On the Crystal Structure of $Na_2[Hg(SO_3)_2].H_2O$

BIRGIT NYBERG and IRENA CYNKIER

Division of Inorganic Chemistry 2, Chemical Center, Box 740, S-220 07 Lund 7, Sweden

The crystal structure of $Na_2[Hg(SO_3)_2].H_2O$ has been determined from three-dimensional X-ray intensity data recorded with the integrating Weissenberg multi-film technique (Mo$K\alpha$ radiation). The intensities of the reflections ($0kl - 9kl$) were measured with a densitometer and were corrected for Lorentz, polarization and absorption effects, the linear absorption coefficient $\mu = 217$ cm^{-1}.

The compound was prepared according to Bogdanov.[1] It forms crystals of space group $P2_1/n$, with $a = 8.434(1)$ Å, $b = 9.345(1)$ Å, $c = 10.543(2)$ Å, and $\beta = 116.14(1)°$, and with a cell content of four formula units. The cell dimensions were obtained from a Guinier-Hägg powder photogram taken with Cu$K\alpha_1$ radiation.

The structure was derived from Patterson and Fourier syntheses. The parameters were refined using least-squares technique, with anisotropic temperature factors for the non-oxygen atoms and isotropic ones for the oxygen atoms.

All the atoms are in the general fourfold position of the space group. The final values of the non-hydrogen atomic parameters and their standard deviations are given in Table 1. The corresponding value of the discrepancy factor is 0.064 for 1355 observed independent reflections. Lists of observed and calculated structure factors are available on request from the Division of Inorganic Chemistry 2. Interatomic distances and angles are given in Table 2.

The infrared absorption spectrum [2] indicated that $Na_2[Hg(SO_3)_2].H_2O$ is a compound with mercury-sulfur bond. This has also been confirmed in the present work. The distances Hg – S (2.402(6), 2.411(6) Å) and the angle S – Hg – S (172.8(2)°) are similar to the values found in the hexagonal modification of mercury(II) sulfide [3] (2 × 2.363(8) Å; 172.5(4)°). In cinnabar the structure is built up of infinite –S–Hg–

Table 1. Fractional atomic coordinates and isotropic temperature factors with standard deviations calculated from the least-squares refinement.

Atom	x	y	z	B (Å^2)
Hg	0.30037(11)	0.07238(9)	0.08637(9)	(1.25)
S1	0.4819(8)	0.1991(6)	0.0011(6)	(1.06)
S2	0.3546(7)	0.4214(7)	0.3200(6)	(1.07)
Na1	0.9465(15)	0.2588(12)	0.1387(12)	(2.00)
Na2	0.8169(14)	0.0047(13)	0.3011(13)	(1.86)
O1	0.6645(26)	0.1464(23)	0.0837(21)	2.0(3)
O2	0.9181(24)	0.3393(21)	0.3497(21)	1.8(3)
O3	0.4592(28)	0.3184(24)	0.4305(23)	2.4(3)
O4	0.2270(26)	0.3529(24)	0.1938(23)	2.2(3)
O5	0.4767(23)	0.3543(21)	0.0193(19)	1.5(2)
O6	0.0256(28)	0.0146(25)	0.2077(23)	2.3(3)
OW	0.6362(30)	0.0093(28)	0.4239(27)	2.9(3)

Anisotropic thermal parameters, and their standard deviations. The temperature factor is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg	0.0060(1)	0.0037(1)	0.0035(1)	– 0.0001(1)	0.0024(1)	0.0004(1)
S1	0.0067(8)	0.0022(5)	0.0029(5)	– 0.0006(5)	0.0018(5)	0.0003(4)
S2	0.0035(8)	0.0039(5)	0.0030(4)	– 0.0002(6)	0.0012(4)	0.0000(5)
Na1	0.0108(19)	0.0050(12)	0.0058(11)	– 0.0004(11)	0.0038(13)	0.0011(10)
Na2	0.0060(17)	0.0068(14)	0.0063(11)	– 0.0004(12)	0.0032(11)	– 0.0007(10)

Table 2. Interatomic distances (Å) and angles (°) with their estimated standard deviations (uncorrected for thermal motion).

Hg–S1	2.402(6)	S1–O5	1.466(20)
–S2	2.411(6)	–O1	1.480(21)
–O3	2.803(21)	–O2	1.486(20)
–O1	2.819(21)	O1–O5	2.408(21)
–O4	3.026(22)	–O2	2.430(28)
–O2	3.070(19)	O5–O2	2.437(27)
Na1–O4	2.344(23)	S2–O4	1.441(22)
–O3	2.357(25)	–O6	1.458(22)
–O6	2.399(25)	–O3	1.469(22)
–O1	2.425(23)	O3–O6	2.380(31)
–OW	2.448(29)	–O4	2.421(30)
–O2	2.458(23)	O4–O6	2.410(30)
Na2–O6	2.368(24)	O2–S1–O1	110(1)
–O5	2.384(22)	O2–S1–O5	111(1)
–OW	2.395(27)	O1–S1–O5	110(1)
–O1	2.463(24)		
–O2	2.463(22)	O6–S2–O4	112(1)
–O5	2.472(22)	O4–S2–O3	112(1)
		O6–S2–O3	109(1)
		S1–Hg–S2:	172.8(2)

Distances O–O<3.0 Å outside the polyhedra

O4–OW	2.902(33)
O5–OW	2.887(30)

S– chains, but in the present compound the structure consists of discrete $Hg(SO_3)_2^{2-}$ groups. The present structure is held together by sodium ions. Two independent distorted NaO_6 octahedra exist. The oxygen atoms belong to five different sulfite groups and to one water molecule. A projection of the structure along the *b* axis is given in Fig. 1.

The mean sulfur-oxygen distance of 1.466 Å in the two independent sulfite groups is the shortest S–O distance hitherto found in a metal sulfite. The mean O–S–O angle of 110.8° is consistent with this S–O distance.[4] The oxygen atoms of the sulfite group are at such long distance from mercury (> 2.80 Å) that the influence of the metal-oxygen bond on the sulfite group is probably small. Hydrogen bonding to one oxygen atom in the sulfite groups is likely, as seen from Table 2, but the influence of this upon the S–O distances is not noticeable. As discussed by Kierkegaard *et al.*,[4] the expected S–O distance in a metal sulfite with a metal-sulfur bond and a weak bond to the oxygen atoms in the sulfite group should be shorter than the distance in Na_2SO_3 (1.504 Å).[5]

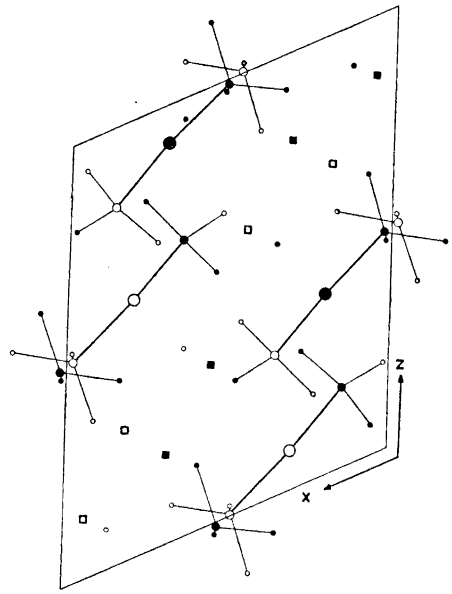

Fig. 1. A schematic drawing showing the structure of $Na_2[Hg(SO_3)_2].H_2O$. The structure is viewed along the *b* axis. Large circles denote mercury atoms, small circles oxygen atoms and squares sodium atoms. Filled figures denote atoms with $0.5 \leq y < 1.0$, unfilled denote atoms with $0 \leq y < 0.5$.

The S–O distance found in $Na_2[Hg(SO_3)_2].H_2O$ is even shorter than that found in many sulfates (*cf.* $Li_2SO_4.H_2O$ with the mean distance 1.472 Å). Diffractometer data will therefore be collected for the present compound to get better standard deviations for a further discussion of the bonding in metal sulfites.

Financial support from the *Swedish Natural Science Research Council* is gratefully acknowledged.

1. Bogdanov, S. V. *J. Gen. Chem. USSR* **16** (1946) 1535.
2. Nyberg, B. and Larsson, R. *Acta Chem. Scand. In press.*
3. Aurivillius, K. *Trans. Royal Inst. Technol. Stockholm 1972. In press.*
4. Kierkegaard, P., Larsson, L. O. and Nyberg, B. *Acta Chem. Scand.* **26** (1972) 218.
5. Larsson, L. O. and Kierkegaard, P. *Acta Chem. Scand.* **23** (1969) 2253.
6. Larsson, A. C. *Acta Cryst.* **18** (1965) 717.

Received November 17, 1972.