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## SHORT STRUCTURAL PAPERS

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## Structure of Cadmium Selenate Monohydrate

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**Abstract.** CdSeO<sub>4</sub>·H<sub>2</sub>O, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.679 (2), *b* = 7.723 (2), *c* = 8.207 (3) Å, β = 120.96 (4)°, *V* = 417.37 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 3.78 Mg m<sup>-3</sup>, μ(Mo *K*α) = 12.6 mm<sup>-1</sup>. For 1281 observed reflexions the final *R* = 0.023. The Cd atom is octahedrally coordinated by four selenate groups and two water molecules at Cd–O distances of 2.25–2.42 Å.

**Introduction.** The structures of CdSeO<sub>4</sub>·H<sub>2</sub>O and CdSO<sub>4</sub>·H<sub>2</sub>O are isomorphous with HgSeO<sub>4</sub>·H<sub>2</sub>O (Stålhandske, 1978) but different from HgSO<sub>4</sub>·H<sub>2</sub>O (Stålhandske, 1980). In order to understand better the differences in coordination of Hg<sup>II</sup> and Cd<sup>II</sup>, a structural study of Hg and Cd compounds with the same stoichiometry has been started. Isomorphous pairs investigated earlier are CdSO<sub>4</sub>, HgSO<sub>4</sub> (Aurivillius & Stålhandske, 1981) and CdF(OH) (Stålhandske, 1979*a*), HgF(OH) (Stålhandske, 1979*b*).

Crystals of CdSeO<sub>4</sub>·H<sub>2</sub>O were obtained by dissolving CdO in concentrated H<sub>2</sub>SeO<sub>4</sub> according to Herpin & Bregéault (1968). A single crystal 0.11 × 0.11 × 0.26 mm was used for the data collection on a CAD-4 diffractometer with Zr-filtered Mo *K* radiation at room temperature. The ω–2θ scan technique was used with variable scan speeds and peak-scan intervals Δω = (0.75 + 0.75 tan θ)°. The maximum time spent on a reflexion was 4 min. Intensities of the 1694 unique reflexions with 3° ≤ θ ≤ 32.5° were measured within

one quadrant of reciprocal space. Of these, 1281 with *I* > 3σ(*I*) were corrected for Lorentz–polarization and absorption effects and used in the analysis. The transmission factors, evaluated by numerical integration, varied from 0.27 to 0.36. Three standard reflexions were measured during the data collection. They showed a maximum deviation from the mean of 3%.

The atomic positions for the non-hydrogen atoms were taken from the structure of HgSeO<sub>4</sub>·H<sub>2</sub>O and refined by full-matrix least squares with anisotropic temperature factors and a parameter to correct for secondary extinction (Zachariasen, 1967). The H-atom positions, as found in difference syntheses, could not be

Table 1. Fractional atomic coordinates and *B*<sub>eq</sub> values (Å<sup>2</sup>) with estimated standard deviations in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub>
Cd	0.21101 (3)	0.23809 (3)	0.25817 (3)	1.19 (1)
Se	0.26096 (4)	0.61488 (4)	0.51574 (4)	0.87 (1)
O(1)	0.1209 (3)	0.4895 (3)	0.3326 (3)	1.46 (6)
O(2)	0.3410 (3)	0.5054 (3)	0.7136 (3)	1.40 (6)
O(3)	0.4554 (4)	0.6970 (3)	0.5158 (4)	1.58 (6)
O(4)	0.1056 (4)	0.7707 (3)	0.4990 (4)	1.43 (6)
O( <i>W</i> )	0.2700 (3)	0.1010 (3)	0.5378 (3)	1.24 (6)
H(1)	0.212	0.024	0.516	
H(2)	0.404	0.086	0.613	

refined and were therefore included with fixed parameters in the final refinement, which gave  $R = 0.023$ ,  $R_w = 0.029$ ,  $S = 1.03$ . The extinction parameter  $g$  was  $0.67(3) \times 10^4$  and the corrections applied to  $|F_o| > 1.10$  for 3% of the reflexions. The form factors of Doyle & Turner (1968) were used for the Cd, Se and O atoms and for H that of Stewart, Davidson & Simpson (1965) was used. The anomalous-dispersion parameters for Cd and Se were taken from Cromer & Liberman (1970). The function minimized was  $\sum w_i(|F_o| - |F_c|)^2$ , with  $w_i^{-1} = \sigma^2(F_o) + (0.020|F_o|)^2$

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

In the $\text{CdO}_4(\text{OH}_2)_2$ polyhedron			
Cd—O(1)	2.249 (2)	O(1)—Cd—O(2 <sup>h</sup> )	172.8 (1)
Cd—O(2 <sup>h</sup> )	2.246 (2)	O(3 <sup>hh</sup> )—Cd—O(W)	74.8 (1)
Cd—O(3 <sup>hh</sup> )	2.316 (3)	O(W)—Cd—O(4 <sup>hh</sup> )	122.3 (1)
Cd—O(4 <sup>hh</sup> )	2.269 (3)	O(4 <sup>hh</sup> )—Cd—O(W <sup>h</sup> )	76.8 (1)
Cd—O(W)	2.350 (2)	O(W <sup>h</sup> )—Cd—O(3 <sup>hh</sup> )	86.1 (1)
Cd—O(W <sup>h</sup> )	2.421 (2)		
In the $\text{SeO}_4$ group			
Se—O(1)	1.640 (2)	O(1)—Se—O(2)	109.7 (1)
Se—O(2)	1.644 (2)	O(1)—Se—O(3)	113.6 (1)
Se—O(3)	1.622 (2)	O(1)—Se—O(4)	104.4 (1)
Se—O(4)	1.650 (2)	O(2)—Se—O(3)	108.9 (1)
		O(2)—Se—O(4)	110.2 (1)
		O(3)—Se—O(4)	109.9 (1)
In the water molecule and hydrogen bonds			
O(W)—H(1)	0.71	H(1)—O(W)—H(2)	114.6
O(W)—H(2)	0.89		
O(W)...O(4 <sup>y</sup> )	2.791 (3)		
O(W)...O(2 <sup>h</sup> )	2.713 (3)		
H(1)...O(4 <sup>y</sup> )	2.10		
H(2)...O(2 <sup>h</sup> )	1.84	O(2 <sup>h</sup> )...O(W)...O(4 <sup>y</sup> )	95.5 (1)
Symmetry code			
None	$x, y, z$	(iii)	$1-x, 1-y, 1-z$
(i)	$x, \frac{1}{2}-y, z-\frac{1}{2}$	(iv)	$1-x, y-\frac{1}{2}, \frac{1}{2}-z$
(ii)	$-x, y-\frac{1}{2}, \frac{1}{2}-z$	(v)	$x, y-1, z$

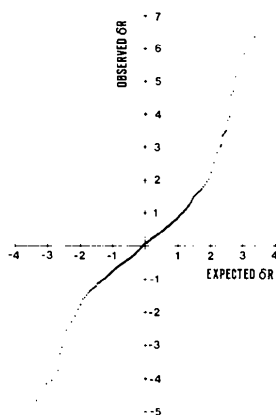


Fig. 1. Normal probability plot of 1281  $\delta R_i$  terms.

+ 0.20. The final parameters are given in Table 1,\* selected interatomic distances in Table 2.

Fig. 1 shows the normal probability plot  $\delta R(i) = [|F_o(i)| - |F_c(i)|]/\sigma|F_o(i)|$  versus the values expected for a normal distribution (Abrahams & Keve, 1971). The slope (0.97) and the intercept (0.07) of the least-squares line fitted to all data indicate that on average  $\sigma(|F_o|)$  is correctly estimated. However, about 20  $\delta R$  terms, mainly from weak reflexions, show systematic errors. This could partly be due to the method used in the measurements, which seems to give values for the background which are too small.

The unit-cell dimensions were calculated from a least-squares analysis of 35  $\theta$  values measured on the diffractometer at room temperature.

**Discussion.** Among the compounds of the Group IIb elements with formula  $M\text{SeO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  and  $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$  are isomorphous but differ from  $\text{ZnSeO}_4 \cdot \text{H}_2\text{O}$  (Pistorius, 1966). The metal atom in  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  is coordinated by four different selenate groups and two water molecules, forming  $\text{CdO}_4(\text{OH}_2)_2$  octahedra. The water molecules link the octahedra in the  $c$  direction to form chains, which are further connected by the selenate groups and hydrogen bonds to form a three-dimensional structure (Fig. 2).

The Cd—O bond lengths within the distorted  $\text{CdO}_4(\text{OH}_2)_2$  octahedron vary between 2.246 and 2.421 Å with an average of 2.31 Å; corresponding Hg—O distances in  $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$  are 2.260–2.499 Å and 2.37 Å. The difference in average bond length, 0.06 Å, is close to the difference in ionic radius for  $\text{Cd}^{2+}$  (0.95 Å) and  $\text{Hg}^{2+}$  (1.02 Å) (Shannon, 1976). The variation in the corresponding bond lengths between the two compounds is, however, considerable, ranging from 0.014 to 0.156 Å (Fig. 3). A closer comparison between  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  and  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  (Bregéault & Herpin, 1970) is not possible as the e.s.d.'s in the Cd—O bonds (2.21–2.36 Å) are 0.02–0.06 Å in the sulphate.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36156 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

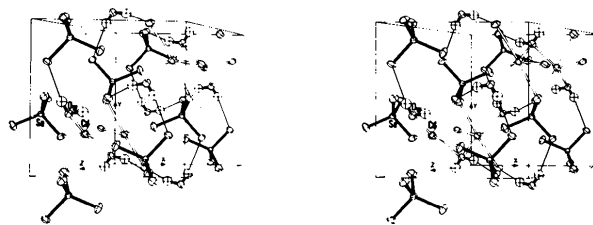


Fig. 2. The structure of  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$ . The O...H bonds are drawn with thin lines.

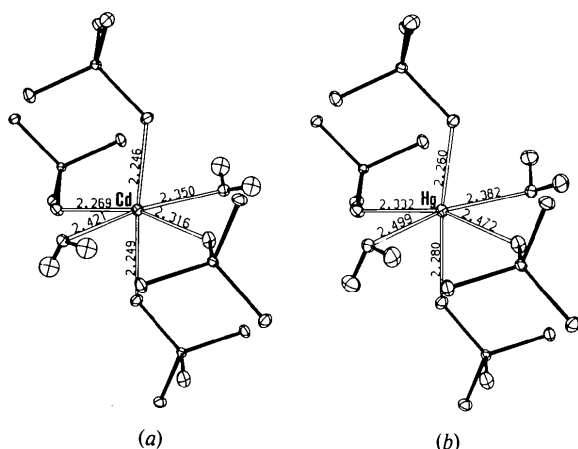


Fig. 3. The metal coordination in (a)  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  and (b)  $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ . (Distances in Å.)

Octahedra of formula  $\text{CdO}_4(\text{OH}_2)_2$  are also building elements in  $\text{K}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$  (Peytavin, Philippot & Lindqvist, 1974) and in  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (Lipson, 1936; Caminiti & Johansson, 1981). The Cd—O bonds range from 2.253 (6)\* to 2.316 (6) Å in  $\text{K}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$  and from 2.268 (3) to 2.303 (3) Å for the two non-equivalent Cd atoms in  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ . In both these compounds the water molecules are non-bridging with Cd—OH<sub>2</sub> distances much shorter than in  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$ . Octahedral coordination is also found for the two independent Cd atoms in  $\text{K}_2\text{Cd}(\text{SO}_4)_2 \cdot 1.5\text{H}_2\text{O}$  (Borène & Solery, 1972). Each Cd atom is coordinated by five sulphate O atoms (Cd—O 2.18–2.30 Å) and one water molecule (Cd—OH<sub>2</sub> 2.37, 2.42 Å) bridging the two octahedra.

The selenate tetrahedron in  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  is only slightly distorted, with O—Se—O angles of 104–114° and Se—O distances of 1.622–1.650 Å (Table 2). The mean value of the Se—O distances, 1.639 Å, is in very good agreement with the mean value of 1.64 Å calculated from a number of selenate structures by Valkonen, Niinistö, Eriksson, Larsson & Skoglund (1975). As the selenate tetrahedra in both  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  and  $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$  are almost regular,

the considerable distortion of the sulphate group (S—O 1.42–1.61 Å) found in the isomorphous  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  is probably not correct. In  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  the four selenate groups are coordinated to Cd with bond angles Se—O—Cd of 112–136° with an average value of 126°; corresponding S—O—Cd angles in  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  are 125–136° and 131°.

The hydrogen bonds in  $\text{CdSeO}_4 \cdot \text{H}_2\text{O}$  (Table 2), which occur between the water molecule and the selenate atoms O(2) and O(4), are of normal strength, with O...O distances of 2.71 and 2.79 Å.

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\* Misprinted as 2.153 (6) Å in the original paper.