

Short Communications

On the Crystal Structure of Neodymium Oxalate

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The complex formation in solution between some three-valent lanthanoids and the oxalate ion have been studied at this Institute.¹ In this connection crystal structure analyses of related solid oxalate compounds have been started.

Single crystals of neodymium oxalate were prepared according to Wylie.² Dilute solutions of oxalic acid (50 mM) and neodymium nitrate (15 mM) were slowly added, at the same rate, to water maintained at 50°C. Analyses for neodymium, carbon, and hydrogen gave: 39.3 % Nd, 9.5 % C, and 3.0 % H; calculated for $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$: 39.3 % Nd, 9.8 % C, and 2.7 % H.

The compound $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ crystallizes in the monoclinic system with unit cell dimensions $a = 11.90 \text{ \AA}$, $b = 9.88 \text{ \AA}$, $c = 10.40 \text{ \AA}$, and $\beta = 119^\circ$, determined from rotation and Weissenberg photographs. The systematically absent reflexions ($h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$) show the space group to be $P2_1/c$ (No. 14). The elementary cell contains two formula units. These results are consistent with those reported by previous authors.³

The intensity data were recorded using a crystal with the approximate dimensions $0.1 \times 0.01 \times 0.25 \text{ mm}^3$, mounted in the elongated direction, $[001]$. Non-integrated Weissenberg photographs were taken with $\text{CuK}\alpha$ radiation for the layers $hk0 - hk5$. The intensity of 479 independent reflexions were measured. The spots were rather ill-shaped and some of them were even split. Because of this

we decided upon using the obtained intensity material for preliminary work only.

The positions of the neodymium atoms were determined from a three-dimensional Patterson synthesis, computed with the data reduction and Fourier calculation program, DRF.⁴ The preliminary atomic coordinates and isotropic temperature factor of neodymium were refined together with the interlayer scale factors using the least-squares program LALS.⁴ A three-dimensional ($F_o - F_c$) synthesis based upon the improved neodymium positions was then calculated. Fig. 1 gives a part of the result in a composite diagram showing the relevant peaks around the neodymium atom at (0.190, 0.046, 0.358).

From geometrical considerations, preliminary positions of the oxygen and carbon atoms of the oxalate ions and of three of the five independent water oxygen atoms

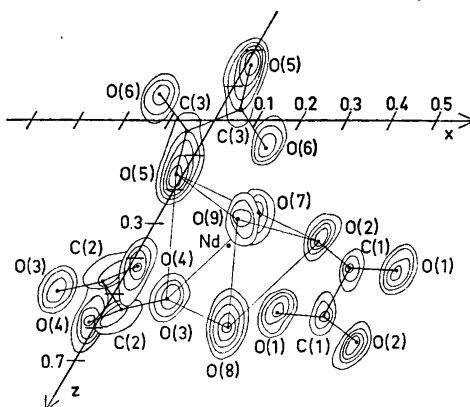


Fig. 1. Part of the electron density in a composite diagram on (010) showing the coordination around the neodymium atom at (0.190, 0.046, 0.358). The contours are drawn at an interval of $1 \text{ e} \cdot \text{\AA}^{-3}$, the zero contours being omitted.

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) $-\text{COO}^-$	0.606	0.080	0.445	3.13
O(2) $-\text{COO}^-$	0.393	0.100	0.357	2.82
O(3) $-\text{COO}^-$	0.866	0.099	0.491	2.89
O(4) $-\text{COO}^-$	0.009	0.145	0.400	2.31
O(5) $-\text{COO}^-$	0.017	0.478	0.345	3.34
O(6) $-\text{COO}^-$	0.160	0.060	0.087	6.41
O(7) H_2O	0.781	0.301	0.218	4.06
O(8) H_2O	0.296	0.310	0.092	4.23
O(9) H_2O	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

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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.