *bc* plane, connected by hydrogen bonds to a three-dimensional network and further supported by the Hg—O contacts of 2·47 and 2·50 Å.

In $HgSeO_4.H_2O$ the angles O—Se—O of the selenate tetrahedron are between 104 and 115°. The mean value of the Se—O distances in the SeO_4 group is 1·645 Å, close to the value 1·64 Å given by Valkonen, Niinistö, Eriksson, Larsson & Skoglund (1975) as a mean value calculated from a number of selenate structures. The variation of the Se—O distances, 1·618–1·651 Å (Table 2), is smaller than in most other selenate structures. The Se—O distance of 1·618 (1) Å is, however, appreciably shorter than the others in the range 1·645 (1)–1·651 (1) Å. This can be explained by the different strengths of the Hg—O bonds, the bond to this selenate O atom being weak (Hg—O 2·47 Å). An example of the same effect, but more pronounced, was found in $Hg_3(OH)_2(SO_4)_2.H_2O$ (Aurivillius & Stålhandske, 1976*a*), where one S—O bond in the sulphate group is 1·537 (2) Å and the others are between 1·451 (2) and 1·465 (2) Å. The O atom of the elongated S—O bond is coordinated to a Hg atom at a short distance of 2·15 Å, while the other sulphate O atoms are in contact with Hg atoms at distances ≥2·46 Å.

The water molecule in the present structure has a tetrahedral environment including two hydrogen-bonded O atoms and two Hg atoms bonded in the direction of the lone pairs of the O(*W*) atom (Fig. 3). The hydrate belongs to class 2*B* according to Ferraris & Franchini-Angela (1972) as do, for example, $HgCrO_4.\frac{1}{2}H_2O$ and $Hg_3(OH)_2(SO_4)_2.H_2O$ (Aurivillius & Stålhandske, 1975, 1976*a*).

In the water molecule the uncorrected O—H distances are 0·983 (2) and 0·984 (2) Å and the angle H—O—H is 104·8 (2)°. Ferraris & Franchini-Angela (1972) have found, in their survey of the water-molecule geometry in crystalline hydrates, studied by neutron diffraction, average values of 0·956 Å for the O—H bond length and 107·8° for the H—O—H angle. The O—H bonds in the present structure are thus stretched about 0·03 Å and the angle is 3·0° smaller than for the average water molecule.

Two selenate O atoms, O(2) and O(4), (Table 2) are acceptors of hydrogen bonds from the water molecule. The hydrogen bonds are of normal strength with O···O distances of 2·706 and 2·734 Å, but they are shorter than those found in other Hg^{II} hydrates (Aurivillius & Stålhandske, 1975, 1976*a,b*). Hydrogen bonds O—H···O shorter than 2·7 Å, according to Brown (1976), are strong, involve strain and are linear, while those longer than 2·7 Å are weak and generally bent. Brown (1976), from a bond-valence analysis of the repulsion between the O atoms in a O—H···O bond, has predicted a correlation between the O···H distance and the O—H···O angle. The O—H···O angles, 167·3 and 172·9°, are smaller than suggested from the O···H distances of 1·738 and 1·756 Å, probably because of crystal-packing effects.

The effect of the hydrogen bonds on the Se—O distances is small. This conclusion can be drawn assuming the elongations of the Se—O(2) and Se—O(4) bonds compared with the Se—O(1) bond distance, 0·005 and 0·006 Å, are mainly due to the hydrogen bonds.

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References

AURIVILLIUS, K. (1968). *Ark. Kemi*, **28**, 279–288.
AURIVILLIUS, K. & MALMROS, B. (1961). *Acta Chem. Scand.* **15**, 1932–1938.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1975). *Z. Kristallogr.* **142**, 129–141.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1976*a*). *Z. Kristallogr.* **144**, 1–15.
AURIVILLIUS, K. & STÅLHANDSKE, C. (1976*b*). *Acta Chem. Scand. Ser. A*, **30**, 735–739.
BACON, G. E. (1972). *Acta Cryst.* A**28**, 357–358.
BRÉGEAULT, J.-M. & HERPIN, P. (1968). *Bull. Soc. Fr. Minéral. Cristallogr.* **91**, 296–297.
BRÉGEAULT, J.-M. & HERPIN, P. (1970). *Bull. Soc. Fr. Minéral. Cristallogr.* **93**, 37–42.
BROWN, I. D. (1976). *Acta Cryst.* A**32**, 24–31.
CARLIN, R. L., ROITMAN, J., DANKLEFF, M. & EDWARDS, J. O. (1962). *Inorg. Chem.* **1**, 182–184.
FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B**28**, 3572–3583.
KEPERT, D. L., TAYLOR, D. & WHITE, A. H. (1973). *J. Chem. Soc. Dalton Trans.* pp. 670–673.
LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.
LINDGREN, O., LINDQVIST, O. & NYBORG, J. (1970). *Acta Chem. Scand.* **24**, 732–733.
PEYTAVIN, S., PHILIPPOT, E. & LINDQVIST, O. (1974). *Rev. Chim. Minér.* **11**, 37–47.
PEYTAVIN, S., PHILIPPOT, E. & MAURIN, M. (1974). *J. Solid State Chem.* **9**, 63–68.
SANDSTRÖM, M. & PERSSON, I. (1978). *Acta Chem. Scand.* To be published.
SLEIGHT, A. W. & PREWITT, C. T. (1973). *J. Solid State Chem.* **6**, 509–512.
TEMPLETON, L. K., TEMPLETON, D. H. & ZALKIN, A. (1964). *Acta Cryst.* **17**, 933–936.
VALKONEN, J., NIINISTÖ, L., ERIKSSON, B., LARSSON, L. O. & SKOGLUND, U. (1975). *Acta Chem. Scand. Ser. A*, **29**, 866–872.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 556–564.