Crystal Structure of Copper Hydrogenselenite Monohydrate *

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Divalent metals may form hydrogenselenites $M(HSeO_3)_2$ and diselenites MSe_2O_5 with selenious acid as well as normal selenites $MSeO_3$. The number of possible solid compounds crystallizing from the $M^{2+}-H_2SeO_3-H_2O$ system is still larger, since the different selenite ligands may be simultaneously present in the solid compounds, and water usually plays an active role either as the aqua ligand or as the water of crystallization.

In the case of selenites formed with divalent copper, the structure of $CuSeO_3 \cdot 2H_2O$ has been reported earlier;[1] this compound also occurs in nature as chalcomenite mineral. More recently, its structure has been determined in connection with an optical and magnetic study.[2] The structures of the anhydious Cu(II) selenite and diselenite are also known.[3,4] Here we present the structure of a Cu(II) hydrogenselenite, $Cu(HSeO_3)_2 \cdot H_2O$, as part of our investigation into the structural chemistry of metal selenites.[5,6]

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Table 1. Summary of crystal data, intensity collection and structure refinement of $Cu(HSeO_3)_2.H_2O$.

(a)	Crystal data	
	Formula	$Cu(HSeO_3)_2 \cdot H_2O$
	Mol wt	337.5
	Crystal system	monoclinic
	Space group	$P2_1/c$ (No. 14)
	a, Å	6.280(2)
	b, Å	6.255(1)
	c, Å	9.087(3)
	β, deg	91.01(3)
	V, Å^3	356.9
	Z	2
	d_{calcd}, g cm^{-3}	3.14
	radiation	$MoK\alpha$ ($\lambda=0.71069$ Å)
	$\mu(MoK\alpha)$, cm^{-1}	141.2
(b)	Data collection and structure refinement[a]	
	2θ scan speed, deg min^{-1}	variable 2.0–29.3 ($\theta/2\theta$)
	No. of data collected	1644 ($3<2\theta<70$)
	No. of unique data ($I_{obs}>3\sigma(I_{obs})$)	1246
	Abs correction	empirical (max. reduction in intensity 36 %)
	Structure solution	direct methods
	No. of variables	65
	R, %	4.1
	R_w, % ($w=1/\sigma^2$)	3.8

[a] Computations were performed with the programs MULTAN 80[10], SHELX-76.[11]

Table 2. Fractional positional parameters and isotropic thermal parameters for $Cu(HSeO_3)_2 \cdot H_2O$.

Atom	x	y	z	$100 \cdot U_{eq}{}^a$
Cu	0	0	0	1.23(5)
Se	0.2347(1)	0.2283(1)	0.7426(1)	0.90(3)
O1	0.2012(7)	0.2178(8)	0.9253(4)	1.52(20)
O2	0.1004(7)	0.0490(8)	0.1988(5)	1.70(24)
O3	0.4955(8)	0.3371(9)	0.7511(6)	1.67(24)
O4	0.7224(8)	0.3000(9)	1.0251(5)	2.13(26)
H1	0.639(14)	0.307(16)	0.939(8)	4(3)
H2	0.784(12)	0.425(12)	1.064(9)	2(2)
H3	0.558(15)	0.306(17)	0.717(11)	2(3)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Transparent blue-green $Cu(HSeO_3)_2 \cdot H_2O$ crystals were prepared by dissolving copper carbonate in a 1 mol dm^{-3} H_2SeO_3 solution, filtering the warm (40 °C) saturated solution and evaporating it at room temperature. The monohydrate phase is apparently not stable at higher temperature, as it was not detected in a recent study of the $CuO-SeO_2-H_2O$ system at 100 °C.[7] The structure of the compound, including hydrogen atom positions, was determined from single crystal X-ray data collected on a Syntex P2₁ diffractometer and refined to an R value of 4.1 % (R_w=3.8 %). Details of crystal data and structure refinement are given in Table 1. In the refinement, the temperature factors for nonhydrogen atoms were anisotropic, while hydrogen atoms had individual isotropic temperature factors; the O−H distances involving the water molecule were refined constraining them to be equal. The final positional and thermal parameters are presented in Table 2; a listing of the observed and calculated structure factors and anisotropic thermal parameters are available from the authors upon request.

Copper atoms are located at the centre of the CuO_6 coordination octahedron, which shows typical elongation due to Jahn-Teller effect (Fig. 1). Four oxygen atoms, from two

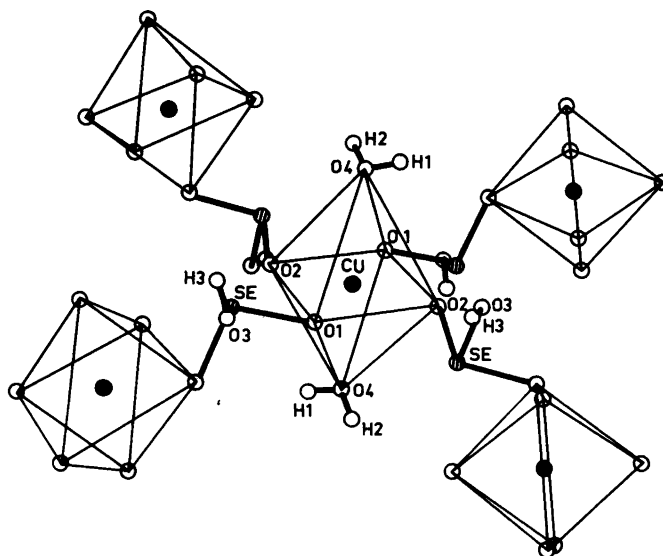*Fig. 1.* A perspective view along x-axis showing the coordination around Cu^{2+} and the joining of the CuO_6 octahedra.

Table 3. Bond distances (Å) and angles (°) in $Cu(HSeO_3)_2 \cdot H_2O$.

Cu−O1 (2x)	1.986(4)	O1−Cu−O2	90.7(2)
Cu−O2 (2x)	1.927(4)	O1−Cu−O4	88.1(2)
Cu−O4 (2x)	2.574(5)	O2−Cu−O4	89.3(2)
Se−O1	1.678(4)	O1−Se−O2	101.3(2)
Se−O2	1.673(5)	O1−Se−O3	96.0(2)
Se−O3	1.773(5)	O2−Se−O3	98.8(2)
O3−H3[a]	0.542(9)	Se−O3−H3	121(10)
O4−H1	0.936(6)		
O4−H2	0.936(6)		
(H1) O4···O3	2.856(7)	O4−H1−O3	173(8)
(H2) O4···O1[i]	3.086(7)	O4−H2−O1	150(7)
(H2) O4···O2[iii]	3.140(7)	O4−H2−O2	136(6)
(H3) O3···O4[ii]	2.662(7)	O3−H3−O4	160(12)

Symmetry code: none x, y, z
        (*i*) $\bar{x}$, $\bar{y}$, $\bar{z}$
        (*ii*) x, $\frac{1}{2}-y, \frac{1}{2}+z$
        (*iii*) $\bar{x}$, $y-\frac{1}{2}, \frac{1}{2}-z$

[a] The O3−H3 distance is unreasonably short owing to the difficulties of refining correctly the hydrogen atom positions when there are heavy atoms in the structure. However, the Se−O3−H3 and O3−H3−O4 angles indicate the basic correctness of the position.

didentately coordinated hydrogenselenite ions, form a plane with Cu. The planar Cu−O distances are 1.927 and 1.986 Å, while the axial Cu−O distance to water molecules is 2.574 Å (Table 3). These values may be compared with those of $CuSeO_3 \cdot 2H_2O$, where copper has a 4+1 coordination and the Cu−O distances in the basal plane are in the range 1.946−1.985 Å, the largest distance involving a water molecule. The topical distance to the other water molecule is significantly larger, *viz.* 2.325 Å.[2]

Hydrogenselenite ions have the shape of a trigonal pyramid but the Se−O3 bond is stretched (1.773 Å) due to the hydrogen atom bonded to this oxygen. The two other Se−O bonds are symmetrical (1.673 and 1.678 Å). The difference between the average Se−O distances, $d_{Se-OH}-d_{Se-O}$, is 0.10 Å, which is comparable to the difference of 0.12 Å found in a neutron diffraction study for $Zn(HSeO_3)_2 \cdot 2H_2O$.[8] In $CuSeO_3 \cdot 2H_2O$ the Se−O(SeO3) mean distance is 1.705 Å,[2] which is equal to the mean value found in the octahedrally coordinated $MnSeO_3 \cdot 2H_2O$ (1.704 Å),[9] and slightly larger than the Se−O distances in both the present compound and $Zn(HSeO_3)_2 \cdot 2H_2O$. The Cu-centred polyhedra are joined into a three-dimensional network by bridging $HSeO_3^-$-ions. There are, however, large tunnels in the network running parallel to the rows of Cu atoms in the [001] direction. The Cu−Cu separation within the rows is 4.3 Å and between them 6.3 Å. All H atoms are involved in hydrogen bonding; the bonds involving H1 and H3 in particular appear strong (*cf.* Table 3).

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