Crystal and Molecular Structure of Hexakis(dimethyl sulfoxide)cadmium(II) Perchlorate, [Cd((CH₃)₂SO)₆](ClO₄)₂

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The title compound crystallizes in the orthorhombic space group $Fd2d$ with $a=12.54(1)$, $b=20.23(1)$, $c=25.53(1)$ Å, and $Z=8$. The X-ray data were collected at room temperature by a computer-controlled Syntex $P2_1$ four-circle diffractometer using MoKα radiation. The structure determination was performed on a data-set with 1244 independent reflections and refined by least-squares methods to a conventional R value of 0.039.

The structure is built up of discrete $[Cd(DMSO)_6]^{2+}$ and perchlorate ions. Six DMSO oxygen atoms are coordinated to each Cd atom, forming an almost regular octahedron. The average Cd−O bond length is 2.27 Å. Two symmetry-related DMSO ligands and one of the two crystallographically different perchlorate groups are disordered between two alternative positions. Both perchlorate groups perform large librational movements.

As part of an investigation into the structures of solvated Cd(II) and Hg(II) ions in solutions and in crystals,[1−4] the crystal structure of the compound $[Cd(DMSO)_6](ClO_4)_2$ was determined.

EXPERIMENTAL

Preparation. The compound $Cd(ClO_4)_2.6DMSO$, prepared as described previously,[5] was recrystallized from DMSO. On slow evaporation, colourless prismatic crystals were formed from a saturated 0.70 M solution at room temperature. They were filtered off and washed with cold acetone. Methods and results of analyses are given elsewhere.[1,5]

X-Ray data collection and reduction. The lattice parameters were determined and refined using 15 centred reflections, by the standard method on the computer-controlled Syntex $P2_1$ diffractometer.[2] The unit cell was found to be orthorhombic with

$a=12.54(1)$, $b=20.23(1)$, $c=25.53(1)$ Å, $D_m=1.58(1)$, and $D_x=1.60$ for $Z=8$. Graphite-monochromatized MoKα radiation ($\lambda=0.71069$ Å) was used.

Two separate data sets were collected using two different crystals enclosed in capillaries. Both data collections were performed in three parts, 0−20, 20−40 and 40−50° in 2θ for one octant (*hkl*). Different scan speeds were used, the lowest speed being 1° min^{-1}. After every 50th reflection four check reflections were measured. For the first set their intensity variations were within $\pm 3\sigma(I)$, for the second set within $\pm 3\%$ in the first two parts ($2\theta<40°$) but a decrease of 10% occurred in the last part.

The first data set was collected on a prismatic crystal of maximum dimensions about 0.15 mm. The ω scan method was used. The second data set was measured using the $\theta-2\theta$ scan technique on a crystal of maximum dimensions 0.3 mm.

All reflections within the first part ($2\theta<20°$) were recorded for both data sets. Conditions limiting possible reflections were found to be: *hkl*: $h+k=2n$, $k+l=2n$, *hk0*: $h+k=4n$ ($h,k=2n$), *0kl*: $k+l=4n$ ($k,l=2n$). This is characteristic of the non-centro-symmetric space group $Fd2d$, non-standard setting of No. 43. The general position is 16-fold with coordinates of equivalent positions (x,y,z), $(\bar{x},y,\bar{z})$, $(1/4-x, 1/4+y, 1/4+z)$ and $(1/4+x, 1/4+y, 1/4-z)$ with translations $(0,\frac{1}{2},\frac{1}{2})$, $(\frac{1}{2},0,\frac{1}{2})$, $(\frac{1}{2},\frac{1}{2},0)$. There were in both data sets about 10 reflections with intensities larger than $3\sigma(I)$ violating the condition $h+k=2n$. Since they were not the same in the two sets and most of them were not centred in the scan range, they were considered spurious. For $2\theta<50°$, 1467 independent reflections are possible. Of these, 1244 in the first and 1218 in the second data set had intensities larger than 1.96 $\sigma(I)$ and were considered observed.

The data were reduced and converted to scaled $|F_o|$ values as described previously using the same computer programs.[2]

STRUCTURE DETERMINATION AND REFINEMENTS

The first data set. The structure was solved using this data set which was considered to be the better. From a three-dimensional Patterson synthesis, the 8 Cd and the 16 Cl atoms of the unit cell were found to occupy the special positions 8(*a*) on two-fold rotation axes. The origin was fixed by giving the Cd atoms the *y* coordinate 0. Possible starting parameters for the Cl and two of the three expected 16-fold S positions could then be obtained. Full-matrix least-squares refinements with these atoms isotropic gave $R = 0.20$ ($R_w = 0.27$), where the conventional R-value is $R = \Sigma \|F_o| - |F_c\| / \Sigma |F_o|$ and the weighted $R_w = (\Sigma w \|F_o| - |F_c\|^2 / \Sigma w |F_o|^2)^{\frac{1}{2}}$.

A difference Fourier map revealed two peaks with heights 4.5 and 3.0 e Å^{-3} corresponding to two different possible locations S3 and S4, of the third S atom. They were both included and refined. Subsequent Fourier difference peak listings revealed possible positions of all non-H atoms. A refinement with Cd anisotropic varying the occupancy factors of S3 and S4 gave $R = 0.082$ ($R_w = 0.12$). All atoms anisotropic lowered the R value to 0.042 ($R_w = 0.053$).

From geometric considerations of the symmetry of the disordered DMSO ligands, it became evident that the very elongated thermal ellipsoid obtained for their DMSO oxygen atoms was very probably caused by two alternative positions, O3 and O4, about 0.8 Å apart.

A Fourier map showed alternative oxygen positions for one of the two different perchlorate groups. Refinements with only O3 and O4 isotropic, including the occupancy factors of all alternative positions, gave $R = 0.039$ ($R_w = 0.047$). The parameter values obtained are given in Tables 1 and 2.

The largest remaining peak found in a final difference Fourier map was 0.43 eÅ^{-3}. Definite H-atom positions could not be ascertained.

The semi-empirical absorption correction[6] discussed previously[2] was tested on this data set, but did not improve the results ($\mu(MoK\alpha) = 12.6$ cm^{-1}).

The second data set. For comparisons, especially of the parameters of the disordered groups, refinements were also performed with this data set. The final refinements with only O3 and O4 isotropic gave $R = 0.13$ ($R_w = 0.17$). No significant differences between any parameter values of this set and those

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

Atom	x	y	z	G	B/Å^2
Cd	0	0	0		
Cl1	0	0.3380(5)	0		
Cl2	0	0.6839(3)	0		
S1	0.2389(2)	−0.0437(1)	0.0441(1)		
S2	0.1840(3)	0.1091(2)	−0.0385(1)		
S3	0.0769(4)	−0.1263(3)	−0.0847(2)	0.67(1)	
S4	0.1547(7)	−0.0945(4)	−0.0827(3)	0.32(1)	
O1	0.1416(5)	−0.0015(5)	0.0557(3)		
O2	0.0798(8)	0.0751(6)	−0.0522(4)		
O3	0.1046(17)	−0.0641(14)	−0.0517(9)	0.57(6)	7.5(8)
O4	0.0691(17)	−0.0916(11)	−0.0377(8)	0.48(5)	5.6(7)
O5	0.457(3)	−0.111(1)	−0.028(1)	0.77(6)	
O6	0.099(4)	0.327(3)	−0.023(3)	0.57(10)	
O5A	0.436(5)	−0.224(3)	−0.019(3)	0.32(6)	
O6A	−0.020(7)	0.328(3)	0.049(1)	0.35(9)	
O7	0.071(2)	0.654(1)	−0.033(7)		
O8	0.0573(15)	0.7217(10)	0.0340(6)		
C1	0.3421(9)	−0.0082(8)	0.0829(6)		
C2	0.2156(13)	−0.1198(8)	0.0786(6)		
C3	0.1811(14)	0.1846(8)	−0.0754(8)		
C4	0.2831(16)	0.0700(10)	−0.0760(6)		
C5	0.1498(20)	0.1586(8)	0.1036(6)		
C6	0.0638(14)	0.0716(7)	0.1712(6)		

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

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd	3.28(3)	3.55(3)	2.73(3)	0	0.23(4)	0
Cl1	5.5(2)	10.4(4)	6.7(3)	0	1.3(2)	0
Cl2	7.5(3)	7.7(3)	4.8(2)	0	−1.0(2)	0
S1	4.6(1)	5.9(1)	4.0(1)	1.37(11)	−0.62(9)	−0.20(9)
S2	6.2(1)	8.6(2)	4.9(1)	−3.10(15)	0.62(12)	0.02(13)
S3	5.0(3)	6.9(3)	5.7(2)	−0.75(20)	0.50(17)	−2.64(19)
S4	4.5(5)	4.5(4)	4.3(4)	0.05(31)	−0.90(29)	−1.56(27)
O1	5.0(3)	7.0(4)	4.7(3)	2.2(4)	−1.6(3)	−1.4(4)
O2	8.3(6)	11.7(7)	6.5(5)	−6.0(5)	−1.5(4)	5.0(5)
O5	18(3)	14(2)	21(3)	4.8(18)	0.4(20)	4.2(19)
O6	9(2)	21(5)	16(4)	−2.8(21)	5.4(26)	−6.8(32)
O5A	10(4)	10(3)	23(7)	−5.2(25)	−2.5(39)	−1.4(34)
O6A	11(5)	20(5)	5(2)	−2.2(34)	2.6(18)	1.4(19)
O7	27(3)	21(2)	12(1)	8.7(2)	7.6(16)	−5.0(15)
O8	12(1)	15(1)	11(1)	−2.0(10)	−2.5(10)	−3.3(9)
C1	5.1(5)	7.7(8)	7.8(7)	0.3(6)	−2.3(5)	−0.1(7)
C2	9.2(9)	6.6(8)	8.1(8)	0.7(7)	0.6(7)	2.8(7)
C3	8.5(9)	6.2(8)	14(1)	−2.1(7)	3.3(10)	0.8(9)
C4	11(1)	10(1)	6.1(7)	−2.2(9)	1.6(7)	−0.1(7)
C5	18(2)	7.3(9)	6.3(8)	−3.8(10)	0.7(10)	−0.1(7)
C6	10(1)	6.2(7)	6.6(7)	−2.6(7)	−0.6(7)	−0.6(6)

of the first set were found. The temperature factors, however, increased about 20 % on the average.

Refinement conditions and scattering factors. The least-squares refinements minimized the sum $\Sigma w\|F_o|-|F_c\|^2$ for all reflections with $|F_o|>3.92\sigma(F_o)$. The weighting function was $w=\{\sigma^2(F_o)+0.03(F_o)^2\}^{-1}$, which, according to analyses of the error distribution, gave a satisfactory weighting scheme. A total of 193 parameters was varied in the final refinements with a largest parameter shift in the last cycle of refinement less than 0.2σ for the first and 1.0σ for the second data set.

The scattering factors were calculated from analytical expressions for the neutral atoms.[7] Anomalous dispersion corrections were included for Cd, Cl and S.[7]

DESCRIPTION AND DISCUSSIONS OF THE STRUCTURE

General. The crystal structure comprises discrete Cd(DMSO)$_6^{2+}$ cations and ClO$_4^-$ anions. Both the Cd and the Cl atoms are found in layers with $z=n/4$ ($n=0, 1, 2,...$) parallel to the xy-plane. Each Cd(DMSO)$_6^{2+}$ complex ion is almost circularly surrounded by six perchlorate groups within such a layer but is in contact with other Cd-complexes

diagonally. The closest intermolecular approaches between the Cd-complexes are Cd − C5 of 4.36(2) Å and Cd − C6 of 4.75(2) Å, which are shorter than some of the intramolecular Cd − C distances given in Table 3.

A stereoscopic view of the Cd(DMSO)$_6^{2+}$ complex ion is shown in Fig. 1 and a unit cell view in Fig. 2.

The Cd(DMSO)$_6^{2+}$ complex ion. Each Cd atom is coordinated to six DMSO oxygen atoms forming a fairly regular octahedron around Cd (Table 3). The arrangement of the DMSO ligands is more irregular than the rather symmetric distribution found for the Hg(DMSO)$_6^{2+}$ ion, in which also the S atoms surround the Hg atom almost octahedrally.[2] In the Cd complex, several of the ligands are closer together giving it a more flattened shape.

A peculiar feature is the alternative orientations found for two symmetry-related DMSO ligands (Fig. 1), with the apex atoms, S3 and S4, of the pyramidal DMSO groups in opposite directions. The C atom positions, C5 and C6, of the two orientations almost coincide and cannot be resolved, but the O atom positions, O3 and O4, are 0.81(4) Å apart. Since there were no provisions in the programs for coupling the occupancy factors within the al-

Table 3. Some intramolecular atomic distances (Å) and angles (degrees). Estimated standard deviations are given in parentheses. The superscript *i* refers to the equivalent position $-x,y,-z$ relative to x,y,z in Table 1.

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Cd–O1	2.278(7)	O1–Cd–O1^i	178.5(3)
Cd–O2	2.257(11)	O1–Cd–O2	91.9(3)
Cd–O3	2.270(24)	O1–Cd–O2^i	89.2(3)
Cd–O4	2.262(22)	O1–Cd–O3	84.5(7)
Cd–S1	3.323(3)	O1–Cd–O3^i	94.6(7)
Cd–S2	3.343(4)	O1–Cd–O4	87.5(6)
Cd–S3	3.485(5)	O1–Cd–O4^i	91.3(6)
Cd–S4	3.448(8)	O2–Cd–O2^i	95.3(4)
Cd–C1	4.791(12)	O2–Cd–O3	77.6(7)
Cd–C2	4.152(16)	O2–Cd–O3^i	170.3(7)
Cd–C3	4.779(17)	O2–Cd–O4	97.5(6)
Cd–C4	4.290(19)	O2–Cd–O4^i	166.9(6)
Cd–C5	4.565(18)	O3–Cd–O3^i	110.3(9)
Cd–C6	4.678(15)	O3–Cd–O4	20.3(8)
S1–O1	1.519(8)	O3–Cd–O4^i	90.1(8)
S2–O2	1.520(11)	O4–Cd–O4^i	69.9(8)
S3–O3	1.554(26)	Cd–O1–S1	120.9(4)
S4–O4	1.574(22)	Cd–O2–S2	123.4(6)
S1–C1	1.782(13)	Cd–O3–S3	130.5(14)
S1–C2	1.800(16)	Cd–O4–S4	127.1(12)
S2–C3	1.796(18)	O1–S1–C1	104.5(6)
S2–C4	1.759(19)	O1–S1–C2	104.8(6)
S3–C5	1.754(16)	C1–S1–C2	101.0(7)
S3–C6	1.737(17)	O2–S2–C3	104.2(7)
S4–C5	1.769(18)	O2–S2–C4	106.2(8)
S4–C6	1.747(17)	C3–S2–C4	96.4(9)
Cl1–O5	1.37(3)	O3–S3–C5	97.2(11)
Cl1–O6	1.39(5)	O3–S3–C6	105.6(11)
Cl1–O5A	1.58(6)	C5–S3–C6	101.0(9)
Cl1–O6A	1.30(4)	O4–S4–C5	114.1(11)
Cl2–O7	1.36(3)	O4–S4–C6	98.6(10)
Cl2–O8	1.36(2)	C5–S4–C6	100.0(9)
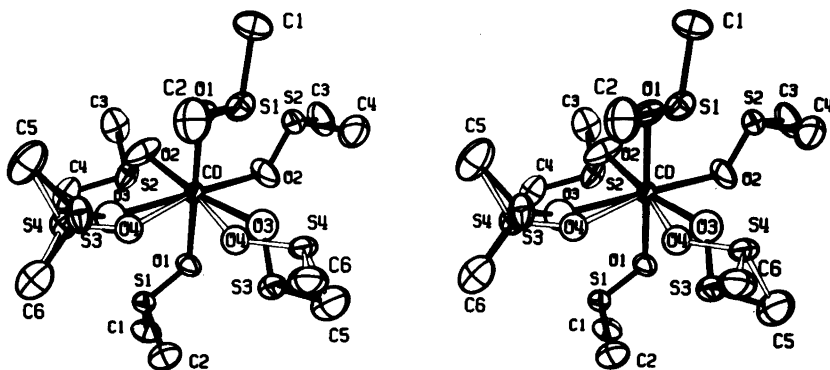
Fig. 1. A stereoscopic view of the $Cd(DMSO)_6^{2+}$ cation. The alternative positions of the two symmetry-related ligands are marked by unfilled bonds. The thermal ellipsoids enclose regions of 30 % probability.
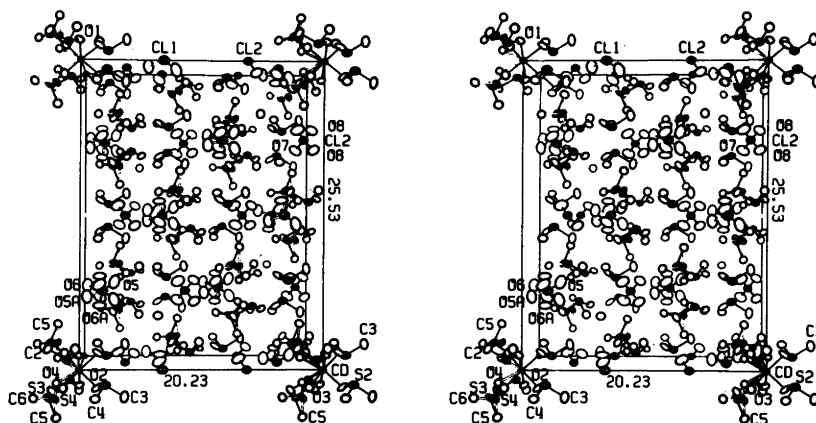
Fig. 2. A stereoscopic view along the *a* edge of the unit cell. The lengths in Å of the *b* and *c* edges are plotted. The alternative positions of the DMSO and $Cl1-O_4$ groups are indicated by unfilled bonds. All atoms are represented by 20 % probability ellipsoids. For the C and O atoms the boundary ellipsoids only are shown.

ternative orientations, they were independently refined. For S3 and O3 their values were found to be 0.67(1) and 0.57(6) for the first and 0.62(4) and 0.41(13) for the second data set, respectively. Corresponding values for S4 and O4 are 0.32(1) and 0.48(5) for the first and 0.29(4) and 0.50(12) for the second data set. The values obtained are not significantly different within each DMSO orientation or between the data sets and show that the DMSO ligands are indeed statistically distributed between the two alternative orientations, approximately in the ratio 2:1. The thermal parameters for the disordered ligands (Tables 1 and 2) are of the same order of magnitude as for the non-disordered ones, which supports the correctness of the occupancy factors obtained (Table 1).

There is sufficient room in the structure to allow for the different orientations. The closest non-bonded interatomic distances to S3 are: C2 3.68(2), O7 3.69(2), O1 3.80(1), and O8 3.74(2) Å. To S4 they are: S1 3.56(1), O2 3.64(1) and C4 3.70(2) Å. However, the rather short distance S1−S4 (van der Waals radius of S 1.75 to 1.85 Å)[8] may explain why the S3 position is preferred.

The disorder observed could also possibly be explained by ordered layers, the stacking of which is disordered in the *z*-direction (*cf.* Fig. 2). The structure would then be of the order-disorder (OD) type, which would give streaks within additional layer lines in the intensity data. However, neither by Weissenberg films and oscillation photos on the

diffractometer, nor by the statistical distribution of errors in F_c caused by removal of one of the disordered DMSO positions, could any indications of an OD-structure be found.

The average values of the well-defined S − O and S − C bond distances within the non-disordered DMSO ligands are 1.52 and 1.77 Å, respectively, in good agreement with previously reported results.[2,9,10] The corresponding values for the disordered groups are not significantly different (Table 3).

None of the Cd − O bond lengths differs significantly from their average value, 2.27 Å, but the thermal ellipsoids of the O2 and S2 atoms of the DMSO ligands are elongated (Fig. 1). This is probably due to a slight disorder, corresponding to the alternative O3 or O4 positions opposite O2, and causes a slight apparent shortening of the calculated Cd − O2 bond length. Only the well-defined Cd − O1 bond distance, 2.276(7) Å, seems to be unaffected by the disorder. This value is also close to the mean Cd − O bond length, 2.28 Å, found for the $Cd(H_2O)_6^{2+}$ ion in the structure of $[Cd(H_2O)_6](NH_4)_2(SO_4)_2$,[11] and is not significantly different from the value 2.291(4) Å found for the $Cd(DMSO)_6^{2+}$ ion in solution.[1]

The ClO_4^- ions. There are two crystallographically different perchlorate groups in the structure, $Cl1 − O_4$ and $Cl2 − O_4$. An examination of a Fourier map showed large librational movements of both groups and also two alternative positions of the $Cl1 − O_4$

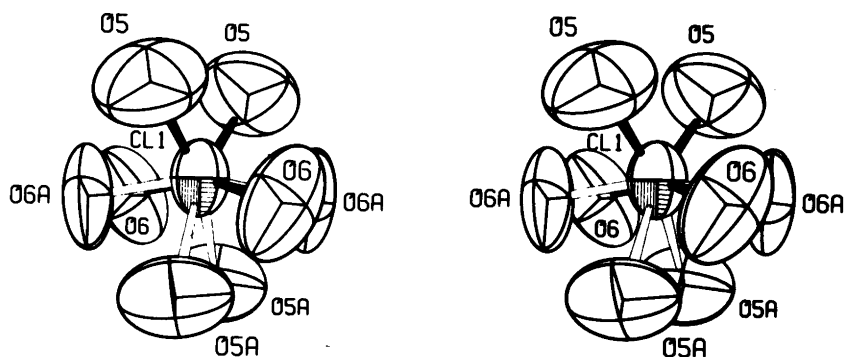*Fig. 3.* A stereoscopic view of the disordered Cl1 − O_4 perchlorate ion. The unfilled Cl − O bonds correspond to the alternative oxygen positions, O5A and O6A. The two-fold rotational axis through the Cl atom is vertical in the picture. The thermal ellipsoids are shown at the 30 % probability level.

group. These positions are approximately related to each other by a 180° rotation perpendicular to the twofold rotational axis through the Cl1 atom and a displacement along this axis of about 0.4 Å (Fig. 3). The resulting new oxygen positions are denoted O5A and O6A. The two slightly displaced Cl1 positions could not be resolved by least squares refinements, but are shown by the elongation of the thermal ellipsoid of the Cl1 atom (Fig. 3) and by the asymmetry of the Cl1 − O bond lengths (Table 3).

The apparent shortening of the average Cl − O bond length, 1.38 Å, from the expected value of 1.42_6 Å,[12] is certainly an effect of the large librational movements, as discussed for the disordered perchlorate ion found in the structure of $[Hg(DMSO)_6](ClO_4)_2$.[2] The thermal ellipsoids of the perchlorate oxygens are also here very large (Fig. 3 and Table 2). The bond angles within the two positions of the disordered Cl1 − O_4 group show large deviations from tetrahedral values, probably mainly due to the displacement of the Cl1 atom position. They range from 71 to 163°. For Cl2 − O_4 the bond angles range from 102 to 127°.

The sum of the refined occupancy factors of the symmetry-related oxygen positions in Cl1 − O_4 for the first data set is 2.06(16), close to the expected value of 2.0. The sum for the second data set is 1.5(3).

Judging from the refined occupancy factors (Table 1) there seems to be a correlation between the alternative positions of the DMSO and the Cl1 − O_4 groups. This perchlorate ion is situated between the disordered DMSO ligands of two different Cd-complexes, as can be seen in Fig. 2. The simultaneously occupied positions would then

be S3,O3 and O5,O6 or S4,O4 and O5A,O6A, with the shortest distance S4 − O5A 4.52(8) Å. It is noticeable that for the other configuration the closest distance would be much shorter, *viz.* S4 − O5 4.05(4) Å, although still much longer than the sum of the van der Waals radii.[8]

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