

# Crystal and Molecular Structure of $\text{Hg}(\text{ClO}_4)_2 \cdot 4(\text{CH}_3)_2\text{SO}$ , a Dimeric Addition Compound

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The crystal structure of the compound  $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$  has been determined from three-dimensional X-ray diffraction data collected at room temperature on an automatic Syntex  $P2_1$  four-circle diffractometer. The unit cell is monoclinic, space group  $P2_1/n$ , with  $a = 12.490(6)$ ,  $b = 22.88(1)$ ,  $c = 17.27(1)$  Å,  $\beta = 105.67(4)^\circ$  and  $Z = 8$ . The structure, refined to a conventional  $R$ -value of 0.087 for 1812 independent reflections, is built up of dimeric  $\text{Hg}_2(\text{DMSO})_8^{4+}$  entities and perchlorate ions. Two dimethyl sulfoxide (DMSO) oxygen atoms form a double bridge between the mercury atoms, with the distances 2.54(4) and 2.51(3) Å to Hg1, and 2.45(4) and 2.37(3) Å to Hg2. The Hg1 atom coordinates four more DMSO oxygen atoms at 2.17(7), 2.25(5), 2.29(4), and 2.40(6) Å, completing a distorted octahedron. The Hg2 atom is bonded to only two more DMSO oxygen atoms at 2.13(4) and 2.16(4) Å in a highly distorted tetrahedral configuration. Two long perchlorate oxygen contacts to Hg2 at 2.78(5) and 3.04(9) Å complete a very distorted octahedral arrangement.

All four crystallographically independent perchlorate groups in the structure perform large librational movements.

A series of X-ray diffraction and spectroscopic investigations of the structures of the hexasolvated Hg(II) and Cd(II) ions, coordinating water and DMSO molecules, have been performed.<sup>1–4</sup> Discrete octahedral complexes, with six oxygen atoms bonded to the metal atoms both in solution and in solid perchlorates, were found. In order to investigate how this regular octahedral coordination, for mercury rarely found, had changed in the novel tetrasolvate,  $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$ ,<sup>1</sup> its structure was determined.

## EXPERIMENTAL

**Preparations.** The crystals were prepared and analyzed as described previously.<sup>2</sup> The recrystallization from methanol solutions was performed at about 5 °C. At room temperature another phase was formed, large colourless crystals with almost quadratic faces. They were found to be monoclinic with  $a = 11.18(1)$ ,  $b = 10.83(1)$ ,  $c = 22.90(1)$  Å, and  $\beta = 91.18(7)^\circ$ . No analyses of this compound were performed.

From large colourless twinned crystals of the  $\text{Hg}(\text{ClO}_4)_2 \cdot 4\text{DMSO}$  phase, obtained at about 5 °C, single crystals of irregular shape were cut out and sealed into capillaries.

**X-Ray data collection and reduction.** The lattice parameters were determined and refined for 25 centred reflections by the standard method on the automatic Syntex four-circle diffractometer of type  $P2_1$ .<sup>2</sup> A monoclinic unit cell with  $a = 12.490(6)$ ,  $b = 22.88(1)$ ,  $c = 17.27(1)$  Å,  $\beta = 105.67(4)^\circ$ ,  $D_m = 1.96(2)$  and  $D_x = 1.99$  g cm<sup>-3</sup> for  $Z = 8$  was found. Two separate data sets on different crystals, both with maximum dimensions less than 0.2 mm, were collected at room temperature. Graphite-monochromatized MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å) was used.

For the first set, all 3232 possible independent reflections below 35° in  $2\theta$  were measured by the  $\omega$  scan technique using variable scan speeds, from 1°/min upwards.

For the second set, only 2251 of the independent reflections for  $2\theta < 35^\circ$  (but all below 30°) were collected. The  $\theta - 2\theta$  scan mode was used with 2°/min as the lowest scan speed.

The  $h0l$  reflections for  $h+l = 2n+1$  and  $0k0$  for  $k = 2n+1$  were systematically absent. This is characteristic of the space group  $P2_1/n$ , non-standard setting of No. 14. The general setting is four-fold:  $\pm(x, y, z; 1/2 - x, 1/2 + y, 1/2 - z)$ . Of the 3027 possible non-extinct reflections for  $2\theta < 35^\circ$  1812 in the first

data set and 1229 in the second had intensities larger than  $1.96 \sigma(I)$ , and were considered observed. Nine strong reflections, apparently suffering from effects of extinction or double diffraction, were removed from the first set of data.

Check reflections were measured regularly every 100th reflection, four for the first data set and three others for the second set. All their intensities decreased almost linearly at nearly the same relative rate as a function of the exposure time. The total decrease was 32% for the first and 25% for the second set.

A linear correction therefore seemed to be justified and was applied on intensities and sigma-values of the first data set.

The absorption coefficient  $\mu(\text{MoK}\alpha)$  is  $72.2 \text{ cm}^{-1}$ . A semi-empirical absorption correction method<sup>5</sup> was applied on both data sets in the way described previously.<sup>2</sup> The largest measured intensity ratio was 1:0.51 for the first and 1:0.59 for the second data set.

The data reduction was performed as described previously. The same computer programs were used.<sup>2</sup>

## STRUCTURE DETERMINATION AND REFINEMENTS

*First data set.* A three-dimensional Patterson function was calculated. The eight Hg atoms of the unit cell were assumed to occupy two of the general four-fold positions. Due to overlapping vectors, several different choices of parameter sets of these positions were possible. One of them gave markedly lower  $R$  values than the others. Isotropic least-squares refinements gave the conventional  $R$  value 0.29 and the weighted  $R_w = 0.34$ , defined as in the

preceding paper.<sup>4</sup> Subsequent difference Fourier syntheses followed by full-matrix least-squares refinements revealed possible positions of all 54 non-H atoms of the asymmetric unit. Refinements with anisotropic temperature factors for the Hg, S and Cl atoms gave  $R = 0.087$  ( $R_w = 0.099$ ). The corresponding parameter values are given in Tables 1 and 2. A subsequent difference Fourier synthesis showed a seemingly random background variation not exceeding  $1.2 \text{ e } \text{Å}^{-3}$ .

When these final refinements were repeated for data without the linear intensity correction,  $R = 0.10$  ( $R_w = 0.13$ ) was obtained. The corresponding difference Fourier map had peaks up to  $1.8 \text{ e } \text{Å}^{-3}$  around the Hg atoms.

*Second data set.* Refinements with the final model gave  $R = 0.089$  ( $R_w = 0.091$ ). No significant differences between any of the parameter values of the two data sets were obtained, but the estimated standard deviations were on the average 50% larger in the second set. The background variation in the final difference Fourier map did not exceed  $1.1 \text{ e } \text{Å}^{-3}$ .

*Refinement conditions.* The least-squares refinements were based on the minimization of  $\sum w \|F_o\| - |F_c|^2$  for all reflections with  $|F_o| > 3.92\sigma(F_o)$  using the same weighting function,  $w$ , and scattering factors as previously.<sup>2</sup> A total of 287 parameters was varied in the final refinements. The largest shift of the parameter values in the last refinement cycle was  $0.1\sigma$  for the first data set and  $1.0\sigma$  for the second.

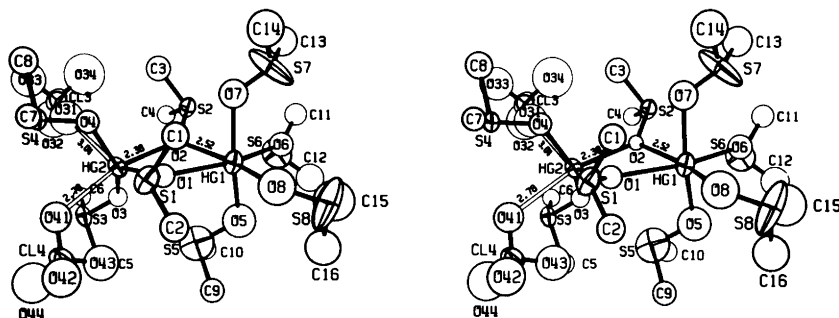


Fig. 1. A stereoscopic view of the dimeric  $\text{Hg}_2(\text{DMSO})_8^{2+}$  complex ion (filled bonds). The long interactions from Hg2 to the perchlorate oxygen atoms O31 and O41 are shown by unfilled bonds. The distances are given in Å. The thermal ellipsoids are drawn at the 30% probability level.

Table 1. Final fractional atomic positional parameters and isotropic temperature factor coefficients in Å<sup>2</sup>. Estimated standard deviations are given in parentheses.

Atom	x	y	z	B
Hg1	0.2494(2)	0.1377(1)	0.2572(1)	
Hg2	-0.0608(2)	0.1330(1)	0.2646(1)	
S1	0.1238(14)	0.2256(6)	0.3882(9)	
S2	0.0363(13)	0.1199(6)	0.0894(8)	
S3	-0.1994(13)	0.0193(6)	0.2847(9)	
S4	-0.2124(14)	0.2465(7)	0.2728(9)	
S5	0.1772(26)	0.0301(10)	0.3543(17)	
S6	0.3003(24)	0.0342(10)	0.1245(16)	
S7	0.3050(31)	0.2419(13)	0.1431(16)	
S8	0.5275(20)	0.1671(13)	0.3774(21)	
Cl1	0.5330(15)	0.3659(9)	0.3561(10)	
Cl2	-0.0256(24)	0.3949(11)	0.1459(11)	
Cl3	0.6317(19)	0.1294(10)	0.0738(14)	
Cl4	-0.0807(17)	0.1259(8)	0.4719(9)	
O1	0.1173(30)	0.1791(17)	0.3320(20)	6.7(9)
O2	0.0538(24)	0.1150(11)	0.1777(16)	3.5(7)
O3	-0.1054(31)	0.0414(15)	0.2526(19)	6.6(10)
O4	-0.1098(32)	0.2224(15)	0.2499(19)	6.7(9)
O5	0.2816(55)	0.0541(29)	0.3179(36)	16.7(21)
O6	0.3318(34)	0.0922(21)	0.1630(22)	8.9(11)
O7	0.2252(41)	0.2169(21)	0.1768(26)	11.0(14)
O8	0.4041(55)	0.1801(26)	0.3542(32)	15.5(19)
O11	0.426(6)	0.360(3)	0.355(4)	17(2)
O12	0.597(6)	0.327(3)	0.403(4)	18(2)
O13	0.547(4)	0.365(2)	0.282(3)	13(2)
O14	0.562(7)	0.418(4)	0.401(5)	23(3)
O21	0.044(11)	0.417(7)	0.126(8)	34(6)
O22	-0.084(11)	0.441(7)	0.132(8)	38(8)
O23	-0.026(7)	0.385(3)	0.222(5)	22(3)
O24	-0.085(8)	0.357(4)	0.098(6)	25(4)
O31	0.715(7)	0.139(3)	0.141(5)	20(3)
O32	0.583(9)	0.073(5)	0.063(6)	29(4)
O33	0.567(7)	0.172(4)	0.068(4)	20(3)
O34	0.677(10)	0.135(5)	0.004(7)	33(5)
O41	-0.129(4)	0.152(2)	0.403(3)	11.9(15)
O42	-0.020(5)	0.160(3)	0.535(4)	16(2)
O43	-0.006(6)	0.090(3)	0.453(3)	16(2)
O44	-0.155(7)	0.095(4)	0.502(4)	21(3)
C1	0.188(5)	0.280(3)	0.351(3)	7.2(16)
C2	0.230(5)	0.211(3)	0.469(3)	7.7(16)
C3	-0.042(6)	0.187(3)	0.061(4)	10.0(20)
C4	-0.068(5)	0.066(2)	0.046(3)	7.2(16)
C5	-0.130(5)	-0.040(3)	0.357(3)	8.3(17)
C6	-0.280(5)	-0.016(2)	0.200(3)	6.7(15)
C7	-0.149(4)	0.308(2)	0.340(3)	5.8(14)
C8	-0.280(6)	0.295(3)	0.187(4)	9.4(19)
C9	0.267(5)	0.019(2)	0.452(3)	7.5(16)
C10	0.171(5)	-0.034(3)	0.317(3)	7.2(16)
C11	0.315(5)	0.042(3)	0.018(4)	9.3(18)
C12	0.407(8)	-0.002(4)	0.154(5)	13.8(28)
C13	0.297(7)	0.229(3)	0.054(5)	11.7(23)
C14	0.296(8)	0.312(4)	0.146(5)	14.9(29)
C15	0.526(10)	0.114(6)	0.321(8)	22.7(49)
C16	0.530(7)	0.095(5)	0.408(5)	14.5(27)

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

Atom	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Hg1	4.7(1)	6.7(2)	6.5(2)	0.47(16)	1.40(11)	-1.19(14)
Hg2	6.9(2)	2.7(1)	6.8(2)	-0.76(12)	4.02(12)	-0.65(10)
S1	6.4(11)	4.7(9)	6.8(9)	0.7(8)	1.0(9)	-2.6(7)
S2	5.1(9)	7.0(11)	5.1(8)	0.9(8)	1.1(7)	-0.9(7)
S3	6.0(10)	2.6(7)	9.2(10)	-1.1(7)	4.6(9)	-0.4(7)
S4	7.5(12)	6.9(10)	7.0(10)	3.2(9)	4.6(9)	1.8(7)
S5	19.0(26)	8.3(15)	17.3(22)	-0.7(16)	4.4(20)	-4.0(14)
S6	17.3(23)	7.0(13)	17.0(20)	-1.1(15)	7.5(18)	-3.0(13)
S7	31.7(37)	14.9(23)	15.1(20)	-8.5(23)	18.0(24)	-1.7(16)
S8	6.3(15)	15.1(22)	28.7(33)	4.5(14)	-1.0(17)	-7.3(23)
Cl1	6.8(12)	8.4(11)	6.4(9)	1.5(11)	1.9(8)	-0.2(9)
Cl2	12.6(18)	11.2(16)	6.7(11)	-4.0(15)	2.2(12)	0.9(10)
Cl3	8.7(14)	7.2(12)	12.7(15)	2.1(12)	3.3(13)	1.0(11)
Cl4	9.9(12)	6.9(10)	5.3(9)	0.7(11)	3.1(9)	0.0(8)

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure is composed of  $\text{Hg}_2\text{(DMSO)}_8^{4+}$  entities, di- $\mu$ -dimethyl sulfoxide- $O$ -[[bis(dimethyl sulfoxide)mercury(II)] [tetra(dimethyl sulfoxide)mercury(II)]] ions, and perchlorate ions. A stereoscopic view of the molecular geometry of the dimeric complex is given in Fig. 1. A unit cell view is shown in Fig. 2. Some interatomic distances and angles are given in Table 3.

*The dimeric complex.* The two unique Hg atoms within the asymmetric unit are joined by a double DMSO oxygen bridge to discrete dimeric entities. Four more DMSO oxygen atoms complete a distorted octahedral coordination around the Hg1 atom with a largest deviation of  $19^\circ$  from regular octahedral angles. The Hg2 atom is bonded to only two more DMSO oxygen atoms in a highly distorted tetrahedral coordination with the angles at Hg2 between 76 and  $149^\circ$ . There are, however, two long

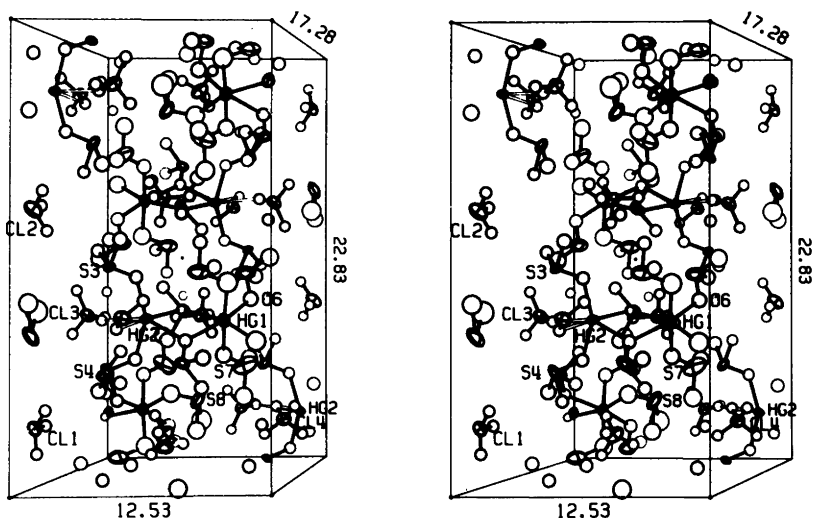


Fig. 2. A stereoscopic unit cell view. The lengths in  $\text{\AA}$  of the unit cell edges are plotted. The thermal ellipsoids enclose 20% probability. The perchlorate oxygen atoms have for clarity been given the  $B$  value  $5 \text{\AA}^2$ .

Table 3. Selected interatomic distances (Å) and angles (degrees). Estimated standard deviations are given in parentheses.

Hg1—O1	2.54(4)	O1—Hg1—O2	72(1)
Hg1—O2	2.51(3)	O1—Hg1—O5	98(2)
Hg1—O5	2.17(7)	O1—Hg1—O6	166(1)
Hg1—O6	2.39(4)	O1—Hg1—O7	91(2)
Hg1—O7	2.25(5)	O1—Hg1—O8	90(2)
Hg1—O8	2.40(6)		
Hg2—O1	2.45(4)	O1—Hg2—O2	76(1)
Hg2—O2	2.37(3)	O1—Hg2—O3	130(1)
Hg2—O3	2.16(4)	O1—Hg2—O4	81(1)
Hg2—O4	2.13(4)	O1—Hg2—O31	149(2)
Hg2—O31	3.04(9)	O1—Hg2—O41	89(1)
Hg2—O41	2.78(5)	O31—Hg2—O41	99(2)
Hg1—O1—Hg2	103(1)	Hg2—O4—S4	123(2)
Hg1—O1—S1	134(2)	Hg1—O5—S5	114(4)
Hg2—O1—S1	121(2)	Hg1—O6—S6	126(3)
Hg1—O2—Hg2	106(1)	Hg1—O7—S7	126(3)
Hg1—O2—S2	113(2)	Hg1—O8—S8	133(4)
Hg2—O2—S2	134(2)	Hg2—O31—Cl3	161(5)
Hg2—O3—S3	120(2)	Hg2—O41—Cl4	123(3)

interactions between Hg2 and the perchlorate oxygen atoms O41 and O31. The distances Hg2—O41 and Hg2—O31 are found to be 2.78(5) and 3.04(9) Å, respectively, from the first set of data, and 2.62(7) and 2.92(9) Å from the second. At least the O41 atom seems to be within the effective coordination sphere of Hg2. The sum of the van der Waals radii for Hg and O is  $1.5 + 1.4 = 2.9$  Å.<sup>6</sup> These contacts complete a very distorted octahedral oxygen coordination around Hg2. The largest angular deviation from a regular symmetry is 40°.

Dimeric complexes with almost symmetrical double bridges, formed by oxygen donor atoms, have also been found in the crystal structures of the adducts  $3\text{HgCl}_2 \cdot \text{SDMSO}$  and  $[(\text{HgCl}_2 \cdot (\text{C}_6\text{H}_5)_3\text{AsO})_2]$ .<sup>7,8</sup> The bridging Hg—O bonds for a specific Hg atom are found to be longer in all three compounds than the non-bridging where the oxygen atom forms only one donor-acceptor bond, as was first observed by Bränden.<sup>8</sup>

The Hg—Hg distance is significantly shorter in the present study, 3.913(4) Å, than in  $3\text{HgCl}_2 \cdot 2\text{DMSO}$ , 4.01<sub>6</sub> Å.<sup>7</sup> This is due to the lower coordination number for Hg2 than for Hg1, which causes a shortening of the Hg2—O bond lengths.

In the DMSO molecules the average distances found, S—O 1.51(9) Å and S—C 1.72(13) Å, do not differ significantly from the expected values, 1.52 and 1.77 Å, respectively. The sulfur atoms S7 and

S8 are found to be extremely anisotropic (Fig. 1) from refinements for both data sets. Approximate anisotropic thermal parameters obtained for the DMSO oxygen atoms show similar elongated thermal ellipsoids of the O5, O7 and O8 atoms, the two latter parallel to the ellipsoids of the corresponding sulfur atoms. This may be an effect of a slight disorder of these DMSO ligands or of the decomposition of the crystal during the data collection.

*The perchlorate ions.* There are four crystallographically different  $\text{ClO}_4^-$  ions in the structure.

Examination of Fourier maps showed that all perchlorate groups performed large librational movements. Distinct alternative positions were not found, however. All perchlorate oxygen atoms have large temperature factors (Table 1), of which the smallest is found for O41 which is within the coordination sphere of the Hg2 atom, as discussed above. Meaningful refinements of anisotropic temperature factors could not be performed, since the standard deviations became too large compared with the parameter values.

The apparent shortening of the average Cl—O bond length, 1.33(8) Å, from the expected value 1.42<sub>6</sub> Å,<sup>9</sup> is probably an effect of this freedom of movement in the absence of hydrogen bonds, as discussed previously.<sup>2</sup> The bond angles obtained did not differ significantly from tetrahedral values.

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