Short Communication

The Crystal Structure of Hexaaquacadmium(II) Perchlorate, [Cd(H$_2$O)$_6$](ClO$_4$)$_2$

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In aqueous and in dimethylsulfoxide (DMSO) solutions, cadmium(II) and mercury(II) are octahedrally coordinated by the solvent molecules in the absence of complex-forming anions.[1] The same regular octahedral coordination is found in the solid mercury(II) compounds [Hg(H$_2$O)$_6$](ClO$_4$)$_2$ (Hg–O distance 2.341(6) Å)[2] and [Hg{(CH$_3$)$_2$SO}$_6$](ClO$_4$)$_2$ (Hg–O: 2.317(6), 2.320(6) and 2.376(6) Å, average distance 2.34 Å),[3] as well as in the cadmium compound [Cd{(CH$_3$)$_2$SO}$_6$](ClO$_4$)$_2$ (Cd–O distances 2.278(7), 2.257(11), and 2.270(24) or 2.262(22) Å).[4] For mercury(II), the corresponding distances in perchlorate solutions have been found to be slightly longer, viz. 2.41(1) Å in water and 2.393(5) Å in DMSO.[1,5] For the cadmium ion in a perchlorate solution in DMSO the Cd–O distance, 2.291(2) Å, does not, however, differ significantly from that found in the crystals, especially when corrections for thermal motion effects are made.[1] In order to make a similar comparison between the Cd–O distance in an aqueous perchlorate solution [2.292(5) Å][6] and in the solid state, the crystal structure of [Cd(H$_2$O)$_6$](ClO$_4$)$_2$ has been determined.

Experimental

Crystals were prepared from acidic or neutral cadmium perchlorate solutions by evaporation. Guinier powder photographs showed them to be isomorphous with the corresponding mercury(II) compound, and this was confirmed by Weissenberg and precession photographs. It appeared,

however, that different crystals had significant differences in their relative intensities, which in some cases led to equivalence between *hkl* and *hkl̄* reflections, even though the correct Laue symmetry is 3*m*. This seemed to indicate disorder in the crystals, and four different sets of data were therefore collected using four crystals (**A**, **B**, **C** and **D**) having different degrees of disorder as judged from their intensities. Crystals with edges less than 0.25 mm enclosed in capillary tubes were used in all cases.

A Syntex *P*2$_1$ four-circle automatic diffractometer was used for data collection, which was carried out in the same way as described for the corresponding mercury compound.[2] Mo*K*α radiation (λ = 0.7107 Å) was used. The trigonal unit cell was found to have the dimensions $a = b$ = 7.989(2) Å and c = 5.326(1) Å by least-squares refinement of 25 centered reflections. Careful checking revealed no doubling of these parameters. The unit cell volume of 294.4(1) Å^3 corresponds to a density D_x = 2.366 g cm^{-3}, in agreement with the measured value (D_m = 2.368 g cm^{-3}).[7] Repeatedly measured check reflections showed no systematic variation in their intensities during the data collection. A semi-empirical absorption correction[8] was applied to all data. For crystal **A**, the number of observed independent reflections was 433 (2θ < 65°) with 6 of these below 1.96σ(I). Corresponding values were 124 and 1 for crystal **B** (2θ < 40°), 352 and 4 for crystal **C** (2θ < 60°), and 351 and 2 for crystal **D** (2θ < 60°), the last values being based on an average of 2607 measured intensities. Comparisons of intensities

of *hkl* and *hkl* reflections indicated that crystals **C** and **D** should be those least affected by the disorder, and should therefore give the best sets of diffraction data.

Structure refinement and results

All calculations were carried out in the same way as described previously.[2,3] Three-dimensional Patterson functions were calculated, and could be explained for crystals **C** and **D** on the basis of the structure found previously for the corresponding mercury(II) compound (space group No. 164 = $P\bar{3}m1$). The Patterson functions for the other two crystals **A** and **B** showed pronounced extra peaks; these could, however, be interpreted by assuming a mixture of two structures related by a mirror plane perpendicular to the *c* axis (and a mirror-plane containing the *c*-axis and the *ab*-diagonal).

A least-squares refinement of the data, taking the parameter values for the mercury(II) compound as a starting point and using isotropic temperature factors for all atoms except Cd, led to an *R* value of 0.14 for crystal **A**. Corresponding refinements gave *R* factors of 0.20, 0.08 and 0.07 for crystals **B**, **C** and **D**, respectively. Difference Fourier maps calculated at this stage for crystals **A**, **B** and **C** revealed the presence of well-defined peaks at positions expected for a structure related

to the main structure by a mirror plane at $z = 0$, in agreement with the conclusions made from the Patterson functions. This was taken into account in the subsequent refinements, allowing also occupancy factors to be varied. For crystal **C**, an *R* factor of 0.051 was obtained using anisotropic temperature factors for all atoms and with a ratio of 0.82:0.18 between the main and the alternate structure. A similar refinement for crystal **A** gave $R = 0.069$ for a ratio of 0.60:0.40. The limited data set for crystal **B** did not allow a complete refinement to be made, but the result indicated a ratio of 0.53:0.47 between the two structures. For the last crystal investigated (**D**), no trace of alternate atom positions, corresponding to a mirror-plane related structure, could be found. A refinement using anisotropic temperature factors gave $R = 0.040$.

Apart from the apparent disorder or twinning, the structure is the same as that of $[Hg(H_2O_6)](ClO_4)_2$. It is built up of $Cd(H_2O)_6$ octahedra and ClO_4 tetrahedra (Fig. 1). The water molecules form a string of octahedra running along the *c*-axis, every second of which is occupied by a Cd atom. The ClO_4^- ions fill up the channels formed between the strings of octahedra and are probably held loosely by hydrogen bonds, as discussed for the mercury compound.[2] They are stacked on top of each other in columns along the three-fold axes with their apex oxygens
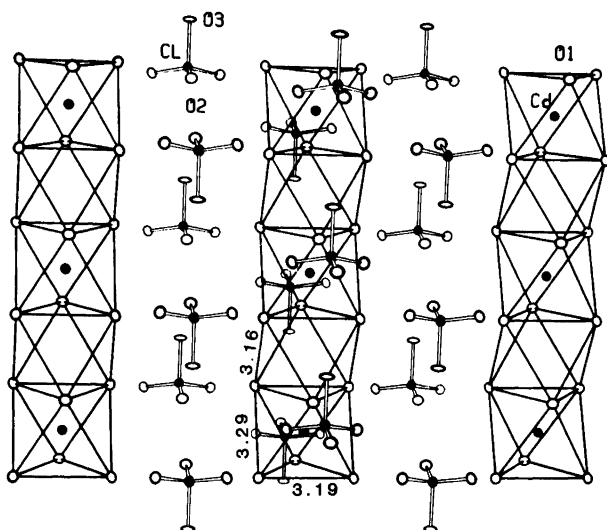

Fig. 1. The water oxygen atoms O1 form, along the *c*-axis, a string of face-sharing octahedra, every second of which contains a Cd atom. Around the central string of octahedra in the figure the six surrounding columns of perchlorate ions are indicated. The thermal ellipsoids correspond to 95 % probability. Distances in Å.

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Table 1. Fractional positional parameters and equivalent isotropic temperature factors $B/\text{Å}^2$ for crystal **D**, with estimated standard deviations given in parentheses. The alternative positions of the perchlorate oxygen atoms are labelled O2A and O3A. Space group No. 164 ($P\bar{3}m1$).

Atom	Position	x	y	z	B
Cd	1(a)	0	0	0	3.06(1)
Cl	2(d)	1/3	2/3	0.2195(3)	3.53(3)
O1	6(i)	0.1316(2)	−0.1316	−0.2566(5)	5.23(9)
O2	6(i)	0.4293(4)	−0.4293	0.3079(12)	7.1(3)
O3	2(d)	1/3	2/3	−0.0530(16)	7.1(4)
O2A	6(i)	0.5730(11)	−0.5730	−0.168(5)	11.3(1.3)
O3A	2(d)	1/3	2/3	0.509(7)	6.7(2.4)

pointing in the same direction. In the Cd-structure there is, however, space enough for the perchlorate ions to have the inverted orientation, that is with the O3 atom pointing in the opposite direction without any noticeable change in the Cl position. Electron density maps for crystals C and **D** indicated that some of the ClO_4 tetrahedra had, in fact, this orientation. A least-squares refinement made on this assumption lowered the R value for the data for crystal C to 0.036 and showed that about 20 % of the tetrahedra had this type of disorder. The corresponding calculation for crystal **D** gave a final R value of 0.029 ($R_w = 0.039$) for a disorder of about 25 %. Changes in other parameter values did not exceed the calculated standard deviations. The highest peaks in a final difference Fourier calculation for crystal **D** were less than 0.4 $e/\text{Å}^3$, and could not be related to possible H atom positions.

Lists of F_o and F_c values and anisotropic temperature factors are available from the authors on request.

Table 2. Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

Within a $M(OH_2)_6^{2+}$ octahedron:

	Cd	Hg
M–O1	2.277(2)	2.341(6)
O1–O1	3.155(1)	3.188(6)
	3.285(3)	3.430(9)
O1–M–O1	87.69(6)	85.81(18)

Between the octahedra:

	Cd	Hg
O1···O1	3.169(3)	3.059(9)

Discussion

The final atom parameter values for crystal **D**, which do not differ significantly from those obtained for the other crystals, are given in Table 1. The Cd–O bond length is 2.277(2) Å (2.285 Å when corrected for thermal effects assuming riding motion) and thus does not differ significantly from the value found for aqueous solutions [2.292(5) Å].[6] The thermal parameters are similar to those for the mercury compound,[2] except for the disordered perchlorate oxygen atoms which have large values. Although the Hg–O bond length [2.341(6) Å] is significantly longer than that of Cd–O [2.277(2) Å], the unit cell of $[Hg(H_2O)_6](ClO_4)_2$ is only marginally larger than that of the Cd analogue, with the edges $a = b = 8.005(5)$ Å and $c = 5.344(2)$ Å. This can be related to the smaller distortion of the $Cd(H_2O)_6$ octahedron (Table 2). The more regular repeat distances between the triangular octahedral faces perpendicular to the c-axis (the z-parameter for O1 is closer to 1/4) is probably the reason why the space is sufficient for the inversion of perchlorate in the $[Cd(H_2O)_6](ClO_4)_2$ structure but not in that of the corresponding mercury compound.

For the perchlorate ions, the Cl–O distances obtained are Cl–O2 1.409(3) Å [Cl–O2A 1.33(1) Å] and Cl–O3 1.451(8) Å [Cl–O3A 1.54(4) Å]. Although the disorder possibly causes some systematic error in the Cl-position, these distances are similar to those found in the mercury compound, viz. 1.394(9) Å and 1.472(24) Å, respectively. The smallest distance between neighbouring columns of tetrahedra is O2–O2 2.83(1) Å in the main part of the structure. For the inverted tetrahedral position the contact distances are

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shorter, with O2A–O2 2.39(1) Å and O3A–O3 (distance to the next tetrahedron in the same column) 2.34(4) Å, which are only slightly larger than the internal O–O distances within a tetrahedron. An inversion of all ClO_4 tetrahedra in a column with a slight shift in the Cl position towards the O3A atom would give a more regular tetrahedral structure and eliminate the short O3A–O3 contacts. The possible H-bond distances are found to be O3···O1 2.994(3) Å and O3A···O1 3.06(2) Å, which are close to the corresponding O3···O1 distance of 2.98(1) Å in the mercury compound.

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