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Crystallographic Study of Neodymium Nitrate Hexahydrate

Crystallographic studies of $Ln(NO_3)_3 \cdot 6H_2O$ compounds have pointed out that rare earth nitrate hexahydrates, Ln = Pr, Nd, and Sm, are isotypic. However, their triclinic crystals were not described and no indexed X-ray diffractograms were published. In addition no crystalline parameter values were proposed for $Nd(NO_3)_3 \cdot 6H_2O$. Known results are shown in Table I. Consequently, we tried to index the neodymium compound powder diffractogram with average parameters corresponding to praseodymium and samarium compounds, bearing in mind the lanthanidic contraction. The results obtained were unsatisfactory and the need for a complete $Nd(NO_3)_3 \cdot 6H_2O$ crystallographic study was obvious.

Preparation and Morphology of Crystals

Starting materials for the synthesis are:

—neodymium oxyde of 99.99% purity previously calcinated at 1300 K for 24 hr.

—pure 49% nitric acid "pro analyst" filtered through Millipore Fluoropore FH, 0.5-μm-porosity filter;

—demineralized water of 4×10^{-6} ohm^{-1} cm^{-1} conductivity filtered through 0.1-μm-porosity Millipore filter.

Fifteen grams of powdered Nd_2O_3 were gradually dissolved at 340 K in 400 ml of nitric acid. The solution was filtered and reduced to 100 ml by slow evaporation then thermostatically cooled to 278 K at a rate of 0.5 K min^{-1}. The resulting syrupy solution was then reheated to 296 K and solidified after 48 hr. The agglomerated mass was dissolved with a minimum of water and heated back to 323 K. The crystals collected after four such thermal cycles were washed in dichloroethane (*4*), dried, and analyzed. Part of the crystals with stoichiometric composition were preserved for seeding nuclei. Seeding and final growth of crystals took place in thermostated surroundings at 306 K. Chemical and radiocrystallographic analyses of the final crystals were identical to those of seeding crystals.

Mauve-colored crystals several millimeters in size were obtained and most of them were elongated along [001] and flattened along [100]. Their morphology was studied with a two-circle optical goniometer NEDINSCO. The precision measurements were sometimes limited, the reflected image being disturbed by small surface irregularities. This is true in particular for $\{h\ k\ 0\}$ forms with growth striations parallel to [001]. The most frequent form of these crystals is represented in Fig. 1. This morphology is compatible with the centrosymmetric triclinic system.

X-Ray Powder and Unit-Cell Data

The triclinic system was confirmed by rotation, Weissenberg, precession, and cone–axis films. The existence of reciprocal vectors with extremely close modulus obliged us to carry out a powder diffractogram under the best possible conditions in order to index it without any ambiguity. The powder diffraction patterns of crushed single crystals were obtained with a Philips PW 1050/25 counter diffractometer using Ni-filtered copper radiation (λ = 1.5418 Å). Silicon was used as an internal standard. The powder diffraction data are recorded in Table II. Unit-cell constants were refined by a classical least-squares program (*5*). Several successive refinement cycles were carried out. During the first stage, 15 streaks

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TABLE I

CRYSTAL DATA FOR $Ln(NO_3)_3 \cdot 6H_2O$ WITH Ln = Pr, Nd, Sm

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	V (Å^3)
$Pr(NO_3)_3 \cdot 6H_2O$ (*1*)	9.19(3)	11.70(4)	6.78(3)	89.0(5)	110.7(5)	110.2(5)	635.4
(*2*)	9.23(3)	11.77(4)	6.78(2)	91.17(8)	110.72(5)	69.5(1)	640.8
$Nd(NO_3)_3 \cdot 6H_2O$ (this work)	9.308(1)	11.745(1)	6.789(1)	91.26(1)	112.03(1)	109.11(1)	641.19
$Sm(NO_3)_3 \cdot 6H_2O$ (*3*)	9.20	11.7	6.78	91	112	109	632

were indexed with certainty. Supplementary streaks were added in every new cycle. Refined unit-cell data at 293 K from the first 90 streaks of the powder diffraction pattern are given in Table I. In order to test the quality of our results, we evaluated the reliability of our powder spectrum indexing. Calculation of the figure of merit (*6*) gives the satisfying value of F_{30} = 104(0.006,48). This result compares favorably with the high-quality criterion for triclinic compounds (*7*).

The experimental density, measured at 293 K by xylene displacement in a picnom-

TABLE II

PORTION OF POWDER DIFFRACTION DATA OF $Nd(NO_3)_3 \cdot 6H_2O$

d_{obsd} (Å)	d_{calcd} (Å)	h	k	l	I/I_0	d_{obsd} (Å)	d_{calcd} (Å)	h	k	l	I/I_0
10.96	10.95	0	1	0	11	3.269	3.267	1	1	$\bar{2}$	25
8.05	8.04	1	0	0	73	3.219	3.216	$\bar{1}$	1	2	4
8.02	8.01	1	$\bar{1}$	0	79	3.151	3.150	2	0	$\bar{2}$	4
6.31	6.30	1	0	$\bar{1}$	18	3.121	3.124	0	1	$\bar{2}$	7
6.21	6.21	0	0	1	31	3.003	3.002	2	$\bar{2}$	1	4
5.824	5.828	0	1	$\bar{1}$	22	2.935	2.935	1	$\bar{4}$	0	20
5.764	5.756	$\bar{1}$	1	1	35	2.914	2.914	0	2	$\bar{2}$	13
5.562	5.556	1	$\bar{2}$	0	100	2.877	2.878	$\bar{2}$	2	2	7
5.480	5.473	0	2	0	79	2.868	2.864	0	1	2	6
5.208	5.205	1	1	$\bar{1}$	27	2.855	2.854	3	$\bar{1}$	0	13
5.052	5.053	0	1	1	5	2.850	2.850	3	$\bar{2}$	0	12
4.485	4.489	0	2	$\bar{1}$	13	2.778	2.778	2	$\bar{4}$	0	7
4.388	4.391	$\bar{1}$	2	1	24	2.751	2.751	$\bar{3}$	3	1	16
4.346	4.348	1	$\bar{1}$	1	5	2.736	2.736	0	4	0	7
4.316	4.314	2	$\bar{1}$	0	5	2.670	2.671	3	$\bar{3}$	0	8
4.255	4.250	2	0	$\bar{1}$	11	2.647	2.649	$\bar{2}$	4	1	8
4.160	4.165	1	0	1	9	2.620	2.620	3	0	$\bar{2}$	13
4.005	4.006	2	$\bar{2}$	0	15	2.592	2.589 2.589	$\bar{3}$ 1	2 $\bar{2}$	2 2	4
3.914	3.913 3.913	1 1	2 2	0 $\bar{1}$	27	2.582	2.583	2	1	1	7
3.805	3.805	0	2	1	24	2.533	2.534	$\bar{2}$	3	2	4
3.648	3.648	0	3	0	9	2.518	2.520	1	3	$\bar{2}$	8
3.401	3.400	0	3	$\bar{1}$	8	2.460	2.460	2	3	$\bar{1}$	7
3.393	3.393	1	0	$\bar{2}$	7	2.451	2.451	$\bar{1}$	3	2	9
3.331	3.329	$\bar{1}$	3	1	22	2.434	2.433	3	1	$\bar{2}$	11
						2.409	2.410 2.410	3 1	1 4	0 $\bar{1}$	17
						2.398	2.398	3	$\bar{4}$	0	10

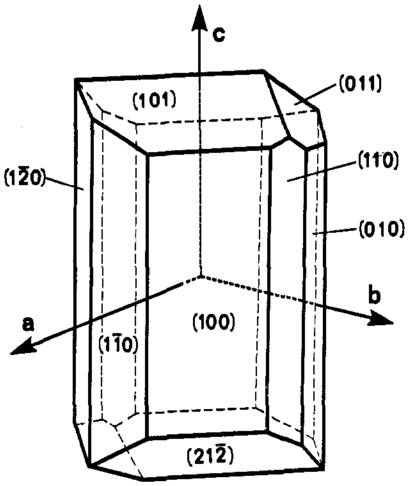

FIG. 1. Morphology of a $Nd(NO_3)_3 \cdot 6H_2O$ idealized crystal.

eter, was found to be $d_{exp} = 2.26$ g cm^{-3}. The calculated density for $Z = 2$ formula units is $d_{th} = 2.270$ g cm^{-3}. This confirms the $P\bar{1}(C_i^1)$ space group since an optical absorption study at 4.2 K reveals only one site for the neodymium atom (*8*).

Conclusion

The limited crystallographic results for $Ln(NO_3)_3 \cdot 6H_2O$ (Ln = Pr, Nd, and Sm) compounds can be mainly explained by two reasons:

—the difficult preparation of really stoichiometric single crystals for X-ray and optical measurements. Excess of NO_3 group was often observed. This fact, already mentioned (*3*, *4*, *9*), is probably due to "nitrosolvates" (*10*).

—the almost equal values of periods along some directions involve some confusion during the spectrum indexing. For instance, after the lanthanidic contraction, the a unit-cell parameter should be superior to the values given in Table I. Probably this is due to a confusion between periods along $[100]^* = 0.1243$ and $[1\bar{1}0]^* = 0.1248$.

However, the isomorphism of $Ln(NO_3)_3 \cdot 6H_2O$ compounds is evident for Ln = Pr, Nd, and Sm. We can easily compare them with the $Ln(HCO_3)_3 \cdot 6H_2O$ compounds. Rohrbaugh and Jacobson (*11*) defined the unit cell of $Ho(HCO_3)_3 \cdot 6H_2O$ as follows: $a = 9.18(2)$, $b = 11.59(1)$, $c = 6.73(1)$ Å, $\alpha = 88.87(6)$, $\beta = 112.45(8)$, and $\gamma = 71.54(6)°$; $V = 619.6$ Å^3 for $Z = 2$ formula units. These values are in agreement with ours for $Nd(NO_3) \cdot 6H_2O$, according to the position of Nd and Ho elements in the rare earth group and the different anions involved in the two compounds.

References

1. G. F. VOLODINA, I. M. RUMANOVA, AND N. V. BELOV, *Sov. Phys. Crystallogr.* **6**, 741 (1962).
2. C. C. FULLER AND R. A. JACOBSON, *Cryst. Struct. Commun.* **5**, 349 (1976).
3. V. I. IVERONOVA, V. P. TARASOVA, AND Z. K. ZOLINA, *Zh. Fiz. Khim.* **29**, 314 (1955).
4. A. P. POPOV AND K. E. MIRONOV, *Rev. Roum. Chim.* **13**, 765 (1968).
5. D. E. WILLIAMS, "LCR-2, a Fortran Lattice Constant Refinement Program," U.S. Atomic Energy Commission Report IS-1052, Institute for Atomic Research, Ames, Iowa (1964).
6. G. S. SMITH AND R. L. SNYDER, *J. Appl. Crystallogr.* **12**, 60 (1979).
7. G. S. SMITH, *J. Appl. Crystallogr.* **9**, 424 (1976).
8. P. CARO, D. R. SVORONOS, E. ANTIC, AND M. QUARTON, *J. Chem. Phys.* **66**, 5284 (1977).
9. K. E. MIRONOV, A. P. POPOV, AND E. M. MOROZ, *Russ. J. Inorg. Chem.* **14**, 165 (1969).
10. K. E. MIRONOV, A. P. POPOV, AND E. D. KARASEVA, *Soc. Cer. Chim. Roman.* **17**, 377 (1969).
11. W. J. ROHRBAUGH AND R. A. JACOBSON, *Inorg. Chem.* **13**, 2535 (1974).

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