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Crystal Structure of Neodymium and Gadolinium Dihydroxy-nitrate, $Ln(OH)_2NO_3$

D. F. MULLICA, E. L. SAPPENFIELD, AND DAVID A. GROSSIE

Departments of Chemistry and Physics, Baylor University,
Waco, Texas 76798

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The crystal structures of $Nd(OH)_2NO_3$ and $Gd(OH)_2NO_3$ have been determined from single-crystal X-ray diffraction techniques. Crystallization occurs in monoclinic space group $P2_1$ (No. 4) with a = 6.420(1), b = 3.838(1), c = 7.746(2) Å, and β = 98.18(2)° for $Nd(OH)_2NO_3$ and a = 6.340(2), b = 3.715(1), c = 7.728(2) Å, and β = 96.95(2)° for $Gd(OH)_2NO_3$. The structures were refined to residual indices of 0.025 and 0.048, respectively, using 372 and 360 unique reflections. The lanthanoid metal atoms are nine-coordinated, having a tricapped trigonal prismatic geometry. The nitrate counter ion acts as a bidentate ligand, while the two hydroxide oxygen atoms link symmetry-related lanthanoid atoms, forming two-dimensional layers.

Introduction

Hydrothermal methods have been extensively used in the crystal growth of lanthanoid compounds. Some of these compounds can have high symmetry, an example being the hexagonal lanthanoid (*Ln*) trihydroxide series (*1*). There is no hydrogen bonding associated with these nine-coordinated $Ln(OH)_3$, where *Ln* = La, Ce, . . . Yb. Only the last member of the lanthanoid series, cubic $Lu(OH)_3$ which is six-coordinated, reveals hydrogen bonding (*2*). In the late 1960s a series of papers (*3–9*) reported the synthesis by hydrothermal methods and the single-crystal analysis of $Ln(OH)_2Cl$ (*Ln* = La–Er, Y). The structure of these dihydroxychloride complexes was described as a series of two-dimensional layers connected by O–H · · · Cl hydrogen bonds. This substitution of a chloride into the $Ln(OH)_3$ structure has the effect of reducing the dimensionality of the crystal lattice. Many other substituted-anion complexes, such as $Pr(OH)CO_3$, $Ln[(OH)_{1-x}F_x]$ (*Ln* = Y, Pr, Nd, Sm–Gd, Dy–Lu), and $Ln(OOCH)_3$ (*Ln* = La–Er), have also been synthesized and studied (*10–12*). The preparation of lanthanoid dihydroxynitrates and the determination of their lattice parameters by means of powder X-ray diffraction have been presented by Haschke (*13*), and the monoclinic phase was thought to be isostructural with $Ln(OH)_2Cl$. In the present work, the structural refinements of two members of the dihydroxynitrate series, $Nd(OH)_2NO_3$ and $Gd(OH)_2NO_3$, are discussed.

Experimental

Single crystals of the title compounds were synthesized by hydrothermal aging of a hydrous gel which was prepared by dis-

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TABLE I

EXPERIMENTAL AND STATISTICAL SUMMARIES

	$Nd(OH)_2NO_3$	$Gd(OH)_2NO_3$
a (Å)	6.420(1)	6.340(2)
b	3.838(1)	3.715(1)
c	7.746(2)	7.728(2)
β (°)	98.18(2)	96.95(2)
V (Å^3)	188.9(1)	180.7(2)
Space group	$P2_1$	$P2_1$
MW	240.26	253.27
Z	2	2
$F(000)$	218	226
D (mg m^{-3})	4.224	4.654
Cryst. dim. (mm)	0.16 × 0.164 × 0.088	0.192 × 0.198 × 0.3
μ (Mo$K\alpha$) (mm^{-1})	13.71	18.34
$\Delta\omega$ (°) (ω-2θ scan)	1.50 + 0.35 tan θ	1.25 + 0.35 tan θ
$\Delta\theta$ (°)	1.5–25.0	1.5–25.0
Scan limits (°min^{-1})	0.48–3.35	0.38–3.35
Trans. fact. range	0.147–0.333	0.044–0.172
R_{int}	0.032	0.039
Unique refl.	372	360
Sys. abs.	$0k0$, $k = 2n + 1$	$0k0$, $k = 2n + 1$
R	0.025	0.048
Rw	0.025	0.049
GnFt (Σ_2)	1.484	2.643
$g(e^{-2})(10^{-6})$	4.1(1)	4.4(2)
Max$[\Delta\xi i/\sigma(\xi i)]$ (10^{-3})	4.3	4.2
Residual (e Å^{-3})		
max.	1.6(3)	4.1(5)
min.	−2.1(3)	−4.4(5)

solving the appropriate oxide in nitric acid and subsequent neutralization by ammonium hydroxide. Crystals used in the X-ray analysis were selected on the basis of optical quality and mounted on an Enraf-Nonius CAD-4F automated diffractometer equipped with a Si(Li) solid-state detector (*14*). The energy dispersive detector was employed to obtain X-ray fluorescence data from the same sample from which single-crystal data were collected. The lanthanoid elements were quickly verified qualitatively from the appropriate $L_{\alpha 1}$, $L_{\beta 1}$, and $L_{\beta 2}$ lines. Cell constants (presented in Table I) were derived from the setting angles of 25 accurately centered reflections. Intensity data were measured using the $\omega - 2\theta$ scan technique in the range and scan limits listed in Table I. All reflections having less than 75 counts above background during a fast prescan (3.35° min^{-1}) were assumed to be unobserved. Selected reflections (0,1,3 and 2,0,0 for $Nd(OH)_2NO_3$ and 3,0,$\bar{4}$ and $\bar{1}$,1,0 for $Gd(OH)_2NO_3$) were monitored periodically (2 h) and revealed only random deviations (<1.2 and <0.6%, respectively) from mean intensities. Lorentz, polarization, and absorption corrections were applied and equivalent reflections were averaged.

The heavy lanthanoid atoms were located by Patterson techniques, and the remaining light atoms by difference Fourier mapping. The model was then refined by the full-matrix least-squares technique employing anisotropic thermal parameters and a secondary extinction correction. The minimized quantity in the refinement program (*15*) was $\Sigma w(\|F_o\| - |F_c\|)^2$, where the weight ($w$) is the reciprocal of the standard deviation on F_o squared, $w = \sigma^{-2}(F_o)$. Refinement was terminated when all parameters had stabilized and the maximum shift-to-error ratio was less than 0.005. The final R-factors for each structure were $R_1 = 0.025$ and $R_2 = 0.025$ for $Nd(OH)_2NO_3$ and $R_1 = 0.048$ and $R_2 = 0.049$ for $Gd(OH)_2NO_3$, where $R_1 = \Sigma \|F_o| - |F_c\|/\Sigma |F_o|$ and $R_2 = \Sigma\sqrt{w}\|F_o| - |F_c\|/\Sigma\sqrt{w}|F_o|$. Final difference Fourier maps revealed some density in the vicinity of the heavy atoms, which is common for the heavy lanthanoid elements. Elsewhere, the electron density maps were virtually featureless, revealing only a random fluctuating background. Atomic scattering factors and anomalous dispersion correction factors were taken from the International Tables (*16*). Crystal data, experimental conditions, and statistical data are listed in Table I. Final atomic positions, equivalent isotropic thermal factors, selected bond and contact distances, and bond angles are presented in Tables II[1] and III.

TABLE II

POSITIONAL PARAMETERS ($x, z \times 10^4$ AND $y \times 10^3$) AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\times 10^4$ FOR *Ln* AND $\times 10^3$ FOR N AND O) FOR $Nd(OH)_2NO_3$ AND $Gd(OH)_2NO_3$

Atom	x	y	z	U_{eq}[a]
Nd	2663(1)	257	955(1)	77(1)
N	2237(16)	646(3)	4363(13)	13(3)
O(1)	1216(10)	758(6)	−738(8)	9(2)
O(2)	5240(11)	786(4)	1436(8)	9(2)
O(3)	1343(11)	768(5)	2891(8)	18(2)
O(4)	3420(15)	390(3)	4307(12)	27(3)
O(5)	1911(13)	799(4)	5726(8)	21(2)
Gd	2631(2)	259	914(1)	112(2)
N	2260(34)	621(8)	4325(30)	23(7)
O(1)	1223(21)	722(4)	−757(19)	1(3)
O(2)	5194(22)	788(10)	1398(19)	16(4)
O(3)	1288(22)	778(9)	2850(19)	25(4)
O(4)	3462(30)	377(6)	4176(28)	26(6)
O(5)	1914(26)	723(8)	5679(19)	22(5)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33} + U_{12}\cos\gamma + U_{13}\cos\beta + U_{23}\cos\alpha)/3$.

Discussion

The experimental lattice parameters for isomorphic $Nd(OH)_2NO_3$ and $Gd(OH)_2NO_3$ are in good agreement with those reported by Haschke (*13*). However, the lanthanoid atoms are nine-coordinated (shown in Figs. 1a and b), as opposed to the suggested isostructural relationship of $Ln(OH)_2NO_3$ with $Ln(OH)_2Cl$ where lanthanoid atoms are eight-coordinated (*13*). This has also been reported by Lundberg and Skarnulis in their analysis of the structure of $Pr(OH)_2NO_3$ (*17*). The average respective Nd—O and Gd—O distances of 2.528 and 2.472 Å are quite reasonable when compared to the sum of radii given by Shannon, 2.53 and 2.48 Å (*18*). Further, all Nd- and Gd-oxygen bond lengths are well within the range of values compiled in BIDICS (*19*) and are in close agreement with the distances found for the lanthanoid trihydroxides (*20*). The coordination polyhedron is a tricapped trigonal prism (*D3h*), which is imperceptively distorted when compared to an idealized model (*21*). The threefold axis of the tricapped trigonal prism lies parallel to the *b* axis of the unit cell. The hydroxyl oxygen

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[1] See NAPS document No. 04373 for 10 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15.00. Foreign orders add $4.50 for postage and handling for the first 20 pages and $1.00 for each additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE III

SELECTED BOND DISTANCES (Å) AND ANGLES (°) FOR $Nd(OH)_2NO_3$ AND $Gd(OH)_2NO_3$

	$Nd(OH)_2NO_3$	$Gd(OH)_2NO_3$		$Nd(OH)_2NO_3$	$Gd(OH)_2NO_3$
Ln—O(1)	2.435(21)	2.267(16)	N—O(3)	1.289(13)	1.360(23)
	2.471(6)	2.435(9)	N—O(4)	1.248(14)	1.197(22)
	2.430(22)	2.485(16)	N—O(5)	1.250(18)	1.158(22)
Ln—O(2)	2.444(15)	2.387(26)	Av	1.262	1.238
	2.442(6)	2.388(9)			
	2.612(16)	2.548(26)			
Ln—O(3)	2.617(14)	2.543(20)	O(3)—N—O(4)	116.9(12)	118.2(18)
	2.679(19)	2.643(27)	O(3)—N—O(5)	118.1(14)	120.1(24)
Ln—O(4)	2.623(8)	2.550(14)	O(4)—N—O(5)	125.0(12)	121.7(22)
Av	2.528	2.472	Av	120.0	120.0

atoms account for six of the vertices, and two of the nitrate oxygen atoms in a bidentate manner occupy the remaining three vertices (see Fig. 1a).

The nitrate counter ion in both neodymium and gadolinium dihydroxynitrate is planar (maximum deviation 0.011 and 0.001 Å, respectively), with only minor distortions in the bond distances and angles around the central nitrogen atom. The angular distortion may be due to the bidentate bonding through O(3) and O(4) to the lanthanoid atoms. In each case, the O(3)–N–O(4) angle is decreased from the expected ideal 120° to 116.9(12)° and 118.2(18)°, respectively. The average nitrogen–oxygen bond distances in both structures (1.262 and 1.238 Å in Nd- and $Gd(OH)_2NO_3$, respectively) are also in good agreement with the summation of ionic radius values obtained from the work of Shannon, 1.25 Å (*18*).

The layered structure is similar to that observed in yttrium and other rare-earth dihydroxychlorides (*3*–*9*). A stereodrawing of the layers viewed down the *b* axis is presented in Fig. 2. Each of the hydroxyl-oxygen atoms has a tetrahedral geometry, being bonded to a hydrogen atom and three lanthanoid atoms. The *Ln*–OH bonding forms a two-dimensional structure which

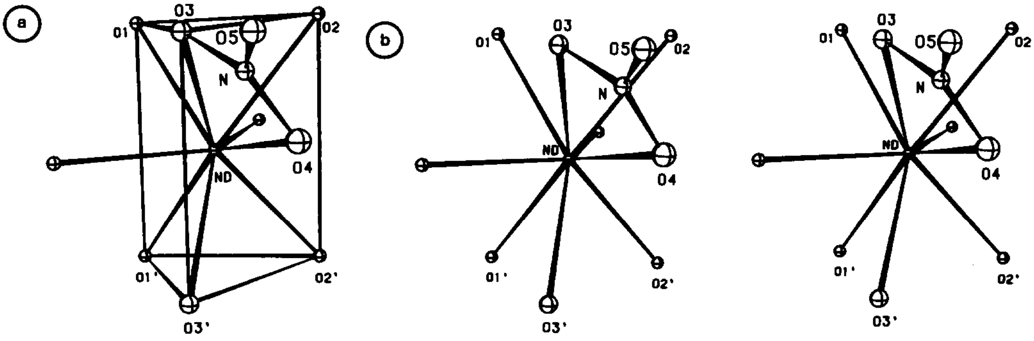

FIG. 1. $Nd(OH)_2NO_3$. (a) A figure showing tricapped prismatic geometry. (b) A stereodrawing of the lanthanoid atom coordination sphere with atoms drawn at 20% thermal probability.

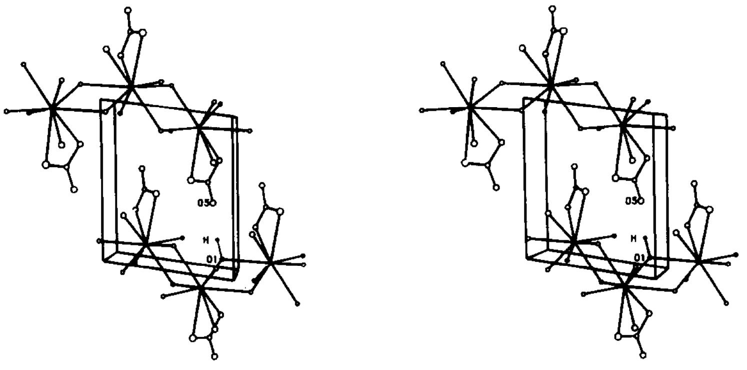

FIG. 2. *Ln*$(OH)_2NO_3$. A stereodrawing of the unit cell showing the layered structure, looking down the *b* axis (*a* axis horizontal and *c* axis vertical) so as to present a view of where hydrogen bonding could occur between atoms O(1) and O(5). The position of the hydrogen atom attached to O(1) was obtained from a geometric calculation and is shown to emphasize where hydrogen bonding could occur.

lies parallel to the ab face of the crystal. The closest contact between symmetry related layers is from hydroxyl–oxygen O(1) to nitrate–oxygen O(5), with distances of 2.842(8) and 2.841(15) Å in the Nd and Gd complexes, respectively. The strength of hydrogen bonding has been shown by Brown (*22*) to be related to the O · · · O interatomic contact distance, which may range from 2.4 to 2.7 Å for a strong hydrogen bond and from 2.7 to approximately 3.1 Å for a weak hydrogen bond. A second consideration with regard to hydrogen bond strength is the O—H · · · O angle, which is ideally 180° for a strong hydrogen bond and as small as 130° for a weak hydrogen bond. From geometric calculations using an O—H distance of 1.0 Å, the hydrogen atom attached to O(1) was found to be directed toward O(5), with an O(1)—H · · · O(5) angle of 172.2° and 169.4° for the two complexes, respectively. The experimental interatomic contact distances and angles indicate that hydrogen bonding could occur between O(1) and O(5).

Infrared studies are often used to detect the presence of hydrogen bonding. Evidence derived from an IR spectrum is the downshift of the O—H stretching frequency from its normal position at 3600 cm^{-1} and the extensive broadening of the absorption peak. The amount of the downward shift is indicative of the strength of a hydrogen bond. In the IR spectra (pressed-disk method) of the Nd– and $Gd(OH)_2NO_3$, the O—H stretching frequency absorption peaks are split into doublets due to the nonequivalence of the two hydroxyl groups. The absorption peaks occur at 3547 and 3533 cm^{-1} for $Nd(OH)_2NO_3$ and 3569 and 3550 cm^{-1} for $Gd(OH)_2NO_3$, and in each case the peaks are very sharp. The lack of appreciable downshifting of these absorptions and the sharpness of the peaks would indicate that there is not any substantial hydrogen bonding present.

The obvious contrast between the structural and infrared evidence regarding the existence of hydrogen bonding in Nd– and $Gd(OH)_2NO_3$ denotes there is a definite need for additional research of other lanthanoid dihydroxynitrate complexes.

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