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Cerium(IV) Oxide Sulphate Hydrate, a New Refinement

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Abstract. $CeOSO_4 . H_2O$, orthorhombic, $P2_12_12_1$, $Z=4$, $a=11{\cdot}987$ (2), $b=8{\cdot}272$ (2), $c=4{\cdot}331$ (1) Å, $V=429{\cdot}1$ Å^3, μ(Mo $K\alpha$) $=101{\cdot}0$ cm^{-1}, $D_x=4{\cdot}182$, $D_m=4{\cdot}2$ g cm^{-3}. The structure was reported previously [Lundgren, *Ark. Kem.* (1953), **5**, 59–75], and is built up by infinite strings of $(CeO^{2+})_n$ parallel to **c**, crosslinked by SO_4 groups. New intensities (2411 non-zero reflexions) have been refined by least squares to a final R of 0·030.

Introduction. Yellow prismatic crystals (elongation **c**) were obtained by hydrothermal hydrolysis of a Ce^{iv} sulphate solution (Lundgren, 1953). A specimen, $0{\cdot}24\times0{\cdot}17\times0{\cdot}47$ mm, was mounted on a Pailred single-crystal diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Intensities for two octants were collected with the ω-scan technique and a scan rate of 2·5° min^{-1}. Systematically absent reflexions and those not fulfilling the criterion $I>3\sigma(I)$ were discarded, leaving 2411 reflexions. The data were corrected for Lorentz, polarization and absorption effects. The crystal volume was 0·0102 mm^3 and transmission factors varied from 0·199 to 0·348.

The parameters of Lundgren (1953) were used as a starting model. Scattering factors of the form $f_o+f'+if''$ for Ce and S and f_o+f' for O (Cromer & Waber, 1965) were used. The initial refinement was performed with a block-diagonal program designed at this Institute: positional parameters and isotropic temperature factors were refined. Moreover, a separate scale factor was used for each layer to allow for systematic errors in F_o as a function of the equi-inclination angle. R fell to 0·035 for the 2411 observed reflexions. In the final refinement, anisotropic temperature factors and an extinction coefficient were refined with the Brookhaven full-matrix least-squares program *LINUS*. Weights were calculated according to $w=(38+|F_o|+0{\cdot}007|F_o|^2+0{\cdot}00054|F_o|^3)^{-1}$. The final R was 0·030. A concluding difference map showed no significant peaks above the general background of $\sim1{\cdot}0$ e Å^{-3}. Atomic parameters are given in Table 1.*

Discussion. The previous investigation (Lundgren, 1953) was based on relatively sparse film data. The coordinates for all atoms except the O^{2-} ion were obtained from electron density projections. The positional parameters for O^{2-} were derived through geometrical considerations. No least-squares adjustment of the parameters was made. The aim of the present investigation was to obtain a more accurate determination of the coordination around Ce.

The structure is built up by infinite strings of empirical composition $(CeO^{2+})_n$ parallel to **c**, crosslinked by SO_4 groups. Fig. 1 is a projection down **a** showing the strings. Ce is in contact with three O^{2-} ions [O(6)] at 2·188 (3), 2·269 (3) and 2·281 (3) Å. The Ce–Ce distance is very short, 3·570 (1) Å, even shorter than the 3·63 Å found in Ce metal (Lawson & Tang, 1949). The string has also a very short O(6)–O(6) distance, 2·680 (4), previously reported as 3·04 Å. Other distances show good agreement with the earlier work.

The SO_4 group has all four O atoms bonded to Ce. It forms an almost regular tetrahedron, with mean S–O

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31956 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Positional and thermal parameters*

The parameters have been multiplied by 10^5 for Ce and S and by 10^4 for 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	17885 (2)	13712 (2)	17002 (4)	632 (6)	710 (7)	647 (5)	90 (10)	−105 (10)	−91 (10)
S	47011 (8)	20358 (11)	34427 (23)	662 (30)	835 (33)	702 (26)	−351 (46)	−210 (49)	145 (50)
O(1)	4570 (3)	483 (4)	5117 (9)	111 (11)	103 (12)	126 (19)	−47 (18)	−48 (19)	62 (18)
O(2)	3652 (3)	2454 (5)	1830 (10)	67 (10)	188 (14)	141 (10)	4 (19)	−68 (18)	102 (19)
O(3)	623 (3)	3152 (5)	8772 (8)	107 (12)	165 (14)	97 (12)	39 (19)	−94 (17)	0 (16)
O(4)	−16 (3)	1677 (4)	4358 (8)	111 (10)	129 (14)	116 (11)	18 (20)	12 (16)	−25 (16)
O(5)	1885 (3)	4421 (4)	2991 (10)	123 (13)	160 (16)	187 (14)	17 (21)	−32 (21)	−64 (20)
O(6)	2267 (2)	892 (4)	6685 (8)	93 (10)	86 (11)	90 (8)	−23 (16)	29 (16)	−15 (19)

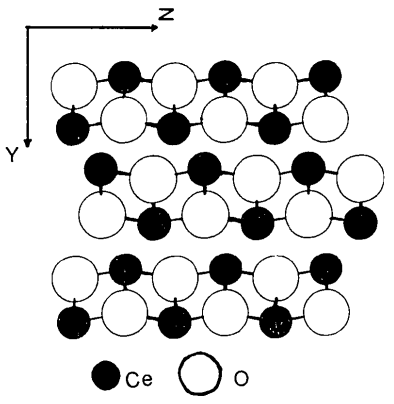

Fig. 1. The $(CeO^{2+})_n$ chains.

and O–O distances 1·476 and 2·409 Å respectively (uncorrected for thermal motion).

A water molecule at 2·587 (4) Å completes the eightfold coordination of Ce. The coordination figure is a distorted Archimedean antiprism. The mean Ce–O distance is 2·366 Å, longer than in CeO_2: 2·343 (Magnéli & Kihlborg, 1951), in $Ce_2(OH)_2(SO_4)_3(H_2O)_4$: 2·328 (Lindgren, 1976) and in $Ce(SO_4).4H_2O$: 2·326 Å (Lindgren, 1976). The water molecules are arranged in zigzag strings also running in the **c** direction.

A stereoscopic packing diagram (Johnson, 1965) is shown in Fig. 2. Distances and angles for the present and previous investigations are given in Table 2.

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

Symmetry code: (i) $\frac{1}{2}-x, -y, z-\frac{1}{2}$; (ii) x, y, z; (iii) $x, y, z-1$.

		This investigation	Lundgren (1953)
Ce—O(1)		2·340 (3)	2·39
Ce—O(2)		2·408 (3)	2·45
Ce—O(3)		2·394 (4)	2·38
Ce—O(4)		2·463 (4)	2·41
Ce—O(5)		2·587 (4)	2·66
Ce—O(6^{i})		2·188 (3)	2·34
Ce—O(6^{ii})		2·269 (3)	2·34
Ce—O(6^{iii})		2·281 (3)	2·34
S—O(1)		1·484 (4)	1·42
S—O(2)		1·479 (4)	1·47
S—O(3)		1·471 (4)	1·46
S—O(4)		1·468 (4)	1·53
O(1)–O(2)		2·428 (5)	2·40
O(1)–O(3)		2·388 (5)	2·37
O(1)–O(4)		2·412 (5)	2·38
O(2)–O(3)		2·428 (5)	2·36
O(2)–O(4)		2·407 (5)	2·45
O(3)–O(4)		2·393 (5)	2·42
O(5)–O(2)		2·719 (5)	2·78
O(5)–O(3)		2·594 (5)	2·63
O(5)–O(5)	(2×)	2·789 (5)	2·73
O(6)–O(6)	(2×)	2·680 (4)	3·04
Ce—Ce	(2×)	3·570 (1)	3·58
O(1)–S–O(2)		110·1 (2)	
O(1)–S–O(3)		107·9 (2)	
O(1)–S–O(4)		109·6 (2)	
O(2)–S–O(3)		110·8 (2)	
O(2)–S–O(4)		109·5 (2)	
O(3)–S–O(4)		109·0 (2)	

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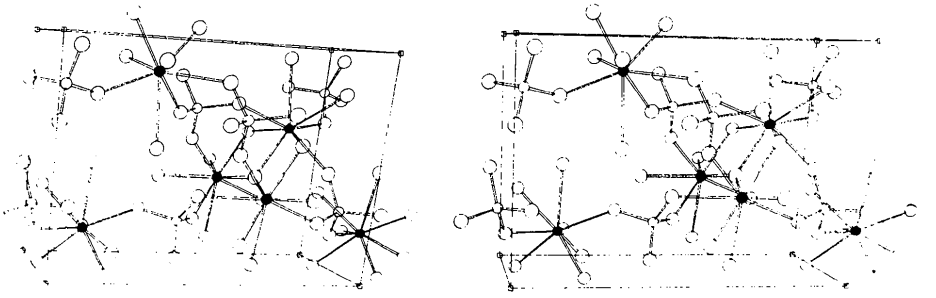

Fig. 2. Stereoscopic drawing of the unit-cell contents viewed approximately along **c**.