Structure of Mercury Disilver Diiodide Dinitrate Monohydrate

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Abstract. $Ag_2HgI_2(NO_3)_2.H_2O$, $M_r = 812.20$, ortho-rhombic, *Pbam*, $a = 10.9470$ (8), $b = 18.9680$ (21), $c = 5.3127$ (8) Å, $D_x = 4.89$ Mg m^{-3}, $Z = 4$. The structure was refined to a final R value of 0.06 from single-crystal diffractometer data (817 independent reflexions). An I–Hg–I segment with an angle of 176.9° and two Hg–I distances of 2.63 Å are found in the structure. Besides the Hg atom, the two independent I atoms also have two Ag atoms as nearest neighbours. These Hg–I_2–Ag_4 units are joined by shared Ag corners, forming sheets in the *ac* plane. There are two such sheets in the unit cell. Two remarkably short Ag–I distances are found: 2.71 and 2.74 Å. The NO_3 groups, of which one is distributed over two positions, are situated in the cavities in this network. The water molecule is distributed over two positions: one is approximately one of the N positions of the disordered nitrate group and the other one is approximately an O position of the alternative nitrate position.

Introduction. For some years structural investigations of the coordination of silver to halide in solid compounds of the general formula $Ag_nX_xA_y$ ($n > x$; $X = $ Cl, Br, or I, and $A = $ F, NO_3, ClO_4) have been performed at this Institute. These investigations have now been extended to compounds of another class *b* metal ion, *i.e.* Hg^{II}.

The structure of $HgINO_3$ has been studied recently (Persson & Holmberg, 1982). A compound containing both Ag^I and Hg^{II} [$2AgI.Hg(NO_3)_2$] had been described earlier (Morse, 1902) and attempts were made to synthesize single crystals with this composition.

A solution of $Hg(NO_3)_2$ (5 *M*) and HNO_3 (4 *M*) was saturated with AgI at about 323 K. After filtration at this temperature single crystals of $Ag_2HgI_2(NO_3)_2.H_2O$ crystallized on cooling. The crystals so obtained were colourless rods with a rhomboidal transverse cross section, and they were stable at room temperature in laboratory air.

Table 1 gives information concerning the collection of intensities, and the refinement. The method employed in data collection has been described elsewhere (Elding, 1976). Weissenberg photographs revealed the Laue class *mmm* and the systematic absences *h0l*: $h = $

$2n + 1$ and $0kl$: $k = 2n + 1$. The Weissenberg photographs gave a slight indication of an *F*-centred unit cell eight times as large as the one described above. Data corresponding to this interpretation were collected but attempts to describe the structure from these have not yet been successful. A single-crystal diffractometer (CAD-4) was used for data collection, and the cell dimensions were improved by the least-squares refinement of 49 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength used for the determination of the cell dimensions was 0.70930 Å (Mo $K\alpha_1$).

Three reflexions ($\bar{5}11$, $4\bar{3}0$, $\bar{3}40$) checked every second hour showed a random fluctuation of less than 6%. The values of I and $\sigma_c(I)$, where $\sigma_c(I)$ is the standard deviation based on counting statistics, were corrected for Lorentz, polarization and absorption effects. The crystal shape was described by six planes [$(00\bar{1})$, $(00\bar{1})$, $(1\bar{1}0)$, $(2\bar{3}0)$, $\{890\}$, $(4\bar{7}0)$].

The positions of the Hg, I and Ag atoms were found by the use of the *MULTAN* 78 system of computer programs (Germain, Main & Woolfson, 1971). One Ag atom is distributed over two possible positions, Ag(2) and Ag(3). Subsequent difference syntheses revealed

Table 1. *Details of the collection and reduction of intensity data, and of the least-squares refinement*

Crystal size (mm)	$0.063 \times 0.075 \times 0.344$
Radiation (Nb filter)	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
Take-off angle (°)	3
$\Delta\omega$ (°) (ω–2θ scan)	$1.00 + 0.50 \tan \theta$
$\Delta\theta$ (°)	3–27
Minimum number of counts in a scan	3000
Maximum recording time (s)	180
μ(Mo $K\alpha$) (mm^{-1})	22.92
Range of transmission factor	0.320–0.413
Number of measured reflexions	1436
Number of reflexions given zero weight	619
Number of independent reflexions used in the final refinements, m	817
Number of parameters refined, n	77
$R = \sum \|F_o\| - \|F_c\|\|/\sum \|F_o\|$	0.063
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.082
$S = [\sum w(\|F_o\| - \|F_c\|)^2/(m - n)]^{1/2}$	1.75
a (weighting function)	0.030
b (weighting function)	3.0
$g \times 10^{-4}$ (extinction coefficient)	0.02 (6)
Mosaic spread (seconds of arc)	291
Domain size (mm)	0.14×10^{-4}

the N and O positions of the nitrate groups; one of these also seemed to be located over more than one position. The calculated electron density, found in a difference synthesis, at the N(2) position exceeded the contribution due only to an N atom with an occupancy factor of 0·5. This observation coupled with a similar high electron density on the O(31) site, an O of the alternative NO_3-group position, indicated the presence of a water O distributed over these two sites. A final difference synthesis showed peaks of height about 3·5 e Å^{-3} in the vicinity of the O(31) atom and one peak at $\frac{1}{2},\frac{1}{2},0$ of height 3·1 e Å^{-3}. These electron densities cannot be explained by the present structure model.

Full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2 + b]$. One scale factor, and positional and anisotropic thermal parameters, for all atoms except those which are disordered, were refined (Table 1). Refinement of the occupancy factors for Ag(2) and Ag(3) gave 0·46 and 0·43 respectively. They were put to 0·5 in the final refinement. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refinement also included correction for secondary extinction (Zachariasen, 1967) and anomalous dispersion by Hg, I and Ag. A normal-probability plot of $\delta R(i) = [|F_o(i)| - |F_c(i)|]/\sigma|F_o(i)|$ *versus* the values expected for a normal distribution was calculated (Abrahams & Keve, 1971) and the slope and intercept of the least-squares line fitted to all data in the range $|\delta R(i)| < 6$ are 1·56 and 0·12. Final positional parameters are given in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and root-mean-square components of thermal displacement along the ellipsoid axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36472 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Positional and isotropic thermal parameters with estimated standard deviations*

The occupancy factor G is also given.

G		x	y	z	B_{eq}/B (Å^2)
1	Hg	0·11178 (14)	0·39031 (8)	0	3·43 (4)*
1	I(1)	−0·10588 (23)	0·33137 (13)	0	4·61 (7)*
1	I(2)	0·32356 (27)	0·45584 (14)	0	5·46 (9)*
1	Ag(1)	0·4596 (6)	0·3117 (2)	0	9·28 (9)*
$\frac{1}{2}$	Ag(2)	0·8452 (7)	0·3233 (4)	$\frac{1}{2}$	5·49 (20)*
$\frac{1}{2}$	Ag(3)	0·3230 (12)	0·4916 (5)	$\frac{1}{2}$	9·4 (4)*
1	N(1)	0·1766 (29)	0·3073 (18)	$\frac{1}{2}$	4·1 (9)*
1	O(11)	0·1324 (29)	0·3670 (14)	$\frac{1}{2}$	5·0 (8)*
1	O(12)	0·1990 (19)	0·2787 (9)	0·2960 (35)	5·4 (6)*
$2 \times \frac{1}{2}$	N(2)	0·0532 (14)	0·1325 (7)	$\frac{1}{2}$	0·6 (2)
$\frac{1}{2}$	O(21)	0·4694 (36)	0·3190 (21)	$\frac{1}{2}$	2·5 (7)
$\frac{1}{2}$	O(22)	0·1007 (29)	0·1252 (16)	0·3058 (68)	3·7 (7)
$\frac{1}{2}$	N(3)	0·4460 (77)	0·0197 (38)	$\frac{1}{2}$	5·8 (1·8)
$2 \times \frac{1}{2}$	O(31)	0·2789 (20)	0·0534 (12)	$\frac{1}{2}$	3·1 (4)
$\frac{1}{2}$	O(32)	$\frac{1}{2}$	0	0·2880 (80)	2·7 (7)

* For these atoms $B_{eq} = \frac{4}{3}\sum_i\sum_j\beta_{ij}\,\mathbf{a}_i\cdot\mathbf{a}_j$.

Discussion. A stereoview of the unit cell is given in Fig. 1. Selected interatomic distances and angles are listed in Table 3. The structure consists of sheets of $Hg-I_2-Ag_4$ units joined by shared Ag corners in the **a** and **c** directions. Two such sheets in the unit cell create cavities where the NO_3 groups and the water molecules reside.
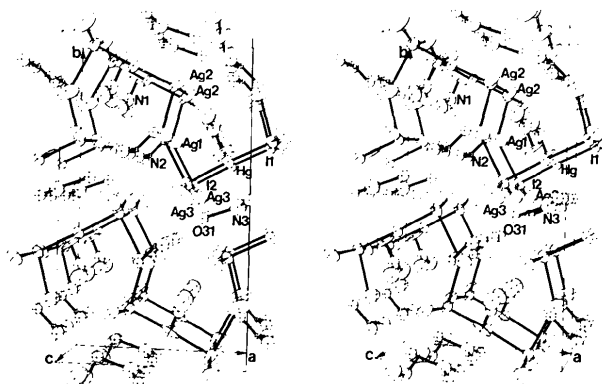

Fig. 1. A stereoscopic pair of drawings showing the contents of the unit cell. Figs. 1 and 3 have been drawn by the program *ORTEP* II (Johnson, 1971).

Table 3. *Selected interatomic distances (Å) and angles (°) with estimated standard deviations*

Hg–I(1)	2·632 (3)	Ag(3)–O(11)	3·15 (3)
Hg–I(2)	2·631 (3)	Ag(3)–O(21)	3·65 (4)
Hg–O(11)	2·702 (5) × 2		
Hg–O(12)	2·80 (2) × 2	I(1)–I(2)	4·687 (4)
Hg–O(32)	2·86 (2) × 2	I(1)–I(2)	5·261 (4)
		I(2)–I(2)	4·211 (4)
Ag(1)–I(1)	2·808 (5)		
Ag(1)–I(2)	3·112 (6)	N(1)–O(11)	1·23 (4)
Ag(2)–I(1)	2·714 (2)	N(1)–O(12)	1·24 (2) × 2
Ag(3)–I(2)	2·742 (3)	N(2)–O(21)	1·30 (4)
		N(2)–O(22)	1·16 (4) × 2
Ag(1)–O(22)	2·54 (3)	N(3)–O(31)	1·94 (9)
Ag(1)–O(21)	2·662 (3)	N(3)–O(32)	1·33 (6) × 2
Ag(1)–O(12)	3·32 (2)		
Ag(2)–O(31)	2·45 (2)	O(11)–O(12)	2·12 (3) × 2
Ag(2)–O(12)	2·73 (2)	O(12)–O(12)	2·17 (4)
Ag(2)–O(21)	3·02 (4)	O(21)–O(22)	2·06 (5) × 2
Ag(2)–O(22)	3·03 (3)	O(22)–O(22)	2·06 (7)
Ag(3)–O(31)	1·62 (3)	O(31)–O(32)	2·85 (3) × 2
Ag(3)–O(22)	2·86 (3)	O(32)–O(32)	2·25 (8)

I(1)–Hg–I(2)	176·9 (1)	Hg–I(1)–Ag(2)	101·7 (2)
		Hg–I(2)–Ag(3)	96·6 (3)
I(2)–Ag(1)–I(2)	136·6 (2)	Hg–I(2)–Ag(1)	90·4 (1)
Hg–I(1)–Ag(1)	100·4 (2)		
Ag(1)–I(1)–Ag(2)	89·8 (2)	O(11)–N(1)–O(12)	119 (2)
Ag(2)–I(1)–Ag(2)	156·3 (39)	O(12)–N(1)–O(12)	122 (3) × 2
Ag(3)–I(2)–Ag(3)	102·6 (3)	O(21)–N(2)–O(22)	114 (2)
Ag(3)–I(2)–Ag(3)	151·3 (5)	O(22)–N(2)–O(22)	125 (3) × 2
		O(31)–N(3)–O(32)	121 (3)
O(11)–Hg–O(11)	159 (1)	O(32)–N(3)–O(32)	116 (6) × 2
O(21)–Ag(1)–O(21)	172 (2)		

The Hg atom is almost linearly (176·9°) coordinated to two I atoms, as is also found in other compounds containing I—Hg—I segments [cf. HgI_2(178·3°) (Jeffrey & Vlasse, 1967) and $Hg_2I_2TiF_6$ (175·8°) (Köhler, Breitinger & Thiele, 1974)]. The Hg—I distances of 2·63 Å (Table 3) are in good agreement with those observed in the compounds mentioned above. By comparison with the structure of $HgINO_3$ (Persson & Holmberg, 1982), a compound containing infinite $[HgI^+]_n$ chains like $Hg_2I_2TiF_6$, it is evident that the introduction of Ag breaks up the chains to form discrete I—Hg—I segments. A comparison may be made with the stoichiometrically related substance $Ag_2Hg(CN)_2(NO_3)_2.2H_2O$ (Mahon & Britton, 1971a) which contains $Hg(CN)_2$ segments bridged by Ag atoms creating an almost linear infinite chain —Ag—NC—Hg—CN—Ag—.

The Ag(2) and Ag(3) atoms alternate in their site occupancy in a way which joins the I—Hg—I segments in the c direction (Fig. 2).

The I(1) and I(2) coordination can be described as a trigonal pyramid with the I atom at the apex and one Hg and two Ag atoms at the corners (Fig. 3), similar to the configuration in $Ag_2IF.H_2O$ (Holmberg & Persson, 1975) where I is coordinated to four Ag atoms to form a square pyramid with the I atom at the apex. The Ag—I distances including Ag(2), Ag(3) are short: 2·71 and 2·74 Å, which are shorter than those of β-AgI
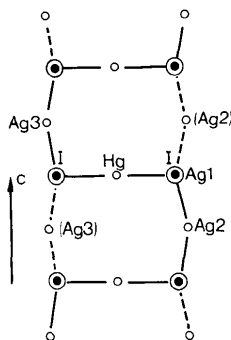

Fig. 2. A schematic projection perpendicular to the I—Hg—I segment parallel to the ab plane. The larger circles represent the I atoms and the smaller ones the cations. The Ag(1) atoms (filled circles) are situated about a plane through the I—Hg—I segment. The alternative positions and bonds for the Ag(2) and Ag(3) atoms are shown by symbols within brackets and by dotted lines.
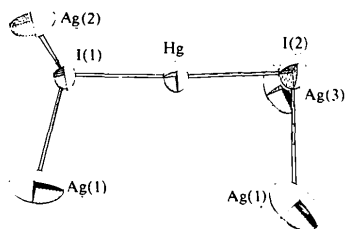

Fig. 3. The environment of the I atoms.

(2·814 Å; Burley, 1963). Such short Ag—I distances have also been found in another compound of general composition $Ag_nX_xA_y$ ($n > x$), viz $Ag_{13}I_9(WO_4)_2$, being a solid Ag^+ electrolyte (Chan & Geller, 1977).

The Hg atom has, besides the two I atoms, six O atoms of the NO_3 groups forming a hexagon in the equatorial plane perpendicular to the I—Hg—I segment. Approximately the same geometrical arrangement of O atoms around the Hg is found in two other substances, i.e. $Hg(CN)NO_3$ (Mahon & Britton, 1971b) and $Ag_2Hg(CN)_2(NO_3)_2.2H_2O$ (Mahon & Britton, 1971a), where six O atoms with Hg—O distances of 2·73 Å and five O atoms with Hg—O distances between 2·55 and 3·06 Å, respectively, surround the Hg atom, in a plane perpendicular to the infinite chain containing Hg, CN and, for the latter substance, Ag atoms. The Hg—O distances in $Ag_2HgI_2(NO_3)_2.H_2O$ vary between 2·70 and 2·86 Å. The nitrate groups around the Hg—I segment are located in exactly the same way as in $HgINO_3$, i.e. one group perpendicular to the segment and the other one parallel with it. The Hg environment is very similar in these two structures. The variation in the equatorial Hg—O distances is, however, smaller in the present compound, which is reflected in the fact that the I—Hg—I segment is closer to linearity than the corresponding bond sequence of the $HgINO_3$ structure (Persson & Holmberg, 1982).

The Ag(1) atom has two I atoms situated above and below a plane of O atoms. This plane is described by a square or hexagon of four or six O atoms, depending on the occupancy of H_2O and NO_3. The Ag—O distances range from 2·54 to 3·32 Å. Ag(2) has a more irregular environment of five or six O atoms with Ag—O distances of 2·44 to 3·03 Å. The Ag(3) atom also has an irregular environment of four O atoms with distances from 1·62 [to O(31)] to 3·13 Å. The short Ag—O(31) distance seems to be an artefact which is mainly due to the inability of the structure model advanced here to account correctly for the electron density in the vicinity of O(31) as described above. An explanation would be a distribution of the O(31) atom over two positions depending on the occupancy of the Ag(2) and Ag(3) sites, but there is no direct evidence for this in the structure refinement.

The distances and angles within the N(1) nitrate group (Table 3) show values normally observed. The N(2) and N(3) groups are more distorted, however. The lower accuracy in the determination of these is probably due to the disorder of parts of the structure.

Finally, it may be instructive to consider the gross packing of the ions in the structure, the chemical and intrastructural differences between NO_3^- and I^- being neglected. All Ag and Hg atoms have a more or less distorted octahedral environment of anions. The anion packing can be approximately described by a hexagonal close-packed arrangement, infinite in the a and c directions and restricted to two hexagons along b.

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Preparation and Structure Refinement of the 2H Polytype of β-Copper(I) Thiocyanate

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Abstract. β-CuNCS, space group $P6_3mc$, $a = 3.850$ (3), $c = 10.937$ (3) Å, $Z = 2$, $V = 140.4$ (3) Å^3, $D_x = 2.877$ Mg m^{-3}. The structure was refined to $R = 0.059$ and $R_w = 0.065$ for a subset of the data (87 reflections). The crystals of β-CuNCS, which normally grow as trigonal or hexagonal pyramids, were obtained as pyramidal-capped hexagonal prisms. These crystals are predominantly the 2H polytype but also contain some 3R polytype in syntactic coalescence, along with disorder and twinning.

Introduction. Copper(I) thiocyanate [poly-μ-(thiocyanato-*N*,*S*)-copper(I)] is polymorphic (Kruger, Bussem & Tschirch, 1936; Kruger & Tschirch, 1941; Garaj & Gazo, 1965). The single-crystal structure of α-CuNCS, which is orthorhombic, was determined by Kabesova, Dunaj-Jurco, Serator, Gazo & Garaj (1976). Recently, we (Smith & Saunders, 1981) determined the structure of β-CuNCS and showed that this form is polytypic. Our β-CuNCS preparations usually produced pyramidal crystals which contained mostly 3R polytype with some 2H polytype in syntactic coalescence. We report here the preparation of hexagonal prisms of β-CuNCS which are predominantly the 2H polytype with some 3R form in syntactic coalescence.

Crystals were grown by vapor dilution of an aqueous solution of CuNCS in NaNCS. To 50 ml of 2·5 M NaNCS solution was added 0·40 g of finely divided CuNCS. After 30 min, the mixture was filtered and brought to 2·0 M NaNCS by the addition of 12 ml of H₂O. Diatomite filter aid (0·5 g) was stirred in and after 5 min the mixture was filtered into an evaporating dish which was then placed on a perforated disk above a supply of water in a closed desiccator. After 46 days, crystals of undecided habit could be seen. In 66 days the peculiar crystals shown in Fig. 1 were harvested. Further growth on crystals that remained in the solution was at the prismatic end of the crystals, indicating that crystal growth had been away from the apex.

Several crystals were examined with a precession camera and each was found to contain primarily the 2H polytype of β-CuNCS together with various small amounts of both *obverse* and *reverse* orientations of the 3R polytype and some disordering. The crystals were of poor quality, especially the larger ones, which gave 0*kl* precession pictures in which the spots were usually split laterally into three nearly equal components. Smaller rhomboid crystals seemed to be of better quality. The crystal chosen for data collection was an irregular hexagon approximately 0·06 mm on an edge and 0·13