Inorganica Chimica Acta, 110 (1985) 83–86

Crystal Structures of Neodymium and Holmium Trifluoromethanesulfonate Enneahydrated

C. O. PAIVA SANTOS, E. E. CASTELLANO

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13.560 São Carlos (SP), Brazil

L. C. MACHADO and G. VICENTINI

Instituto de Química, Universidade de São Paulo, Caixa Postal 20.780, 01498 São Paulo (SP), Brazil

Received January 14, 1985

Abstract

The crystal structures of the title compounds, $[Ln(H_2O)_9](CF_3SO_3)_3$ with Ln = Nd^{3+} and Ho^{3+}, were determined by three-dimensional X-ray diffraction methods and refined anisotropically to final R values of 0.026 and 0.030 from 636 and 676 reflections with $I > 3\sigma(I)$, respectively. The structures are essentially isomorphous; the space group is $P6_3/m$, $Z = 2$. Unit cell dimensions are $a = 13.851(4)$, $c = 7.460(3)$ Å and $a = 13.570(2)$, $c = 7.577(1)$ Å for the Nd and Ho complexes. The cation is coordinated to the oxygen atoms of nine water molecules, which form a tricapped trigonal prism of crystallographic point symmetry $\bar{6}$ (C_{3h}). There are two different Ln–O distances in the coordination polyhedron: 2.568(3) and 2.451(2) Å in the Nd complex and 2.526(4) and 2.367(3) Å in the Ho one. All water molecule oxygens are hydrogen-bonded to two O-atoms of two different anions.

Introduction

Lanthanide complexes having trifluoromethanesulfonate as anions have been prepared and extensively studied by several physicochemical methods [1]. These compounds are normally used to prepare complexes of lanthanides with organic ligands. All previous structures of lanthanide complexes determined in our laboratory show some degree of disorder that restricts the accuracy of the structural model from which interatomic distances are determined. The title compounds are the first exception to this rule, providing therefore the means for accurate determinations of Nd^{3+}–O and Ho^{3+}–O interatomic distances. With this aim and to unambiguously determine the predicted coordination number nine [2] and the non-coordinating character of the $CF_3SO_3^-$ anion, a three-dimensional X-ray analysis of the title complexes was undertaken.

Experimental

Crystal data are given in Table I. Intensities were measured on an Enraf-Nonius CAD-4 diffractometer by the ω–2θ scan technique, with scan rates between 5.0 and 20.0° min^{-1} determined from a fast prescan on each reflection, using graphite monochromated MoKα (λ = 0.71073 Å) radiation. The intensities of three standard reflections were essentially constant over the duration of both experiments. Data were corrected for Lorentz and polarization effects but not for absorption or extinction.

The compounds were prepared by treating an aqueous suspension of hydrated basic carbonates ($Ln(OH)(CO_3)\cdot xH_2O$) with concentrated trifluoromethanesulfonic acid. The solution was filtered, evaporated to near dryness in a water bath and left to stand in a desiccator over anhydrous calcium chloride to crystallize.

Structure Solution and Refinement

Nd Complex

Systematic extinctions were consistent with space groups $P6_3$ or $P6_3/m$. Unit cell volume and observed density provided the value $Z = 2$. With this information a Patterson map was readily interpreted, indicating space group $P6_3/m$ and a heavy atom in special position c (1/3, 2/3, 0; 2/3, 1/3, 0) of point symmetry $\bar{6}$. The rest of the non-hydrogen atoms were obtained from the usual alternate cycles of difference maps and isotropic least squares, which converged to $R = 0.054$. At this stage all hydrogen atoms were obtained from a difference map and included in the molecular model with isotropic temperature factors equal to that of the atom they were bonded to. Anisotropic refinement of all non-hydrogen atoms, with O–H distances constrained to the value 0.950(1) Å [3] and weighting scheme $w = 1/\sigma^2(F)$ ($\sigma^2(F)$ estimated from counting statistics), gave the final values $R = 0.026$ and $R_w = 0.022$.

0020-1693/85/$3.30

TABLE I. Summary of Data Collection and Processing Parameters.

Parameter	Nd	Ho
Space group	$P6_3/m$	$P6_3/m$
Cell constants	$a = 13.851(4)$	13.570(2)
	$c = 7.460(3)$	7.577(1) Å
	$V = 1240(1)$	1208(1) $Å^3$
Crystal size mm (approx.)	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Molecular formula	$NdC_3H_{18}O_{18}F_9S_3$	$HoC_3H_{18}O_{18}F_9S_3$
Molecular weight	753.6	774.3
Molecules per cell	$Z = 2$	2
Density (calcd.)	2.02	2.13 g cm^{-3}
Absorption coefficient	$\mu = 2.32$	3.48 mm^{-1}
Collection range	$0 < \theta < 28°$	$0 < \theta < 28°$
Total data collected	2098	2400
Data with $I > 3\sigma(I)$	636	676
$R = \|\|F_o\| - \|F_c\|\|/\|F_o\|$	0.026	0.030
R_w	0.022	0.022
Weights	$1/\sigma^2(F_o)$	$1/\sigma^2(F_o)$

Ho Complex

The structure was refined with conditions identical to those of the previous case starting from the same positional and thermal parameters. Some relevant information is included in Table I. The final R-values are $R = 0.030$ and $R_w = 0.022$.

In both crystals the function minimized was $\Sigma(|F_o| - |F_c|)^2 w$ by the full-matrix technique, until all parameter shifts were less than 1% of the corresponding standard deviation. Scattering form factors for non-H atoms were taken from [4]; corrections for anomalous dispersion from [5] and form factors for H-atoms from [6]. Most calculations were performed on a VAX computer with the SHELX76 systems of programs [3]. Final positional parameters and equivalent isotropic B values [7] are given in Tables II and III. Interatomic distances and bond angles are given in Tables IV and V.

TABLE II. Atomic Coordinates and B_{eq}'s ($Å^2$) for the Nd Complex.

Atom	x/a	y/b	z/c	B_{eq}
Nd	1/3	2/3	1/4	2.14(1)
O(1)	0.1408(3)	0.4893(3)	1/4	3.6(1)
O(2)	0.3354(2)	0.5431(2)	0.4833(4)	3.31(8)
S(1)	0.3812(1)	0.3190(1)	1/4	3.11(4)
O(3)	0.4320(3)	0.2503(3)	1/4	4.1(1)
O(4)	0.3987(2)	0.3812(2)	0.4123(4)	4.51(9)
C(1)	0.2313(6)	0.2197(7)	1/4	5.8(3)
F(1)	0.1764(3)	0.2742(4)	1/4	8.4(2)
F(2)	0.2048(3)	0.1573(3)	0.3923(5)	10.8(2)
H(11)	0.104(2)	0.452(2)	0.357(2)	3.599
H(21)	0.364(2)	0.494(2)	0.494(5)	3.309
H(22)	0.285(2)	0.510(3)	0.581(3)	3.309

TABLE III. Atomic Coordinates and B_{eq}'s ($Å^2$) for the Ho Complex.

Atom	x/a	y/b	z/c	B_{eq}
Ho	1/3	2/3	1/4	2.21(1)
O(1)	0.1408(4)	0.4875(3)	1/4	3.6(1)
O(2)	0.3350(2)	0.5445(2)	0.4716(4)	3.08(8)
S(1)	0.3837(1)	0.3162(1)	1/4	3.11(5)
O(3)	0.4438(4)	0.2542(4)	1/4	4.4(2)
O(4)	0.3961(3)	0.3779(3)	0.4096(4)	4.4(1)
C(1)	0.2322(8)	0.2052(8)	1/4	6.1(3)
F(1)	0.1700(4)	0.2561(5)	1/4	9.0(2)
F(2)	0.2112(3)	0.1431(3)	0.3901(6)	10.7(2)
H(11)	0.099(3)	0.446(3)	0.356(3)	3.599
H(21)	0.361(3)	0.489(2)	0.466(5)	3.099
H(22)	0.286(3)	0.510(3)	0.575(3)	3.099

TABLE IV. Interatomic Bond Distances (Å).

	Ln = Nd	Ln = Ho
Ln–O(1)	2.568(3)	2.526(4)
Ln–O(2)	2.451(2)	2.367(3)
S(1)–O(3)	1.439(3)	1.435(4)
S(1)–O(4)	1.435(3)	1.432(3)
S(1)–C(1)	1.830(7)	1.8843(9)
C(1)–F(1)	1.311(8)	1.33(1)
C(1)–F(2)	1.301(5)	1.296(5)

Results and Discussion

Figure 1 is a stereoscopic projection of a unit cell contents. The cation is sited on the $\bar{6}$ fold-axis and is coordinated to the oxygen atoms of nine water molecules, only two of which are crystallographically

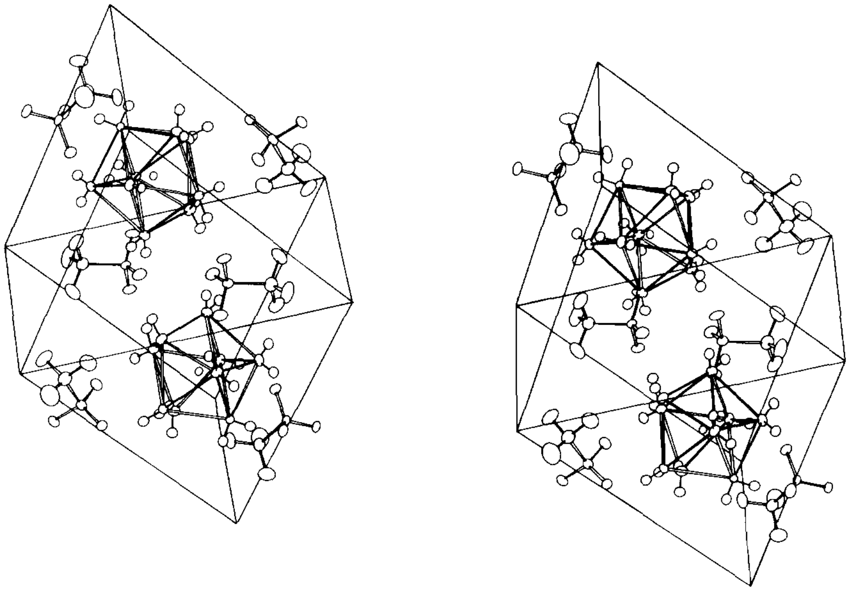

Fig. 1. Stereoscopic projection of a unit cell contents.

TABLE V. Interatomic Bond Angles (°).

	Ln = Nd	Ln = Ho
O(1)–Ln–O(2)	72.6(1)	72.1(1)
O(2)–Ln–O(2)	75.1(1)	75.3(1)[a]
O(2)–Ln–O(2)	90.5(1)	90.3(1)[b]
H(11)–O(1)–H(12)	114.3(8)	109.1(9)
H(21)–O(1)–H(22)	93(3)	95(3)
O(3)–S(1)–O(4)	113.9(1)	114.0(1)
O(4)–S(1)–O(4)	115.1(3)	115.2(4)
O(3)–S(1)–C(1)	104.4(3)	104.5(4)
O(4)–S(1)–C(1)	103.8(2)	103.6(2)
F(1)–C(1)–S(1)	109.5(5)	108.3(6)
F(2)–C(1)–S(1)	109.7(4)	108.9(5)
F(1)–C(1)–F(2)	109.3(5)	110.4(5)
F(2)–C(1)–F(2)	109.4(6)	110.0(7)

[a] O(2)–O(2) normal to $\bar{6}$. [b] O(2)–O(2) parallel to $\bar{6}$.

TABLE VI. Interatomic Distances in the Coordination Polyhedra (Å).

Ln–O distances			
Ln	O(1)	O(2)	Weighted mean value
Nd	2.568(3)	2.451(2)	2.495
Ho	2.526(4)	2.367(3)	2.427
c-edges			
Ln		O(2)	O(2)
Nd	O(1)	2.973(4)	2.745(4)
Ho	O(1)	2.884(4)	2.691(4)
h-edges			
	Nd	Ho	
O(2)–O(2)	2.988(4)	2.891(4)	
ν-edges			
	Nd	Ho	
O(2)–O(2)	3.480(5)	3.357(6)	

independent. The three equatorial O(1) atoms are located on the mirror plane at $Z = 1/4$ forming an equilateral triangle which is rotated (4.9° in Nd and 4.2° in Ho) from the ideal D_{3h} tricapped-trigonal-prism (TCTP). This can be appreciated by the fact that there are two different distances between, say, O(1) and two neighbouring equivalent O(2) atoms (Table VI). This small distortion, which effectively lowers the symmetry of the TCTP to C_{3h}, is probably due to steric requirements of the hydrogen bonds in which both, O(1) and O(2) are involved (Table VII).

Interatomic distances in the coordination polyhedra are given in Table VI. In both structures the prismatic Ln–O(2) distance is shorter than the equatorial Ln–O(1) one. Ln–O(2) is 0.08 Å shorter in the Ho complex, a value close to the difference in ionic radii between Nd^{3+} and Ho^{3+} of 0.09 Å. The equatorial contraction is, however, half that of the prismatic one (0.04 Å). This effect has also been observed in structures of Y^{3+} and Pr^{3+} ennehydrated having BrO_3^- or $C_2H_5SO_4^-$ as anion [8]. In all cases the effect seems to be due to the fact that the O(1)–O(2) (*c*-edges) distances are much shorter than the O(2)–O(2) ones, normal (*h*-edges) and parallel (*ν*-edges) to the $\bar{6}$ axis (see Table VI).

TABLE VII. Relevand Distances (Å) and Angles (°) in Hydrogen Bonds.

	O...O		H...O		Ang. O–H...O	
	Ln = Nd	Ln = Ho	Ln = Nd	Ln = Ho	Hn = Nd	Ln = Ho
O(1)–H(11)...O(4)	2.98	2.98	2.01	2.05	167.5	166.1
O(1)–H(11)...O(4)	2.98	2.98	2.01	2.05	167.5	166.1
O(2)–H(21)...O(4)	2.84	2.81	1.94	1.87	155.7	168.5
O(2)–H(22)...O(3)	2.75	2.74	1.81	1.79	173.4	176.5

Interatomic distances and angles in the anions are within the expected ranges (Tables IV and V) except for distances C(1)–F(1) and C(1)–F(2) which are somewhat too short, probably as a consequence of the high temperature factors associated with the fluorine atoms [9].

The oxygen atoms of all water molecules are hydrogen-bonded to two oxygen atoms of two different $CF_3SO_3^-$ anions. Relevant parameters describing these interactions are given in Table VII.

Acknowledgements

This work was sponsored by grants from FINEP, CNPq, FAPESP and CAPES.

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