The Crystal Structure of Cerium(IV) Sulfate Tetrahydrate, $Ce(SO_4)_2.4H_2O$

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When the common form of $Ce(SO_4)_2.4H_2O$, space group $Fddd$, is treated hydrothermally with $0.3-1.0$ M H_2SO_4, a polymorphic phase, space group $Pnma$, crystallizes. The structure of the latter has been determined from X-ray diffractometer data. The orthorhombic cell has the dimensions $a = 14.5994(17)$ Å, $b = 11.0064(4)$ Å, and $c = 5.6601(5)$ Å; it contains four formula units.

Standard Patterson and Fourier methods were used to solve the structure. Full matrix least-squares refinement based on 1409 reflexions yielded a final R of 0.040.

The structure is composed of layers of the empirical formula $Ce(SO_4)_2$ normal to the a axis. The water molecules link the layers together by hydrogen bonds.

Cerium is eight-coordinated by four water molecules and four sulfate oxygen atoms, giving a square antiprismatic configuration. The average $Ce-O$ distance is 2.326 Å (range $2.292-2.388$ Å).

A number of cerium(IV) sulfates and a cerium-(IV) chromate have been investigated at this Institute.[1-5] They all contain cerium(IV) ions coordinated by eight oxygen atoms. However, the coordination polyhedra are of different kinds, square antiprisms, a dodecahedron and a bicapped trigonal prism. Usually the compounds have been prepared by hydrothermal hydrolysis with varying acid concentration and at different temperatures. Some of the phases obtained are basic, others neutral.

The compound under investigation is the neutral $Ce(SO_4)_2.4H_2O$, which seems to be isostructural with $U(SO_4)_2.4H_2O$.[6] Some crystallographic data for the cerium compound have been reported [7] previously, but not a complete structure determination. The present study is

part of a program concerning the type and dimensions of cerium — oxygen polyhedra

EXPERIMENTAL

A saturated solution of $Ce(SO_4)_2.4H_2O$ (space group $Fddd$,[7] pro analysi quality from Merck) in 1.0 M H_2SO_4 was prepared. The solution was divided in five portions, four of them diluted with H_2O in proportions varying from 1:1 to 1:15. About 25 ml of each solution was sealed in a glass tube and heated to 80 °C in an oven for a week. In the tubes containing the more concentrated solutions bright yellow crystals suitable for X-ray work were obtained.

A crystal with the approximate dimensions $0.09 \times 0.09 \times 0.2$ mm was mounted in the needle axis, [001]. Rotation and Weissenberg recordings showed orthorhombic symmetry. The systematic absences were: $hk0$ for $h \neq 2n$ and $0kl$ for $k + l \neq 2n$, which is characteristic of the space groups $Pnma$ and $Pn2_1a$.

The cell dimensions were determined from a powder photograph recorded with monochromatized $CuK\alpha_1$ radiation in a Guinier camera. Lead nitrate ($a = 7.8566$ Å at 21 °C) [8] was used as an internal standard. Least-squares refinement of 14 indexed lines gave the following cell constants: $a = 14.5994(17)$ Å, $b = 11.0064(4)$ Å, $c = 5.6601(5)$ Å, and $V = 909.5$ Å³. $Z = 4$ leads to a calculated density of 2.952 g cm⁻³.

Ten layers, $hk0$ to $hk9$, were recorded with graphite monochromated $MoK\alpha$ radiation on a PAILRED 2-circle diffractometer. The ω scan technique was employed, and measuring times varied from 72 to 120 s for the peaks, while the background intensities were measured in two 24 s periods, one preceding, one following the scan. Reflexions with $\sigma(I)/I > 0.3$ were considered insignificant, $\sigma(I)/I$ defined as $(I_{tot} + I_{back})^{\frac{1}{2}}/(I_{tot} - I_{back})$. The remaining 1409 independent reflexions were corrected for

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ce	0.17148(3)	0.25	0.12469(9)	91(2)	86(2)	87(2)	0	1(2)	0
S	0.35064(10)	0.05504(13)	0.88347(33)	100(5)	84(5)	111(5)	3(4)	−2(5)	7(5)
O1	0.2606(4)	0.1170(5)	0.9143(10)	170(22)	213(24)	226(28)	39(19)	27(19)	−56(20)
O2	0.3319(4)	0.9230(4)	0.8522(9)	247(22)	111(17)	160(19)	5(18)	4(22)	18(15)
O3	0.4066(4)	0.0691(5)	0.0931(11)	248(25)	144(20)	219(27)	34(19)	−100(21)	22(19)
O4	0.3943(4)	0.1040(5)	0.6713(10)	151(21)	194(23)	209(25)	29(18)	75(18)	73(19)
O5	0.0251(6)	0.25	0.3128(17)	209(36)	122(28)	318(40)	0	160(33)	0
O6	0.2991(5)	0.25	0.3716(17)	149(26)	165(28)	213(29)	0	−46(32)	0
O7	0.0763(4)	0.1249(5)	0.8934(2)	153(21)	216(22)	205(24)	1(17)	−29(20)	−71(22)

Lorentz, polarisation and absorption effects (program: DATAPA [9]). The transmission factors varied from 0.535 to 0.790.

DETERMINATION AND REFINEMENT

To reduce the computation times only half the reflexions were included in all calculations except for the final ones. The major peaks in a Patterson synthesis were all explained as cerium and sulfur vectors assuming the space group to be *Pnma*. A Fourier summation clearly showed seven independent oxygen atoms. Block diagonal refinement (program: BLOCK [9]) was used to adjust the scale factor, the positional and the temperature parameters. In the final refinement, based on all data, the Brookhaven full matrix program LINUS was used. Scattering factors were those of Doyle and Turner,[10] for the uncharged atoms. The effects of anomalous dispersion were neglected since the structure is centrosymmetric. Weights were calculated according to $w=(10.0+|F_o|-0.0025|F_o|^2+0.00002|F_o|^3)^{-1}$ leading to a reasonable agreement between w^{-1} and $(|F_o|-|F_c|)^2$ independent of $|F|$. An isotropic secondary extinction parameter and anisotropic temperature factors were included in the refinement and the conventional R value dropped to 0.040. A final difference Fourier synthesis showed no significant peaks except fluctuations in the vicinity of cerium. The atomic parameters obtained in the last refinement are listed in Table 1. The structure factor list can be obtained from the author on request.

DESCRIPTION AND DISCUSSION

Fig. 1 illustrates the structures viewed along the c axis. Selected interatomic distances and angles are listed in Table 2.
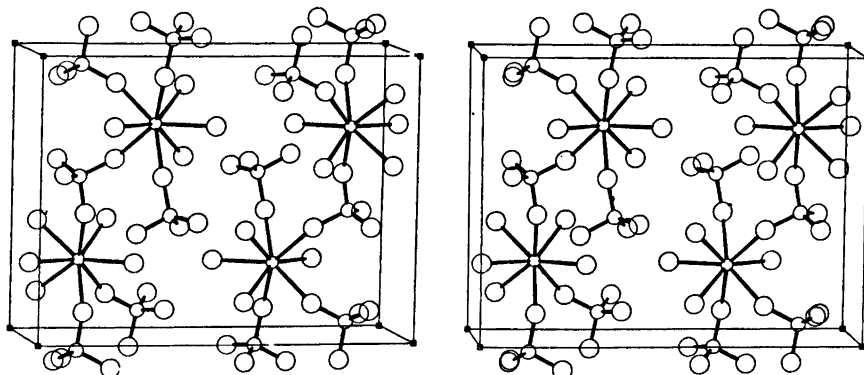

Fig. 1. A stereoscopic drawing of the unit-cell contents viewed approximately along c.

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

Antiprism			Sulfate group	
Ce−O1	(2×)	2.292(6)	S−O1	1.491(6)
−O2	(2×)	2.299(5)	−O2	1.490(5)
−O6		2.329(8)	−O3	1.449(6)
−O7	(2×)	2.354(6)	−O4	1.463(6)
−O5		2.388(9)		
Average:		2.326	O1−S−O2	107.3(3)
			O1−S−O3	110.6(3)
O1−O1		2.927(12)	O1−S−O4	108.2(3)
O1−O7	(2×)	2.695(8)	O2−S−O3	107.8(3)
O7−O7		2.754(12)	O2−S−O4	110.0(3)
O2−O5	(2×)	2.835(8)	O3−S−O4	112.8(3)
O2−O6	(2×)	2.701(7)		
O1−O2		2.856(8)		
O1−O6		3.026(10)		
O7−O2		2.970(8)		
O7−O5		2.844(19)		
Hydrogen bond system				
O5−O3	(2×)	2.691(8)	O3−O5−O3	95.5(4)
O6−O4	(2×)	2.719(9)	O4−O6−O4	72.5(3)
O7−O3		2.740(8)	O3−O7−O4	86.5(3)
O7−O4		2.691(8)		

The structure is made up of layers of the composition $Ce(SO_4)_2$ normal to the a axis, and the water molecules join these layers by hydrogen bonds. The two sulfate oxygen atoms O3 and O4, which are not bonded to centrum, are at distances varying between 2.691 to 2.740 Å from the water molecules O5, O6 and O7. O5 probably has its hydrogen hydrogens directed towards O3, and O6 towards O4, while O7 has one hydrogen directed towards O3 and one towards O4. Both O3 and O4 thus act as acceptors of two hydrogen bonds.

Cerium is eightfold coordinated by oxygen atoms, four water molecules and four sulfate oxygens belonging to different sulfate groups. The coordination polyhedron is a somewhat distorted Archimedean square antiprism. The least-squares planes through the square faces form an angle of only 2.3°. One plane has, due to space group symmetry, all four atoms in the same plane while the other formed by the atoms two O2, O5 and O6 shows a minor deviation (0.02 Å) from an ideal plane.

The average Ce−O distance is 2.326 Å, which agrees with those found in related compounds (*cf.* Table 3).

The sulfate group is in contact with two cerium atoms, the other two sulfate oxygens being involved in hydrogen bonding. This is reflected in the deviation from regularity found in the sulfate group. O1 and O2, linked to cerium, are at significantly longer distances from sulfur than O3 and O4. The average S−O and O−O distances in the sulfate group are 1.473 and 2.405 Å.

Cerium sulfate tetrahydrate has two polymorphic forms. The first crystallizes in the space group *Fddd* and the second in *Pnma*. The analogous uranium compound, reported by Kierkegaard,[6] has only one form, and it is isomorphous with the *Pnma* form. Zirconium sulfate tetrahydrate[12] is isomorphous with the *Fddd* form. However, as described by Singer and Cromer,[12] the structures of the compounds in *Pnma* are closely related to those in *Fddd*.

Table 3. Coordination polyhedra in cerium(IV) compounds.

Compound	Polyhedron	⟨Ce−O⟩ Å	Range Å
$Ce(SO_4)_2.4H_2O$	antiprism	2.326	2.292 − 2.388
CeO_2 [11]	cube	2.343	2.343
$Ce_6O_4(OH)_4(SO_4)_6$ [2]	antiprism	2.33	2.22 − 2.39
$CeOSO_4.H_2O$ [1,3]	antiprism	2.364	2.188 − 2.587
$Ce_2(OH)_2(H_2O)_4(SO_4)_3$ [4]	dodecahedron	2.328	2.223 − 2.406
$Ce(CrO_4)_2.2H_2O$ [5]	bicapped trigonal prism	2.342	2.232 − 2.575

REFERENCES

1. Lundgren, G. *Ark. Kemi 6* (1953) 59.
2. Lundgren, G. *Ark. Kemi 10* (1956) 183.
3. Lindgren, O. *Acta Crystallogr. B 32* (1976) 3347.
4. Lindgren, O. *Acta Chem. Scand. A 31* (1977) 163.
5. Lindgren, O. *Acta Chem. Scand. A 31* (1977) 167.
6. Kierkegaard, P. *Acta Chem. Scand. 10* (1956) 599.
7. Staritzky, E. and Truitt, A. L. *The Actinide Elements*, NNES, McGraw-Hill, New York 1954, Chapter 19.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1959.
9. The Program Library of the Dept. of Inorg. Chem., Göteborg.
10. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A 24* (1968) 390.
11. Magnéli, A. and Kihlborg, L. *Acta Chem. Scand. 5* (1951) 578.
12. Singer, J. and Cromer, D. T. *Acta Crystallogr. 12* (1959) 719.