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The Crystal Structure of a Dimeric Cerium(IV) Sulfate $Ce_2(OH)_2(H_2O)_4(SO_4)_3$

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The crystal structure of $Ce_2(OH)_2(H_2O)_4(SO_4)_3$ has been determined from three-dimensional X-ray diffractometer data. The crystals are monoclinic, space group $A2/a$, with $a = 15.583(11)$ Å, $b = 13.448(13)$ Å, $c = 6.748(4)$ Å, $\gamma = 95.39(6)°$ and $Z = 4$.

The positions of the cerium, sulfur and oxygen atoms were evaluated from a Patterson function and a subsequent electron density summation. Full matrix least-squares refinement based on 1425 reflexions yielded a final R value of 4.25 %.

The structure contains discrete $Ce_2(OH)_2(H_2O)_4^{6+}$ ions, in which the Ce(IV) atoms are connected by double OH^- bridges, the Ce – Ce and $OH^- - OH^-$ distances being 3.769(3) and 2.481(14) Å, respectively. Cerium is eight-coordinated by two OH^- ions, two water molecules and four oxygen atoms belonging to sulfate groups, giving a distorted dodecahedral configuration with Ce – O distances of 2.223 – 2.406 Å (mean 2.328 Å). The $Ce_2(OH)_2(H_2O)_4^{6+}$ ions are linked through SO_4^{2-} ions to form a three dimensional network.

The oxygen coordination of some tetravalent metal ions has been a subject of study at this Department for several years. The work was commenced by Lundgren [1] who investigated some basic salts of Ce^{IV}, Th^{IV}, U^{IV}, Ti^{IV}, and Zr^{IV}, and was continued on essentially the same lines by Hansson [2] and Mark [3] on Hf and Zr, by Lindqvist [4] on Te and by Titze and Allard [5] on Th and Np. The present author has studied the oxygen coordination of cerium in a cerium (III)sulfate,[6a] basic and neutral cerium(IV) sulfates [6b,6c] and a cerium(IV) chromate.[6d] In this paper the investigation of the crystal structure of a dimeric basic cerium(IV) sulfate, *viz.* $Ce_2(OH)_2(H_2O)_4(SO_4)_3$, is reported.

EXPERIMENTAL

The commercially available compound, $Ce(SO_4)_2(H_2O)_4$, (orthorhombic, space group *Fddd*, manufactured by Merck AG), was dissolved in 1 M H_2SO_4. About 100 ml of the solution, still containing some undissolved salt, was transferred to a glass flask which was then sealed. After some months, small yellow prismatic crystals had formed. Oscillation and Weissenberg photographs showed the crystals to be monoclinic. Systematically absent reflexions, *i.e.*

hkl: $k + l = 2n + 1$

$hk0$: $h = 2n + 1$

indicated the space group to be Aa or $A2/a$.

Approximate cell dimensions were calculated from oscillation and Weissenberg photographs. Guinier X-ray powder photographs were taken using $CuK\alpha_1$ radiation and with $Pb(NO_3)_2$ ($a = 7.8566$ Å at 21 °C) [7] as an internal standard. The cell dimensions as calculated from these photographs with the programme POWDER [8] are: $a = 15.583(11)$ Å, $b = 13.448(13)$ Å, $c = 6.748(4)$ Å and $\gamma = 95.39(6)°$.

The crystal chosen for single crystal work had the approximate dimensions $0.08 \times 0.1 \times 0.08$ mm³. Ten layers, $hk0 - hk9$, were recorded on a PAILRED single crystal diffractometer using graphite monochromatized $MoK\alpha$ radiation. The Lorentz and polarisation effects were corrected for, using the programme DATAP1,[9] those reflexions for which $\sigma(I)/I > 0.3$ where $\sigma(I) = (I_t + I_b)^{\frac{1}{2}}$, I_t denoting total intensity and I_b background intensity, being discarded. The remaining 1425 symmetry independent reflexions were used in the refinement of the structure. However, to solve the structure only reflexions from the layers $hk0 - hk4$ were considered necessary. Before the final refinement a correction was made for absorption with the programme DATAPA.[9] The trans-

Table 1. Atomic coordinates and temperature factors for $Ce_2(OH)_2(H_2O)_4(SO_4)_3$. Estimated standard deviations are given in parentheses. The thermal parameters have been multiplied by 10^5 for Ce and by 10^4 for S and O. The temperature factor is of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	0.08607(3)	0.10763(4)	−0.02215(6)	852(21)	722(21)	638(20)	714(26)	−3(37)	66(37)
S1	0.56723(14)	0.20905(16)	0.52131(32)	118(9)	83(8)	66(8)	136(13)	−25(14)	−22(14)
S2	1/4	0	0.27320(44)	121(14)	68(13)	75(12)	62(21)	0	0
O1	−0.0149(5)	0.2472(5)	0.5367(11)	160(32)	137(31)	150(31)	168(51)	−16(51)	−100(51)
O2	0.0517(6)	0.1460(7)	0.3031(12)	271(44)	249(44)	166(34)	323(73)	−11(60)	−160(61)
O3	0.1343(6)	0.2889(6)	0.4426(15)	196(38)	175(38)	395(50)	38(61)	163(70)	246(70)
O4	0.0943(5)	0.1453(6)	0.6409(11)	246(40)	194(38)	108(31)	393(61)	133(53)	101(52)
O5	0.3165(6)	0.0560(6)	0.3931(12)	209(38)	118(35)	214(36)	−11(58)	−98(58)	−88(55)
O6	0.2899(5)	0.4286(6)	0.6431(13)	128(35)	183(38)	276(40)	175(58)	62(58)	−62(61)
W1	0.1439(6)	0.4790(7)	0.2852(12)	344(48)	213(42)	120(34)	341(72)	82(60)	48(56)
W2	0.3949(5)	0.2555(6)	0.4642(14)	197(36)	103(32)	395(48)	63(54)	−8(70)	−128(66)
OH	0.0428(5)	0.4577(5)	0.6239(10)	115(31)	73(30)	154(31)	41(49)	−37(48)	32(50)

mission factors, ranging from 0.71 to 0.82, were calculated using a 6 × 8 × 6 grid.

STRUCTURE DETERMINATION

A Patterson synthesis was calculated using the programme DRF.[9] The interpretation, in terms of space group $A2/a$, gave positions for the cerium atom, one sulfur atom and the OH^- ion, all situated in the general positions of the space group. A subsequent three-dimensional Fourier synthesis based on these three atomic positions, clearly revealed the locations of the remaining nonhydrogen atoms. The final refinement with the full matrix programme LALS[9] was based on all the 1425 recorded reflexions. The scattering factors used were those given by Cromer and Waber,[10] corrected for the real part of the anomalous dispersion, and the reflexions were weighted according to $w = 1/(80+|F_o|+0.001|F_o|^2)$. One scale factor, 34 positional parameters, and 70 anisotropic temperature factors were refined giving a conventional R value of 4.25 %.

Lists of observed and calculated structure factors are available on request from the author. The final atomic parameters are listed in Table 1.

DESCRIPTION AND DISCUSSION

Fig. 1 illustrates the structure viewed along the c-axis. The structure consists of $Ce_2(OH)_2(H_2O)_4{}^{6+}$ ions and $SO_4{}^{2-}$ ions joined in a three-

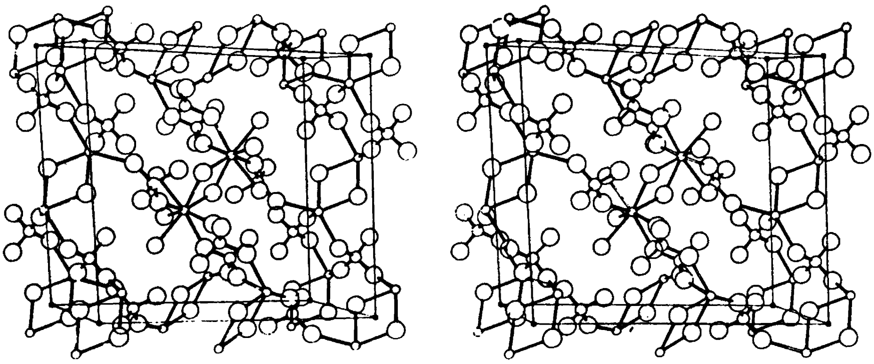

Fig. 1. Stereo drawing of $Ce_2(OH)_2(H_2O)_4(SO_4)_3$ viewed along the c axis. For clarity only two complete cerium-oxygen polyhedra are shown.

Table 2. Interatomic distances (Å) and angles (°).

Ce – Ce	3.769(3)	S1 – O1	1.475(8)
OH^- – OH^-	2.481(14)	– O2	1.464(9)
		– O3	1.446(9)
Ce – O1	2.337(8)	– O4	1.476(8)
– O2	2.329(8)	Average:	1.465
– O4	2.331(7)		
– O6	2.322(8)	S2 – O5(× 2)	1.465(9)
– W1	2.406(9)	– O6(× 2)	1.481(9)
– W2	2.386(8)	Average:	1.473
– OH^-	2.289(7)		
– OH^-	2.223(7)	O1 – O2	2.382(11)
Average:	2.328	– O3	2.423(11)
		– O4	2.388(11)
W1 – O3	2.759(13)	O2 – O3	2.402(13)
– O5	2.768(12)	– O4	2.374(11)
W2 – O3	2.742(12)	O3 – O4	2.383(12)
– O5	2.749(11)	Average:	2.392
O1 – S1 – O2	108.3(5)	O5 – O5	2.444(17)
O1 – S1 – O3	112.1(5)	– O6(× 2)	2.412(12)
O1 – S1 – O4	108.1(5)	– O6(× 2)	2.388(12)
O2 – S1 – O3	111.2(5)	O6 – O6	2.384(17)
O2 – S1 – O4	107.8(5)	Average:	2.407
O3 – S1 – O4	109.2(5)		
O5 – S2 – O5	113.0(7)		
O5 – S2 – O6(× 2)	109.9(5)		
O5 – S2 – O6(× 2)	108.3(5)		
O6 – S2 – O6	107.3(7)		

dimensional network, so that cerium is surrounded by eight oxygen atoms. Distances and angles with their standard deviations are listed in Table 2. No correction has been made for thermal motion.

Fig. 2. shows the bonding viewed in the *y* direction. The dimeric cerium complexes are arranged in a chain along the *a*-axis. Between them are SO_4^{2-} ions situated on the twofold axes. Only half of the oxygen atoms of these groups are involved in bonds to cerium.

The cerium – sulfate bonds, viewed in the *x* direction are illustrated in Fig. 3, a zigzag pattern being formed by cerium atoms and sulfate groups (S1). Two of the oxygen atoms in the S1 group participate in the chain along the *a*-axis. A third oxygen atom, also bonded to S1, is coordinated to a cerium atom in a neighbouring zigzag chain.

Although the square Archimedean antiprism is the usual coordination polyhedron in known compounds with cerium(IV) – oxygen bonds, the eight oxygen atoms in this substance form a dodecahedron. Since they are of four different kinds: OH^- ions, water molecules, and sulfate oxygen atoms bonded to S1 or S2, it could be expected that there would be different bond lengths within the coordination polyhedron and that the cerium – hydroxide bond distances would be shorter than those of Ce – H_2O.

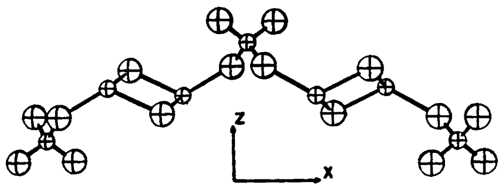

Fig. 2. The bonding viewed in the *y* direction showing the $Ce_2(OH)_2^{6+}$ dimers linked by sulfate ions.

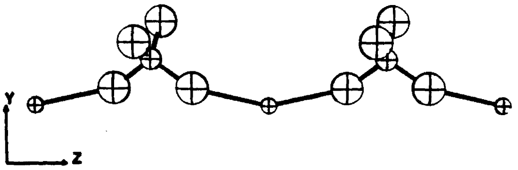

Fig. 3. The cerium-sulfate zig-zag pattern viewed in the *x* direction.

This is, in fact, the case, the former being 2.223(7) and 2.289(7) Å, while the latter are 2.386(8) and 2.406(9) Å. The Ce – O(sulfate) bond lengths are intermediate between these two groups of Ce – O distances. Although three of the oxygen atoms in the S1 group are coordinated to cerium but only two of those in the S2 group are similarly coordinated, there is no significant difference between the $Ce-O_S$ distances (mean $Ce-O_{S1}=$ 2.332(8) Å; $Ce-O_{S2}$ = 2.322(8) Å). The mean Ce – O distance is 2.328 Å. This value is close to those found in $Ce_6O_4(OH)_4(SO_4)_6$[11] (2.33 Å) and in $Ce(CrO_4)_2(H_2O)_2$[6d] (2.342 Å). Although the oxygen atoms in these structures form an antiprism, the mean Ce – O distances ought to be comparable, since a dodecahedron and an antiprism are nearly equivalent energetically. In $CeOSO_4H_2O$[6b] the corresponding mean is 2.364(5) Å, which is probably due to a different type of packing, a fact that is supported by the extremely short Ce – Ce distance: 3.568 Å (3.63 Å in cerium metal). In the cubically coordinated CeO_2[12] the mean Ce – O distance is 2.343(1) Å.

The average S – O distances in the sulfate groups are 1.465(9) Å for S1 and 1.473(9) Å for S2 and the mean O – O distances are 2.392(12) and 2.407(12) Å, respectively. These values agree well with mean S – O, 1.472 Å, and O – O, 2.404 Å, distances obtained in recently determined sulfate structures.[13] The O – S1 – O angles vary between 107.8 and 112.1°, the corresponding range in the O – S2 – O angles being 107.3 – 113.0°. A higher irregularity is to be expected in the latter case, since only two of the oxygen atoms are bonded to cerium.

The unit cell contains two symmetrically independent water molecules, which form hydrogen bonds stabilizing the structure. These water molecules, W1 and W2, probably each form two hydrogen bonds, the W – O distances being short in each case, W1 – O5: 2.768 Å, W1 – O3: 2.759 Å, the O5 – W1 – O3 angle being 101.8°. For W2 the corresponding values are W2 – O5: 2.749 Å, W2 – O3: 2.742 Å, the O5 – W2 – O3 angle being 107.7°. All other short O – O distances are within the coordination polyhedron. Both O3 and O5 may thus act as acceptors in two hydrogen bonds and the fact that O3 and O5 are not coordinated to cerium supports the theory that the hydrogen atoms of W1 and W2 are bonded to O3 and O5.

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