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Intralayer Hydrogen Bonding in $CdSeO_3.H_2O$

Ulrich Bäumer, Bernward Engelen and Holger Müller

Anorganische Chemie II, Universität-GH Siegen, D-57068 Siegen, Germany. E-mail: engelen@chemie.uni-siegen.de

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Abstract

Single crystals of cadmium trioxoselenate(IV) monohydrate were obtained from aqueous solutions of H_2SeO_3 and $[Cd(CH_3COO)_2].2H_2O$. $CdSeO_3.H_2O$ crystallizes in the $MnSeO_3.D_2O$ *oP*32 type. The structure contains buckled *trans* $[CdSeO_3.H_2O]^2_i$ layers consisting of strongly distorted, vertex-sharing $CdO_5(H_2O)$ octahedra and SeO_3^{2-} ions, both of symmetry *m*. The H-atom position was also determined, indicating that the H_2O molecules have pseudo *mm*2 symmetry. They form an intralayer hydrogen-bonding scheme with approximately linear hydrogen bonds of distance $d(OH\cdots O)$ = 2.903 (3) Å. As a consequence, the $[MSeO_3.H_2O]^2_i$ layers of the $[MnSeO_3.D_2O]$ *oP*32-type monohydrates are held together by van der Waals interactions but not by hydrogen bonds.

Comment

The chalcogenite monohydrates $MXO_3.H_2O$ (M = Mg, Mn, Co, Ni, Zn, Cd; X = S, Se) form a series of octahedral layer structures all containing the same type of buckled *trans* $[MXO_3.H_2O]^2_i$ layers (Engelen, 1994; Engelen *et al.*, 1995, 1996). The structures differ mainly in the lateral arrangement of the layers, giving rise to some local pseudosymmetry and related contradictions with respect to the interpretation of the IR spectra (Engelen *et al.*, 1996). The structures are of types a_1 or b_1 (Wells, 1990), *i.e.* the layers are held together either by van der Waals forces, as in $ZnSeO_3.H_2O$ *mP*32 (Engelen *et al.*, 1996), or by hydrogen bonds, as in $MnSO_3.H_2O$ *mP*32 (Engelen, 1994). Thus, the interlayer forces and the type of the resulting structures are determined mainly by the orientation of the apically positioned H_2O molecules (Fig. 1). The orientation of the H_2O molecules is believed to depend on the nature of the chalcogenite (Engelen *et al.*, 1996).

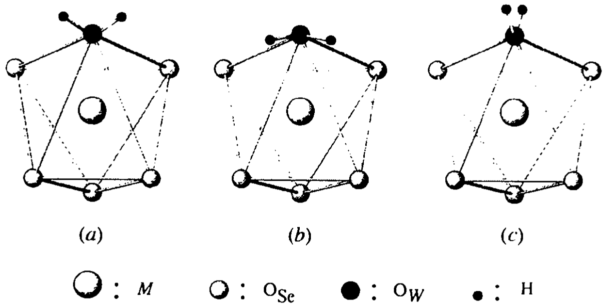

Fig. 1. Possible orientations of the H_2O molecules with respect to the MO_6 octahedra of layer-type hydrates $MXO_3.(H/D)_2O$ (M = Mg, Mn, Co, Ni, Zn, Cd; X = S, Se).

Powder X-ray diffraction and IR measurements (Engelen *et al.*, 1996) imply that $CdSeO_3.H_2O$ is isotypic with $MnSeO_3.D_2O$ *oP*32 (Koskenlinna & Valkonen, 1977; Engelen *et al.*, 1996). In order to determine unambiguously the orientation of the $(H/D)_2O$ molecules of these $MnSeO_3.D_2O$ *oP*32-type monohydrates, the crystal structure of $CdSeO_3.H_2O$ was determined by single-crystal X-ray diffraction. The determination of the H_2O orientation provides evidence for the above-mentioned influence of the nature of the chalcogenite on the structural chemistry of chalcogenite monohydrates. $CdSeO_3.H_2O$ was chosen because the crystal quality of the other $MnSeO_3.D_2O$ *oP*32-type compounds was not sufficient for determination of the H-atom positions (see Koskenlinna & Valkonen, 1977).

The heavy-atom structure (Cd, Se, O) was found to correspond to that of $MnSeO_3.D_2O$ *oP*32 (Koskenlinna & Valkonen, 1977), *i.e.* $CdSeO_3.H_2O$ is built up from $[CdSeO_3.H_2O]^2_i$ layers of symmetry $Pnm2_1$ consisting of distorted vertex-sharing $CdO_5(H_2O)$ octahedra and distorted trigonal pyramidal SeO_3^{2-} ions, both of symmetry *m* (Fig. 2 and Table 2). The layers have a buckled *trans* configuration with non-collinear Cd—O bonds. They are repeated by the 2_1 axes parallel to [100]. The distortion of the CdO_6 and SeO_3 groups is caused by the fact that SeO_3^{2-} acts as both a mono- and a bidentate ligand to Cd (see Fig. 2). The distortion found for $CdSeO_3.H_2O$ is greater than that for $MnSeO_3.D_2O$ (see Müller, 1997). The 'overlap' of the CdO_6 octahedra [see Koskenlinna & Valkonen (1977) and Fig. 2], represented by the Cd—O—Cd angle (Table 2), is the smallest found for chalcogenite monohydrates (Engelen *et al.*, 1996).

The H_2O molecules were found to be oriented with the OH directors nearly parallel to the $[CdSeO_3.H_2O]^2_i$ layers (Fig. 2). With respect to the MO_6 octahedra, the orientation is as given in Fig. 1(*b*) and is the same as that found in $ZnSeO_3.H_2O$ *mP*32 (Engelen *et al.*, 1996). The corresponding intralayer hydrogen-bonding scheme is shown in Fig. 3. In agreement with the IR spectra of isotopically dilute samples (Engelen *et al.*, 1996), the hydrogen bonds are weak, approximately linear and symmetric (Table 2 and Fig.

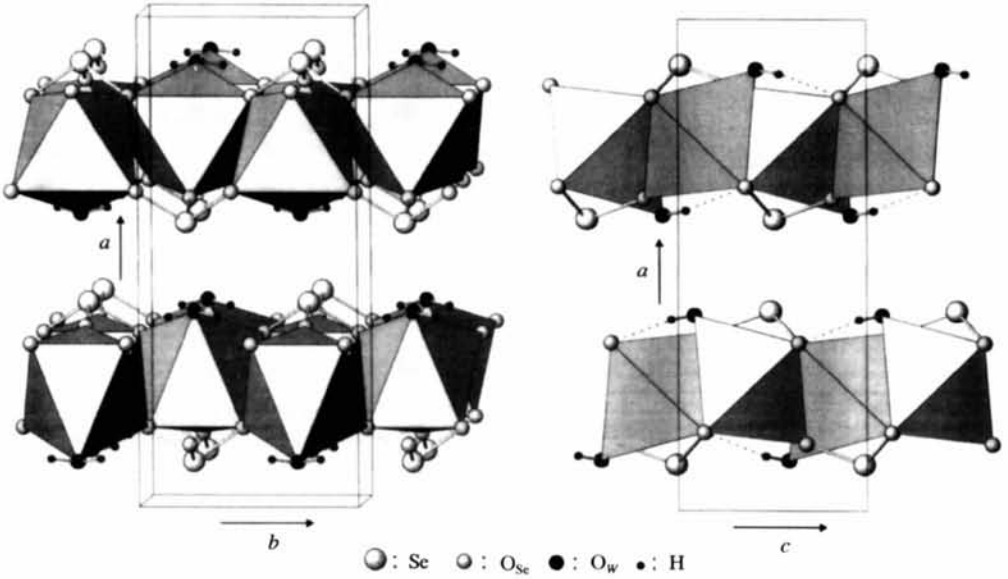

Fig. 2. The crystal structure of $CdSeO_3.H_2O$ viewed approximately (4°) along [001] (left) and along [0$\bar{1}$0] (right) showing the buckled layers $[CdSeO_3.H_2O]^2_\infty$ and the intralayer hydrogen bonds (dashed lines).

3). The orientation of H_2O as given in Fig. 1(*c*), and the resulting interlayer hydrogen-bonding scheme, are still restricted to the corresponding layered sulfite monohydrates (Engelen, 1994; Engelen *et al.*, 1996). This proves the theory that the $[MXO_3.H_2O]^2_\infty$ layers of the chalcogenite monohydrates are held together by van der Waals forces in the case of the selenites and by hydrogen bonds in the case of the sulfites.

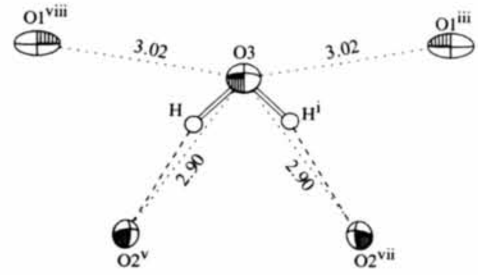

Fig. 3. The hydrogen-bonding scheme and OH···O distances (Å) for $CdSeO_3.H_2O$. The O atoms are drawn at a probability level of 48%. H atoms are shown with arbitrary radii. The symmetry codes are those given in Table 2, plus (viii) $\frac{1}{2} - x, -y, z - \frac{1}{2}$.

As in $MnSeO_3.D_2O$ *oP*32 and $ZnSeO_3.H_2O$ *mP*32 (Engelen *et al.*, 1996), the layers of $CdSeO_3.H_2O$ *oP*32 are limited by the Se atoms and not by the H_2O molecules as in $MnSO_3.H_2O$ (Engelen *et al.*, 1996). In all these selenite hydrates/deuterates, the depths of the layers decrease with the decreasing ionic radii of Cd, Mn and Zn. The interlayer distances increase in the same way by similar amounts (Müller, 1997). This unexpected finding is not caused by metal-dependent electrostatic interactions between the layers, but is attributed to simple geometric reasoning (Müller, 1997).

Experimental

Crystals of the title compound were obtained in the form of colourless prisms, needles or plates by slow evaporation over 2 weeks of an aqueous solution of 0.05 *M* H_2SeO_3 and 0.05 *M* $[Cd(CH_3COO)_2].2H_2O$ at room temperature (see also Engelen *et al.*, 1996).

Crystal data

$CdSeO_3.H_2O$
$M_r = 257.38$
Orthorhombic
Pnma
$a = 13.180\ (2)$ Å
$b = 5.8904\ (8)$ Å
$c = 5.0560\ (5)$ Å
$V = 392.52\ (9)$ Å^3
$Z = 4$
$D_x = 4.355$ Mg m^{-3}
$D_m = 4.30$ Mg m^{-3}
D_m measured by pycnometry

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 10.02$–$46.68°$
$\mu = 14.696$ mm^{-1}
$T = 293\ (2)$ K
Transparent prism
$0.4 \times 0.2 \times 0.1$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North *et al.*, 1968) and spherical (Bond, 1959)
$T_{min} = 0.054$, $T_{max} = 0.116$
2265 measured reflections
609 independent reflections

595 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 29.93°$
$h = -18 \rightarrow 18$
$k = -7 \rightarrow 0$
$l = -6 \rightarrow 6$
3 standard reflections
frequency: 60 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.044$
$S = 1.290$
609 reflections
39 parameters
H atom refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0168P)^2 + 0.5112P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$
$\Delta\rho_{\max} = 1.150$ e Å^{-3}
$\Delta\rho_{\min} = -0.821$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0390 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$U_{\rm iso}$ for H, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
Cd	0.27185 (2)	1/4	0.40234 (5)	0.01666 (12)
Se	0.40643 (3)	3/4	0.48839 (7)	0.01405 (13)
O1	0.1357 (3)	1/4	0.6813 (6)	0.0290 (7)
O2	0.3410 (2)	0.5330 (3)	0.6386 (3)	0.0196 (4)
O3	0.3980 (3)	1/4	0.0846 (6)	0.0233 (6)
H	0.389 (4)	0.137 (8)	−0.037 (8)	0.034 (11)

Table 2. *Selected geometric parameters (Å, °)*

Cd—O1	2.283 (3)	Se—O1$^{\rm iii}$	1.649 (3)
Cd—O2	2.245 (2)	Se—O2	1.719 (2)
Cd—O2$^{\rm i}$	2.245 (2)	Se—O2$^{\rm iv}$	1.719 (2)
Cd—O2$^{\rm ii}$	2.372 (2)	O3—H	0.91 (4)
Cd—O2$^{\rm iii}$	2.372 (2)	H—O2$^{\rm v}$	2.02 (4)
Cd—O3	2.312 (3)	O3—O2$^{\rm v}$	2.903 (3)
O1$^{\rm iii}$—Se—O2	104.32 (10)	H—O—H$^{\rm i}$	93 (5)
O1$^{\rm iii}$—Se—O2$^{\rm iv}$	104.32 (10)	O3—H—O2$^{\rm v}$	161 (4)
O2$^{\rm iv}$—Se—O2	96.09 (13)	O2$^{\rm v}$—O3—O2$^{\rm vii}$	70.10 (10)
Cd—O2—Cd$^{\rm vi}$	116.41 (9)		

Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iv) $x, \frac{3}{2} - y, z$; (v) $x, \frac{1}{2} - y, z - 1$; (vi) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (vii) $x, y, z - 1$.

Lattice parameters were determined from X-ray Guinier powder photographs (Cr $K\alpha_1$ radiation, α-quartz as internal standard) using a Huber–Guinier system 600 and the refinement program *LSUCR* (Evans *et al.*, 1963). The atomic positions were obtained from a Patterson map (Cd, Se) and successive least-squares refinements and ΔF syntheses (O, H).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971), *ATOMS* (Dowty, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1149). Services for accessing these data are described at the back of the journal.

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Tetraammonium Tetrametaphosphimate Tetrahydrate

NORBERT STOCK AND WOLFGANG SCHNICK

Laboratorium für Anorganische Chemie, Universitätsstraße 30, D-95440 Bayreuth, Germany. E-mail: wolfgang.schnick@uni-bayreuth.de

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Abstract

The tetrametaphosphimate ring in the title compound [tetraammonium *cyclo*-tetra-μ-imido-tetraphosphate tetrahydrate, $(NH_4)_4(PO_2NH)_4.4H_2O$] exhibits a chair conformation. The tetrametaphosphimate rings are linked by N—H···O bonds forming columns along [100]. These columns are interconnected by O—H···O and N—H···O hydrogen bonds through water molecules and ammonium ions. All H atoms are involved in hydrogen bonding.

Comment

The synthesis of salts of the tetrametaphosphimic acid $H_4(PO_2NH)_4.2H_2O$ has been well investigated (Stokes, 1896; Lunkwitz & Steger, 1968; Herzog & Nielsen, 1958) but the compounds have been mainly characterized by IR spectroscopy (Corbridge & Lowe, 1954; Lunkwitz & Steger, 1968; Pustinger *et al.*, 1959; Sukova