

Table 1. Approximate atomic parameters for the compound $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10 \text{H}_2\text{O}$. The space group is $P2_1/c$ (No. 14). Two water oxygens are not located. B (\AA^2) denotes the isotropic temperature factor.

Atom Group	x	y	z	B
Nd	0.190	0.046	0.358	1.49
O(1) —COO ⁻	0.606	0.080	0.445	3.13
O(2) —COO ⁻	0.393	0.100	0.357	2.82
O(3) —COO ⁻	0.866	0.099	0.491	2.89
O(4) —COO ⁻	0.009	0.145	0.400	2.31
O(5) —COO ⁻	0.017	0.478	0.345	3.34
O(6) —COO ⁻	0.160	0.060	0.087	6.41
O(7) H ₂ O	0.781	0.301	0.218	4.06
O(8) H ₂ O	0.296	0.310	0.092	4.23
O(9) H ₂ O	0.170	0.288	0.290	4.01
C(1)	0.501	0.050	0.436	2.54
C(2)	0.957	0.080	0.486	3.35
C(3)	0.054	0.478	0.483	1.11

were obtained. The parameters of the atoms and the scale factors were refined in a series of least-squares calculations. After five cycles the discrepancy index $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0.15. The atomic parameters are given in Table 1.

Each neodymium ion is coordinated by six oxalate and three water oxygen atoms at the distances 2.4–2.5 Å. The coordination polyhedron is based upon a somewhat distorted trigonal prism formed by the three water oxygens and three of the carboxylic oxygens (Fig. 1). The remaining three carboxylic oxygens are located opposite the rectangular faces. The same coordination geometry is found, e.g., in $\text{NH}_4\text{Y}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ ⁵ and $\text{Na}_3[\text{M}(\text{OCOCH}_2\text{OCH}_2\text{OCO})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$, M = lanthanoid.⁶ Each oxalate ion is coordinated to two neodymium ions, forming infinite puckered neodymium-oxalate networks perpendicular to the b -axis. The dimensions of the oxalate groups are compatible with those found in other oxalate structures.

It has not been possible to locate the two remaining independent water oxygen atoms from this preliminary intensity material. More suitable single crystals have now been prepared and a better intensity material is being recorded. This continued work will also include the structures of other lanthanoid-oxalates.

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X-Ray Studies on a Hafnium Sulphate

MARGARETA HANSSON and
GEORG LUNDGREN

Department of Inorganic Chemistry,
Chalmers Institute of Technology and the
University of Göteborg, Gibraltargatan 5 A,
P.O.B., S-402 20 Göteborg 5, Sweden

As the first member in a newly begun series of crystal structure determinations of hafnium sulphates, a compound with a formula approximating to $\text{Hf}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_2$ has been investigated, and a short report is given in this note.

Crystals were prepared by hydrothermal hydrolysis: 0.6 g HfO_2 was dissolved in boiling concentrated sulphuric acid, and the resulting solution was evaporated to dryness. A solution of 0.8 g of the residue in 10 ml 0.1 M sulphuric acid was then sealed in a thick-walled Pyrex tube and heated to 100°C for ten days, after which a crystalline precipitate was formed. After cooling, the precipitate (0.2 g) was filtered off and rapidly washed with water. Thin needle-shaped crystals, efflorescent in air, were obtained.

Table 1. Observed and calculated values of $\sin^2\theta$ and corresponding observed intensities for 37 reflections recorded by Guinier powder methods.

hkl	$10^5\sin^2\theta$ obs	$10^5\sin^2\theta$ calc	I_{obs}
1 1 0	206	204	vvs
1 0 1	259	258	s
2 0 0	273	272	w
1 1 1	396	394	vs
2 0 1	464	462	vvs
2 1 0	479	476	s
3 0 0	618	612	m
2 1 1	671	666	w
3 0 1	808	802	s
3 1 0	891	884	w
1 1 2	968	964	w
4 0 0	1087	1089	w
2 1 2	1246	1236	m
3 0 2	1380	1373	m
3 1 2	1657	1645	s
1 1 3	1924	1915	vw
3 0 3	2341	2323	m
3 3 2	2617	2598	m
4 3 1	2694	2708	vw
0 0 4	3032	3042	vw
1 1 4	3252	3246	m
2 0 4	3322	3314	m
3 3 3	3550	3548	m
4 3 3	4229	4229	vw
4 4 3	5001	4978	vw
6 3 2	5072	5048	w
2 7 2	5313	5320	vw
7 3 0	5381	5377	vw
7 1 3	5615	5590	m
6 4 2	5936	5933	w
2 1 6	7310	7321	m
8 1 4	8009	8010	vw
6 6 2	8105	8111	vw
8 4 2	8387	8383	vw
2 0 7	9601	9588	m
6 1 6	9775	9771	vw
11 0 3	9954	9947	w

The compound was analysed for hafnium and water. The hafnium content was determined as HfO_2 by ignition to constant weight, and the amount of water by differential thermal analysis and thermogravimetric analysis using a Mettler Recording Thermoanalyzer. The following results were obtained:

	% HfO_2	% H_2O
Found	63.0	15.8
Calc. for $\text{Hf}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_2$	61.1	15.7

If the remainder is assumed to be sulphate, the compound will have a formula approximating to $\text{Hf}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_2$. Small deviations from this formula could not be determined from the analysis data, since the crystals have a very large unit cell (see below).

Weissenberg and precession photographs corresponding to the reflections $hk0$ – $hk9$ and $0kl$ – $2kl$, respectively, were recorded using $\text{CuK}\alpha$ radiation. The crystals are of hexagonal symmetry, and, since mirror planes are present in the precession photograph $0kl$ but not in the Weissenberg photograph $hk0$, the Laue symmetry group of the crystals should be $6/m$. The only systematically absent reflections are $00l$ with $l = 2n + 1$, which is in accordance with the space groups No. 176 $P6_3/m$ and No. 173 $P6_3$.¹

Accurate cell dimensions were determined from Guinier powder photographs using $\text{Pb}(\text{NO}_3)_2$ as an internal standard and $\text{CuK}\alpha_1$ radiation ($\alpha_{\text{Pb}(\text{NO}_3)_2} = 7.8566$ Å at 21°C).² By means of the programme POWDER³ for IBM 360/50 the following cell parameters were obtained: $a = b = 34.09 \pm 0.016$ Å and $c = 17.66 \pm 0.007$ Å, which gives $V = 1.775 \times 10^4$ Å³. The observed and calculated values of $\sin^2\theta$ are listed in Table 1.

The experimental density determined by the method of flotation (using a mixture of thallium(I) formate, thallium(I) malonate and water) was 3.44 ± 0.03 g/ml, indicating 108 formula units of $\text{Hf}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_2$ per unit cell. The calculated density is then 3.47 g/ml.

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