

Crystal and Molecular Structure of Hexakis(dimethylsulfoxide)-mercury(II) Perchlorate, $[\text{Hg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2$

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The compound $[\text{Hg}(\text{DMSO})_6](\text{ClO}_4)_2$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 7.418(2)$, $b = 10.831(6)$, $c = 11.241(4)$ Å, $\alpha = 118.37(4)^\circ$, $\beta = 93.10(3)^\circ$, $\gamma = 92.60(3)^\circ$ and $Z = 1$. The X-ray investigation was based on 2001 independent reflections collected with a computer-controlled Syntex $P2_1$ four-circle diffractometer using $\text{MoK}\alpha$ radiation. The structural parameters were refined by least-squares methods to a conventional R value of 0.035.

The structure is built up from discrete hexakis(dimethylsulfoxide)mercury(II) complex ions and perchlorate ions. The mercury atom is coordinated to six DMSO molecules through the oxygen atoms in an almost regular octahedron. The average Hg–O bond length is 2.34 Å. The perchlorate group is disordered and performs large librational movements in the absence of hydrogen bonds.

The most common configuration of hexa-coordinated mercury is that of a distorted octahedron, with two short linear bonds.¹ Discrete complexes with regular octahedral coordination seem to be rare, but an example has been found in the compound $[\text{Hg}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$ with an Hg–O bond length of 2.35(2) Å.² Moreover, X-ray diffraction^{3,4} and Raman⁴ measurements on DMSO and aqueous solutions are consistent with a regular coordination of six solvent molecules to the Hg^{2+} ion. The average Hg–O bond lengths are 2.393(5) and 2.41(1) Å,⁴ respectively. For a comparison with the structures found for the solvated ions in solution the crystal structures of the solvates $[\text{Hg}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$,⁵ $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$,⁶ and $[\text{Hg}((\text{CH}_3)_2\text{SO})_6](\text{ClO}_4)_2$ in the present paper, were determined.

EXPERIMENTAL

Preparation of crystals. Saturated DMSO solutions, 0.94 M at 25 °C, were prepared by dissolving the compound $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ in pure DMSO.⁴ By slow evaporation or by cooling, colourless prismatic crystals of the composition $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{DMSO}$ were formed. The crystals were filtered off and washed with cold acetone. Methods and results of analyses of the crystals are given elsewhere.⁴

The crystals were very hygroscopic and decomposed rapidly in air. Even when stored in a closed tube they decomposed slowly losing DMSO. After two months the average number of DMSO molecules per mercury atom was found to be 5.4(1).

X-Ray data collection. The intensity data were collected at 25 ± 2 °C by a computer-controlled four-circle diffractometer of type Syntex $P2_1$, equipped with a scintillation counter. Graphite-monochromatized $\text{MoK}\alpha$ -radiation ($\lambda = 0.71069$ Å) was used.

A prismatic crystal with maximum dimensions of about 0.1 mm, contained in a capillary, was aligned optically. Approximate positions of 20 reflections were obtained from an oscillation photograph on the diffractometer. These reflections were automatically centred and used in an auto-indexing routine to determine the lattice constants, which were refined using least-squares methods. The unit cell was found to be triclinic with the crystal data: $a = 7.418(2)$, $b = 10.831(6)$, $c = 11.241(4)$ Å, $\alpha = 118.37(4)^\circ$, $\beta = 93.10(3)^\circ$, $\gamma = 92.60(3)^\circ$, $V = 790.9(6)$ Å³, $D_m = 1.76(3)$ and $D_x = 1.82$ g cm⁻³ for $Z = 1$.

The $\theta - 2\theta$ scan mode was used for the intensity data collection with different scan speeds, the minimum scan speed being 2° min⁻¹. Stationary background measurements were made on each side of a peak. The total background counting time was equal to the scan time.

The intensity, I , of each reflection was calculated by subtracting the total background count, BG , from the total scan count, SC . The standard deviation, $\sigma(I)$, was obtained from $\sigma(I) = (SC + BG)^{1/2}$. The values obtained were then multiplied with the scan rate to compensate for the different scan speeds. All intensities were corrected for Lorentz and polarization effects and converted to scaled $|F_o|$ values by means of a data reduction program. Of the 2064 possible independent reflections for $2\theta < 45^\circ$, 2001 had intensities larger than $1.96 \sigma(I)$ and were considered observed.

After every 50th reflection three check reflections were measured. Their intensities varied within $\pm 15\%$ during the data collection. They first increased and then slowly decreased, probably due to extinction changes during a gradual decomposition of the crystal. No correction for this was applied.

The absorption coefficient $\mu(\text{MoK}\alpha)$ is 55.7 cm^{-1} . A semi-empirical absorption correction method was used.⁷ The intensities of selected reflections, which had χ values close to 90° and 2θ values evenly distributed over the 2θ range used, were measured for a full flat-cone rotation around the diffraction vector in steps of 10° . The relative intensity variations obtained were used to correct the intensities of all measured reflections in appropriate 2θ -intervals. The largest measured relative reduction in intensity was from 1.00 to 0.63.

Computer programs. The program system supplied by Syntex (XTL version 2)⁸ for a NOVA 24K computer with a disk memory unit, was used for the calculations. In addition, the thermal-ellipsoid plot program for crystal structure illustrations, ORTEP 2, was used.⁹

STRUCTURE DETERMINATION AND REFINEMENTS

Determination of the structure. From a three-dimensional Patterson peak listing one Hg–Cl, three Hg–S and three Hg–O vectors, all with a multiplicity of two, could be identified. The space-group was therefore assumed to be the centrosymmetrical $P\bar{1}$ (No. 2), and the corresponding atomic parameters, with Hg at the origin of the unit cell, were refined by least-squares methods. The positions of the C atoms were found from a subsequent Fourier difference synthesis. Full-matrix least-squares refinements gave $R = 0.070$ ($R_w = 0.096$) with Hg anisotropic.

The conventional R -value is defined as $R = \sum |F_o| - |F_c| / \sum |F_o|$, and the weighted as $R_w = (\sum w |F_o| - |F_c|)^2 / \sum w |F_o|^2$.

A three-dimensional Fourier difference map was calculated and showed regions of increased electron density at about 1.4 \AA from the chlorine atoms. Seven more or less distinct peaks with heights between 1.1 and 2.4 e \AA^{-3} were found. Their locations and relative sizes corresponded approximately to two alternative positions of the ClO_4^- group, obtained by rotating it $\sim 60^\circ$ around an axis through the Cl and the highest of the oxygen peaks. This oxygen, O4, was then given a fixed occupancy number 1.0 and the remaining six positions 0.5. After new refinements another Fourier difference synthesis revealed peaks around the C atoms with heights of 0.4 to 0.8 e \AA^{-3} , which could be ascribed to the 18 H atom positions.

Full-matrix least-squares refinements with all non-H atoms anisotropic and with a fixed B -value of 5 \AA^2 for the H atoms gave $R = 0.036$ ($R_w = 0.048$). Finally, also the occupancy numbers of the perchlorate oxygens were allowed to vary, which gave $R = 0.035$ ($R_w = 0.047$).

Test of the absorption correction. Similar final refinements were also performed for data without the semi-empirical absorption correction described above, and gave $R = 0.036$ ($R_w = 0.047$).

The main effect of this absorption correction was to decrease the largest remaining peaks in the final difference Fourier synthesis, which were located around Hg, from 1.4 to 0.9 e \AA^{-3} . The refined parameters were not significantly affected except for the oxygen atoms coordinated to Hg, where the average Hg–O bond distance increased by 0.01 \AA . The data set with the absorption correction was considered to be the better one and was used for all other calculations reported here.

This semi-empirical absorption correction has, in some cases, been found to give almost identical results as those obtained using a Gaussian integration method, for some highly absorbing compounds.¹⁰

Test of non-centrosymmetry. In order to check if deviations from centrosymmetry would occur for the neighbouring atoms of the perchlorate groups, and if the perchlorate positions could be described in a better way, calculations were also performed in the non-centrosymmetric space-group $P1$ (No. 1). However, the R_w values obtained were not, according to statistical tests,¹¹ significantly lower than the corresponding values for $P\bar{1}$. Moreover, some of the anisotropic temperature coefficients, B_{ii} , of the DMSO oxygens became negative, which is physically meaningless.

Scattering factors and refinement conditions. The scattering factors used for all non-H atoms were calculated from analytical expressions for the neutral atoms.¹¹ For the H atoms the spherical form factors proposed by Stewart *et al.* were used.¹² Anomalous dispersion corrections were included for Hg, Cl and S.¹¹

The least-squares refinements were based on the minimization of $\sum w \|F_o\| - |F_c\|^2$ and 2001 reflections with $F_o > 3.92 \sigma(F_o)$ were used. The weighting scheme used was $w = 1/[\sigma^2(F_o) + (0.04 F_o)^2]$ which,

according to a weight analysis, gave a satisfactory error distribution.

A total of 251 parameters, including one scale factor, was varied in the final refinements. The ratios of the shifts in the last cycle to the standard deviation were less than 0.1 in $P\bar{1}$, except for the thermal parameters of the perchlorate oxygens, where the largest ratio was 0.4.

The final refined parameter values are given in Tables 1 and 2.

Table 1. Final fractional atomic positional parameters with estimated standard deviations in parentheses. The *G* values are the refined occupancy factors.

Atom	x	y	z	G
Hg	0.0	0.0	0.0	
Cl	0.7029(3)	0.6945(3)	0.3486(3)	
S1	0.2146(3)	0.3271(2)	0.1231(2)	
S2	0.3437(3)	-0.0243(3)	0.2147(2)	
S3	-0.1518(3)	0.1841(2)	0.3012(2)	
O1	0.0299(8)	0.2451(5)	0.0709(6)	
O2	0.2391(8)	0.0613(6)	0.1647(6)	
O3	-0.2016(8)	0.0540(6)	0.1651(6)	
O4	0.683(6)	0.661(3)	0.448(3)	0.74(7)
O5	0.747(8)	0.833(3)	0.441(5)	0.61(8)
O6	0.567(5)	0.690(9)	0.386(9)	0.53(10)
O7	0.848(5)	0.628(5)	0.321(5)	0.73(10)
O8	0.640(5)	0.573(3)	0.233(3)	0.74(6)
O9	0.834(6)	0.750(7)	0.312(5)	0.63(10)
O10	0.591(8)	0.758(6)	0.306(6)	0.57(8)
C1	0.2116(7)	0.4286(12)	0.3026(11)	
C2	0.2056(23)	0.4656(16)	0.0841(16)	
C3	0.4053(19)	-0.1725(17)	0.0698(16)	
C4	0.1796(21)	-0.1149(16)	0.2602(15)	
C5	-0.2192(18)	0.1400(15)	0.4258(12)	
C6	-0.3233(24)	0.3007(16)	0.3195(14)	
H1	0.219(12)	0.364(10)	0.345(9)	
H2	0.289(13)	0.496(10)	0.322(10)	
H3	0.108(13)	0.484(10)	0.313(10)	
H4	0.197(15)	0.431(11)	0.011(11)	
H5	0.104(13)	0.527(10)	0.144(10)	
H6	0.318(13)	0.522(10)	0.131(10)	
H7	0.298(13)	-0.221(10)	-0.002(10)	
H8	0.477(15)	-0.150(13)	0.060(13)	
H9	0.488(12)	-0.204(9)	0.144(10)	
H10	0.169(12)	-0.030(10)	0.359(10)	
H11	0.095(13)	-0.166(10)	0.184(10)	
H12	0.266(12)	-0.167(10)	0.288(10)	
H13	-0.130(14)	0.098(10)	0.440(10)	
H14	-0.140(12)	0.233(10)	0.526(10)	
H15	-0.311(14)	0.119(11)	0.414(11)	
H16	-0.311(12)	0.368(10)	0.410(10)	
H17	-0.472(12)	0.235(10)	0.264(10)	
H18	-0.284(14)	0.320(11)	0.277(11)	

Table 2. Final anisotropic thermal parameters (\AA^2) with estimated standard deviations in parentheses. The expression used is $\exp[-1/4(B_{11}h^2a^{*2} + \dots + 2B_{12}hka^*b^* + \dots)]$.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	4.00(2)	2.79(2)	2.51(2)	0.21(1)	0.31(1)	0.92(1)
Cl	4.51(12)	5.33(12)	6.11(13)	-0.20(10)	0.30(10)	3.21(11)
S1	3.74(9)	3.54(9)	4.41(10)	0.19(7)	0.37(7)	1.69(8)
S2	4.89(10)	5.11(11)	4.16(10)	0.60(8)	-0.53(8)	2.26(9)
S3	4.97(10)	4.87(11)	3.09(9)	-0.63(8)	0.63(8)	1.22(8)
O1	4.7(3)	2.7(2)	3.9(3)	-0.15(19)	-0.51(21)	0.60(20)
O2	5.7(3)	4.0(3)	4.5(3)	-0.02(23)	-1.68(24)	1.90(24)
O3	5.2(3)	4.6(3)	3.5(3)	-0.89(22)	1.13(22)	0.97(23)
O4	30.2(42)	19.6(24)	12.5(17)	3.2(24)	2.8(20)	13.1(17)
O5	28.4(50)	7.1(14)	18.1(37)	-4.3(18)	3.6(33)	-0.9(15)
O6	7.4(23)	37.2(94)	32.4(90)	-3.5(28)	11.6(34)	-4.8(60)
O7	12.7(23)	17.6(32)	39.4(61)	7.8(21)	9.8(29)	14.6(35)
O8	20.5(30)	15.5(22)	13.2(19)	-7.1(18)	-4.2(16)	7.2(16)
O9	13.2(27)	20.8(57)	23.7(45)	-6.8(28)	4.0(21)	11.1(39)
O10	25.2(57)	24.2(53)	28.0(54)	7.6(39)	-6.3(40)	19.8(47)
C1	6.2(6)	4.2(5)	4.8(5)	-1.2(4)	0.0(4)	1.2(4)
C2	8.8(8)	6.4(7)	7.4(7)	-2.1(6)	-1.2(7)	4.3(7)
C3	6.0(7)	8.2(8)	6.1(6)	1.8(6)	1.4(6)	2.9(6)
C4	8.7(8)	7.9(7)	5.9(7)	1.5(6)	1.7(6)	4.4(6)
C5	5.7(5)	8.7(8)	4.9(5)	0.7(6)	0.9(5)	4.2(6)
C6	11.0(10)	6.5(7)	4.9(6)	1.6(7)	1.4(6)	2.7(5)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure is composed of discrete $\text{Hg}(\text{DMSO})_6^{2+}$ cations and ClO_4^- anions. Stereoscopic views of the molecular geometry of these ions are given in Figs. 1 and 2, and a unit cell view is

shown in Fig. 3. Some intramolecular distances and angles are given in Table 3.

The $\text{Hg}(\text{DMSO})_6^{2+}$ complex. Each Hg atom coordinates six DMSO molecules through the oxygen atoms. The resulting coordination polyhedron around the mercury(II) ion is a slightly distorted octahedron with an average Hg-O bond length

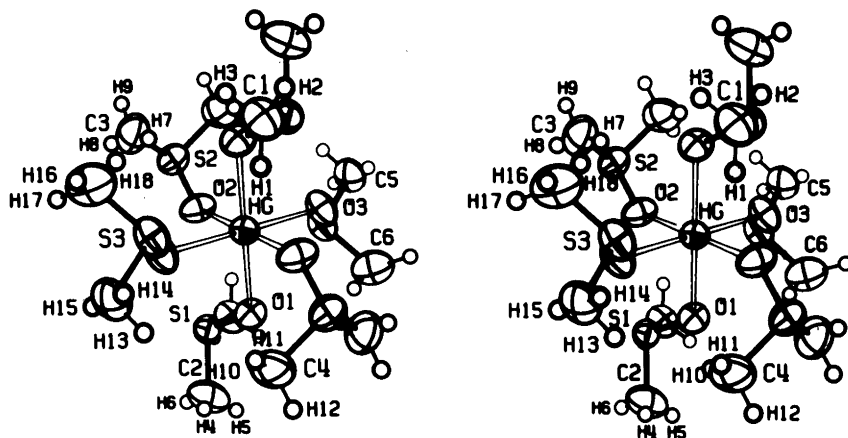


Fig. 1. A stereoscopic view of the centrosymmetrical $\text{Hg}(\text{DMSO})_6^{2+}$ cation. All non-H atoms are represented by 50% probability thermal ellipsoids. The H atoms have for clarity been given a B -value of 1\AA^2 in the figure.

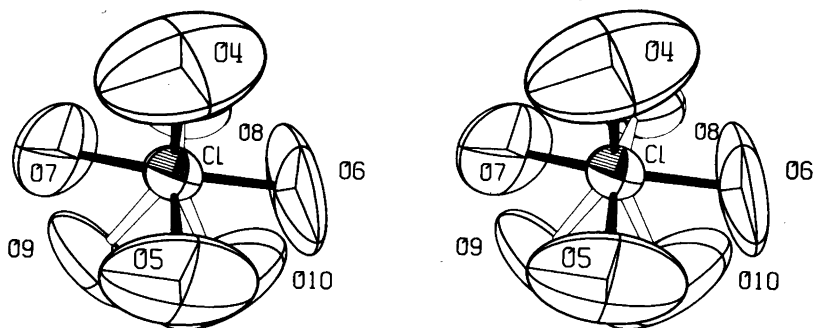


Fig. 2. A stereoscopic view of the disordered perchlorate ion. The thermal ellipsoids enclose 30% probability. The alternative oxygen positions are those with unfilled bonds.

of 2.34 Å. The sulfur atoms also form a somewhat irregular octahedron around mercury, with an average Hg–S distance of 3.41 Å.

The average S–O and S–C distances within the pyramidal DMSO molecules are 1.52 and 1.77 Å, respectively, which are in good agreement with distances found for other compounds with oxygen-coordinated DMSO ligands.^{13,14}

The C–H distances lie in the range 0.6 to 1.3 Å, the average value being 0.95 Å, close to values found by other X-ray diffraction determinations.^{15,12}

The ClO_4^- ion. The seven oxygen positions O4 to O10 (Table 1) all belong to the perchlorate group (Fig. 2). The refined Cl–O distances are between 1.29 and 1.38 Å, except for Cl–O6 which is 1.12(5) Å. However, the corresponding distances for the oxygen peaks found from the Fourier difference map were all between 1.32 and 1.45 Å (Cl–O6 1.39 Å). The expected average Cl–O bond length should be 1.42–1.43 Å.¹⁶ The large deviations from expected values found for bond lengths and angles in the least-squares refinements are probably caused by the inadequate way of representing the librational

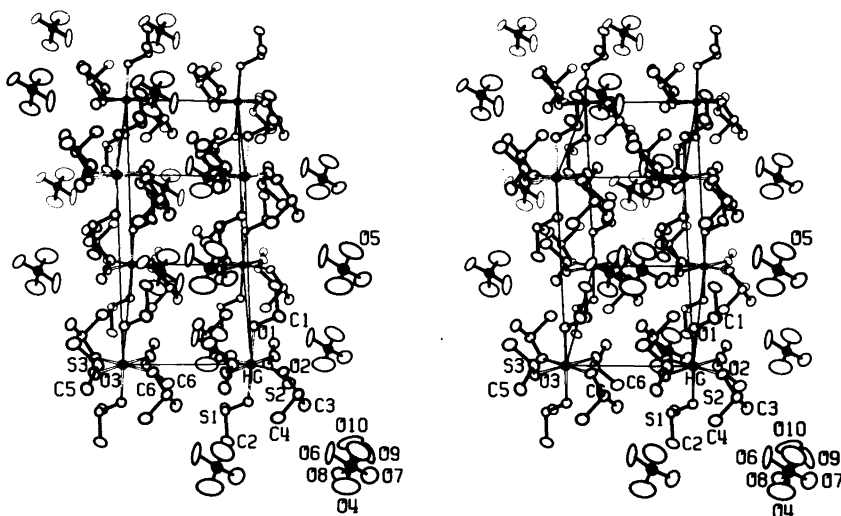


Fig. 3. A stereoscopic view along c^* of the triclinic unit cell. The a axis is horizontal in the figure. The thermal ellipsoids are drawn to enclose 30% probability. For clarity, the H atoms are omitted and only four of the seven oxygen positions are shown but for one of the disordered perchlorate groups.

Table 3. Some intramolecular atomic distances (Å) and angles (degrees) of interest. Estimated standard deviations are given in parentheses.

Hg—O1	2.376(6)	Cl—O4	1.34(3)
Hg—O2	2.320(6)	Cl—O5	1.37(4)
Hg—O3	2.317(6)	Cl—O6	1.12(5)
		Cl—O7	1.29(4)
Hg—S1	3.404(2)	Cl—O8	1.38(3)
Hg—S2	3.520(2)	Cl—O9	1.31(6)
Hg—S3	3.302(2)	Cl—O10	1.31(7)
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Hg—C1	4.40(1)	O1—Hg—O2	82.4(2)
Hg—C2	4.82(2)	O1—Hg—O3	86.3(2)
Hg—C3	3.85(2)	O2—Hg—O3	89.6(2)
Hg—C4	3.88(2)	S1—Hg—S2	81.41(6)
Hg—C5	4.69(1)	S1—Hg—S3	75.71(6)
Hg—C6	4.45(2)	S2—Hg—S3	78.33(6)
		Hg—O1—S1	120.1(3)
S1—O1	1.522(6)	Hg—O2—S2	132.2(4)
S2—O2	1.513(7)	Hg—O3—S3	117.3(4)
S3—O3	1.518(7)	O1—S1—C1	106.2(5)
		O1—S1—C2	105.1(6)
S1—C1	1.78(1)	C1—S1—C2	97.9(7)
S1—C2	1.76(2)	O2—S2—C3	106.8(6)
S2—C3	1.76(2)	O2—S2—C4	106.0(6)
S2—C4	1.77(2)	C3—S2—C4	96.8(8)
S3—C5	1.77(2)	O3—S3—C5	106.2(6)
S3—C6	1.79(2)	O3—S3—C6	105.6(6)
		C5—S3—C6	96.7(7)

movements of the perchlorate oxygens by the ellipsoidal approximation. The thermal ellipsoids obtained for these oxygen atoms are also very large (Fig. 2). The distances were not corrected for thermal motion.

However, the residual electron density in the vicinity of the ClO_4^- group is between 0.5 and $-0.4 \text{ e } \text{Å}^{-3}$ from a Fourier difference map. The sum of the refined occupancy factors of the seven oxygen positions is 4.55(23). This would mean that the refined model still accounts for the electron density of the perchlorate group to a fairly good extent.

The closest intermolecular approaches are O10—H9 2.16(12) and O5—H10 2.28(12) Å. In the absence of hydrogen bonds these intermolecular interactions will hardly cause any serious restraints on the librational movements of the perchlorate group.

Disordered perchlorate ions are also found in the structures of $\text{Ag}(\text{DMSO})_2\text{ClO}_4$ ¹⁴ and $[\text{Cd}(\text{DMSO})_6]_2(\text{ClO}_4)_2$.¹⁷ A survey of different types of disordered perchlorate ions is given in Ref. 14.

Acknowledgements. The authors wish to thank Dr. Georg Johansson and Prof. Sten Ahrland for valuable advice and interest in this work. The work has been financially supported by the Swedish Natural Science Research Council. A generous donation from the foundation Knut och Alice Wallenbergs Stiftelse to the departments of chemistry at the Royal Institute of Technology has made it possible to obtain the computer-controlled four-circle diffractometer with a complete program system for structure determinations.

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Received August 26, 1977.