Synthesis, Properties and Structure of Hexaaquo-tris(*N*,*N*-dimethylformamide)-lanthanide Trifluoromethanesulfonates

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Abstract

The compounds of general formula $[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3$ (Ln = La–Eu, Tb, Dy) were synthesized and characterized by microanalysis, conductance measurements, IR absorption (Nd^{3+}) and emission (Eu^{3+}) spectra. The crystal structure of the neodymium compound was determined by X-ray diffraction techniques. The compound crystallizes in the triclinic system, space group $P1$, $a = 8.589(4)$, $b = 11.222(2)$, $c = 12.271(2)$ Å, $\alpha = 56.83(2)$, $\beta = 62.13(2)$, $\gamma = 75.14(2)°$, $V = 875.2$ Å^3, $M = 918.4$, $Z = 1$, $D_c = 1.73$ g cm^{-3}, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.65$ mm^{-1}, $F(000) = 456$, $R = 0.056$, $R_w = 0.057$, for 2979 independent reflections with $I > 3\sigma(I)$. Nd^{3+} is coordinated to the oxygen atoms of six independent water molecules at a mean distance Nd–O = 2.52(1) Å, and to the oxygen atoms of three independent DMF groups at a mean distance Nd–O = 2.40(2) Å. The coordination polyhedron is a tricapped trigonal prism of point symmetry C_{3v}.

Introduction

Addition compounds of lanthanide iodides [1], acetates [2], nitrates [3], perchlorates [4, 5], chlorides [6], perrhenates [7, 8], hexathiocyanate chromiates(III) [9], isothiocyanates [10], hexafluorophosphates [11] and trifluoroacetates [12] have already been described.

This paper reports the synthesis and characterization of the compounds of composition $[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3$ (Ln = La–Eu, Tb, Dy). The structure of the neodymium compound, isomorphous with the others, is described.

Experimental

Preparation of the Complexes

The hydrated trifluoromethanesulfonates were treated with a small excess of DMF and the mixture was gently warmed, resulting in an oily product. Crystallization of the complexes was obtained by the diffusion method, using chloroform as the outer solvent. The crystals were dried in air, over filter paper.

Characterization of the Complexes

The compounds were characterized by the usual microanalytical procedures, consisting of complexometric titration of the lanthanides with EDTA [13] and determination of carbon, hydrogen and nitrogen with a Perkin-Elmer model 240 CHN system. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Conductance measurements were performed at 25.00 ± 0.02 °C in a system composed of a pointer galvanometer, a resistance box and a cell from Leeds and Northrup ($K_c = 0.10708$ cm^{-1}). Absorption spectra of the neodymium compound were determined on a Cary 17 spectrophotometer and the emission spectrum of the europium compound was taken on a Zeiss ZFM-4 spectrofluorometer. X-ray powder patterns were determined on a Norelco apparatus using a diffractometer from Phillips Electronic Instruments, with copper Kα radiation. Diffraction measurements of the neodymium compound were carried out on a CAD-4 Enraf Nonius diffractometer using a rectangular prismatic crystal of approximate dimensions 0.67 × 0.25 × 0.17 mm. Graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used. Cell dimension and the orientation matrix were calculated by the least-squares method from 25 centered reflections in the range $8.1 < \theta < 14.7°$. Intensities were measured by ω–2θ scans using a variable scan speed between 3.0–5.0° min^{-1}. The intensities of two standard reflections varied ±3% of the mean intensity over the data collection; 6176 reflections were measured; 3100 were unique. Data were corrected for Lorentz and polarization effects.

The heavy atom positions were located from a Patterson synthesis and the rest of the structure was determined by the usual alternate cycles of least-

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TABLE I. Summary of Analytical Results and Conductance Data of the Compounds of Formula $[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3$

Ln	Analysis (%)								Conductance	
	Lanthanide		Carbon		Hydrogen		Nitrogen		Concentration (mM)	Λ_m [a]
	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found		
La	15.21	15.01	15.78	15.83	3.60	3.56	4.60	4.44	1.00	55.8
Ce	15.31	15.01	15.75	15.75	3.60	3.18	4.60	4.89	1.09	56.4
Pr	15.39	15.68	15.74	16.04	3.60	3.67	4.60	4.73	0.99	62.3
Nd	15.69	15.26	15.69	15.82	3.59	3.64	4.57	4.51	0.99	58.2
Sm	16.25	15.35	15.58	15.53	3.57	3.54	4.54	4.18	1.03	61.7
Eu	16.40	16.45	15.56	15.57	3.56	3.51	4.54	4.56	0.99	62.4
Tb	17.03	17.12	15.44	15.58	3.53	3.17	4.50	4.72	0.99	71.2
Dy	17.34	16.92	15.38	15.06	3.52	3.05	4.48	4.94	0.95	72.5

[a] $\Lambda_m = \Omega^{-1}\ cm^2\ mol^{-1}$.

squares refinement and difference maps; 390 parameters were refined. The carbonyl groups were assigned a common isotropic temperature factor, such that the oxygen temperature factor was 1.3 times the value for carbon [14]. An extinction parameter χ in the formula $F_{corr} = F_c(\chi F_c^2/\sin\theta)$ converged to the value 2.32×10^{-6}. Least-squares refinements were carried out minimizing $\Sigma w(|F_o| - |F_c|)^2$ with $w = |\sigma^2(F_o) + 0.001F_o^2|^{-1}$ and σ was obtained from counting statistics. No hydrogen atoms were included in the model. Final R factors were $R = 0.056$ and $R_w = 0.057$. A final difference map showed fluctuations between 1.3 and -1.5 eÅ^{-3}.

Complex form factors for the lanthanide [15] and complex neutral form factors for the remaining atoms [16, 17] were employed. Most of the calculations were performed on a VAX computer with the SHELX76 system of programs [14]. Final positional parameters and isotropic temperature factors [18] are given in Table III. Structure factors tables may be obtained from one of the authors (E.E.C.).

Results and Discussion

Table I contains a summary of the analytical results and conductance data in nitromethane. According to the results, the composition of the complexes is $Ln(CF_3SO_3)_3{\cdot}3DMF{\cdot}6H_2O$ (Ln = La–Eu, Tb, Dy). They behave as 1:1 electrolytes [19] in nitromethane.

The IR spectral frequencies are tabulated in Table II. Strong water bands in the 3500 cm^{-1} region and small shifts of ν(CO) to lower frequencies in relation to the free ligand were observed and ν(CN) was unaltered, indicating the presence of coordinated water and coordination of DMF through the oxygen. Bands attributed to the anion show that $CF_3SO_3^-$ is not bonded to the central ion, meaning that conductance data are due to the existence of ion-pairs in solution.

TABLE II. IR Data (cm^{-1})

Ln	ν_s(CO)	ν(CN)	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$	$\delta_{as}(SO_3)$	$\delta_s(SO_3)$
La	1669	1500	1260	1035	640	521
Ce	1665	1500	1270	1031	640	522
Pr	1661	1500	1275	1032	640	522
Nd	1670	1501	1270	1032	640	522
Sm	1665	1500	1280	1031	641	522
Eu	1665	1500	1270	1031	640	522
Tb	1665	1500	1270	1030	640	522
Dy	1670	1500	1275	1030	635	522
DMF	1675	1500				

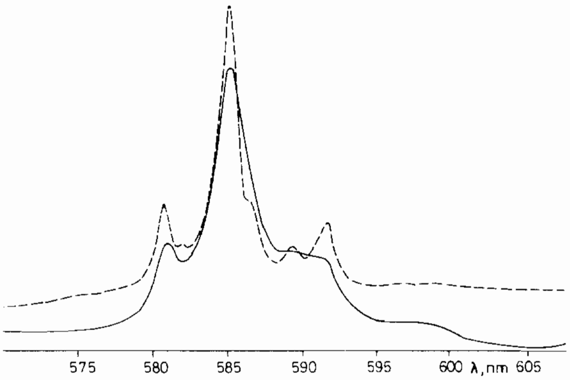

Fig. 1. Absorption spectra of the neodymium compound at room temperature (solid line) and at 77 K (dashed line).

Figure 1 shows the neodymium compound absorption spectra at room temperature (solid line) and at 77 K (dashed line) in the $^4G_{5/2}$, $^2G_{7/2} \leftarrow {}^4I_{9/2}$ transition region. The number of bands at 77 K indicates the existence of non-cubic site symmetry. From the room temperature spectrum, the baricenter of the band was determined applying Simpson's rule [20]

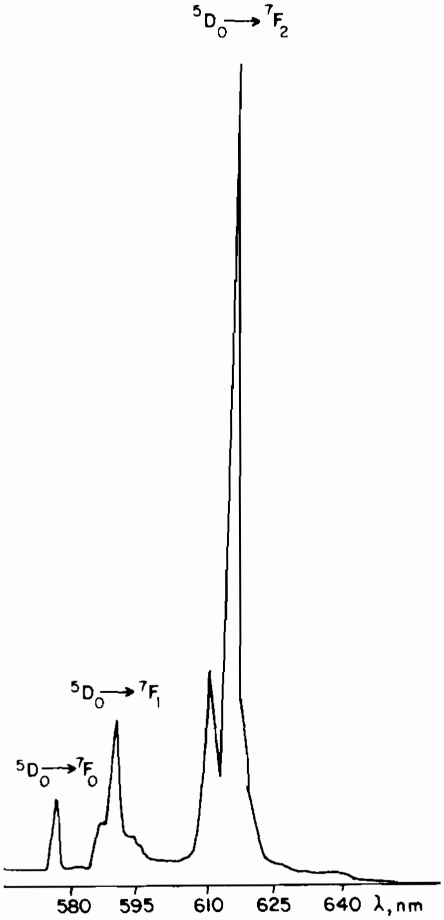

Fig. 2. Emission spectrum of the europium compound at 77 K.

(G = 17227 cm^{-1}) and compared with the same transition in the standard Nd^{3+}:LaF_3 (G = 17329 cm^{-1}). The nephelauxetic parameter ($\beta = 0.994$) was also calculated, indicating an essentially electrostatic bonding between the central ion and the ligands.

Figure 2 presents the emission spectrum of the europium compound at 77 K, which contains one $^5D_0 \rightarrow {}^7F_0$ band (the existence of this band indicating that only C_n, $C_{n,v}$ or C_s symmetries are possible [21]), one peak and shoulders due to the $^5D_0 \rightarrow {}^7F_1$ transition and two peaks and a shoulder due to $^5D_0 \rightarrow {}^7F_2$. The spectrum was interpreted in terms of the existence of C_{3v} symmetry [22].

Description of the Structure of the Neodymium Complex

Fractional atomic coordinates and isotropic temperature factors are given in Table III. Relevant bond distances and angles are presented in Tables IV, V and VI.

TABLE III. Fractional Atomic Coordinates and Isotropic Temperature Factors (Å^2) with Standard Deviations in Parentheses

Atom	x/a	y/b	z/c	B_{eq}
Nd	0	0	0	2.63(4)
OW(1)	−0.094(2)	0.000(1)	−0.163(1)	4.2(8)
OW(2)	0.155(2)	0.165(1)	0.002(1)	4.8(9)
OW(3)	−0.259(1)	−0.166(1)	0.169(1)	4.1(8)
OW(4)	−0.258(1)	0.167(1)	0.002(1)	4.1(8)
OW(5)	0.317(1)	0.001(1)	−0.161(1)	4.4(8)
OW(6)	0.152(2)	−0.165(1)	0.167(1)	4.5(9)
O(1)	0.076(3)	0.221(2)	−0.218(2)	8.3(2)
C(1)	0.119(3)	0.320(2)	−0.313(2)	6.4(2)
N(1)	0.152(2)	0.434(2)	−0.428(2)	7(1)
C(11)	0.256(5)	0.451(4)	−0.564(5)	12(1)
C(12)	0.108(7)	0.549(7)	−0.418(7)	16(1)
O(2)	0.076(3)	−0.221(2)	0.002(2)	8.3(2)
C(2)	0.115(3)	−0.322(2)	0.008(2)	6.4(2)
N(2)	0.153(2)	−0.436(2)	0.007(2)	7(1)
C(21)	0.111(6)	−0.556(6)	0.131(5)	15(1)
C(22)	0.254(5)	−0.453(5)	−0.116(5)	11(1)
O(3)	−0.150(3)	0.002(2)	0.224(2)	8.3(3)
C(3)	−0.198(3)	−0.009(2)	0.320(3)	6.4(3)
N(3)	−0.278(2)	0.000(2)	0.434(2)	6(1)
C(31)	−0.322(6)	−0.132(5)	0.582(5)	12(1)
C(32)	−0.327(6)	0.137(5)	0.445(5)	13(1)
S(1)	−0.3868(7)	−0.6905(5)	−0.3071(5)	5.3(3)
O(11)	−0.356(5)	−0.657(3)	−0.226(3)	14(1)
O(12)	−0.225(4)	−0.767(3)	−0.351(3)	12(1)
O(13)	−0.536(5)	−0.722(4)	−0.275(4)	26(1)
C(111)	−0.346(3)	−0.528(3)	−0.467(3)	7(1)
F(11)	−0.182(5)	−0.508(7)	−0.527(3)	32(1)
F(12)	−0.361(7)	−0.542(4)	−0.559(3)	20(1)
F(13)	−0.453(6)	−0.436(3)	−0.458(4)	19(1)
S(2)	−0.3869(7)	−0.3085(5)	0.0016(6)	5.3(4)
O(21)	−0.226(4)	−0.233(3)	−0.119(3)	12(1)
O(22)	−0.351(4)	−0.347(3)	0.119(3)	13(1)
O(23)	−0.538(5)	−0.281(4)	0.005(8)	27(1)
C(222)	−0.343(3)	−0.470(3)	0.003(3)	7(1)
F(21)	−0.186(6)	−0.498(7)	−0.028(9)	30(1)
F(22)	−0.365(6)	−0.460(4)	−0.099(4)	18(1)
F(23)	−0.452(6)	−0.565(3)	0.107(4)	18(1)
S(3)	−0.6961(6)	0.0003(6)	−0.6890(5)	5.3(4)
O(31)	−0.578(3)	−0.121(3)	−0.644(3)	12(1)
O(32)	−0.580(3)	0.121(3)	−0.766(3)	14(1)
O(33)	0.185(4)	−0.005(7)	0.286(4)	21(1)
C(333)	0.185(3)	0.000(3)	0.471(3)	7(1)
F(31)	0.282(5)	−0.002(6)	0.524(4)	22(1)
F(32)	0.079(4)	0.107(4)	0.459(3)	17(1)
F(33)	0.075(4)	−0.105(3)	0.566(3)	16(1)

The Nd cation is coordinated to the oxygen atoms of six independent water molecules at a mean distance Nd–OW = 2.52(1) Å, and to the oxygen atoms of three independent DMF groups at a mean distance Nd–O = 2.40(2) Å. The coordination number is therefore nine and the coordination polyhedron is a tricapped trigonal prism of point symmetry C_{3v}. The water oxygen atoms are located at the corners of the prism and the oxygen atoms of the DMF groups form the vertices of the caps. The structure is shown in Fig. 3.

TABLE IV. Interatomic Bond Distances (Å) with Standard Deviations in Parentheses

Nd–OW(1)	2.48(1)
Nd–OW(2)	2.56(1)
Nd–OW(3)	2.51(1)
Nd–OW(4)	2.51(1)
Nd–OW(5)	2.51(1)
Nd–OW(6)	2.54(1)
Nd–O(1)	2.38(2)
Nd–O(2)	2.39(2)
Nd–O(3)	2.44(2)
O(1)–C(1)	1.06(3)
C(1)–N(1)	1.24(3)
N(1)–C(11)	1.40(5)
N(1)–C(12)	1.31(9)
O(2)–C(2)	1.07(4)
C(2)–N(2)	1.24(4)
N(2)–C(21)	1.32(6)
N(2)–C(22)	1.44(5)
O(3)–C(3)	0.99(3)
C(3)–N(3)	1.29(3)
N(3)–C(31)	1.53(5)
N(3)–C(32)	1.55(7)
S(1)–O(11)	1.38(4)
S(1)–O(12)	1.47(4)
S(1)–O(13)	1.24(5)
S(1)–C(111)	1.75(3)
C(111)–F(11)	1.26(6)
C(111)–F(12)	1.29(5)
C(111)–F(13)	1.21(5)
S(2)–O(21)	1.46(3)
S(2)–O(22)	1.42(3)
S(2)–O(23)	1.24(6)
S(2)–C(222)	1.75(3)
C(222)–F(21)	1.22(8)
C(222)–F(22)	1.29(5)
C(222)–F(23)	1.24(5)
S(3)–O(31)	1.48(3)
S(3)–O(32)	1.46(3)
S(3)–O(33)	1.22(4)
C(333)–F(31)	1.26(6)
C(333)–F(32)	1.29(6)
C(333)–F(33)	1.30(4)
S(3)–C(333)	1.74(3)

TABLE V. Interatomic Bond Angles (°) in the Coordination Polyhedron with Standard Deviations in Parentheses

OW(1)–Nd–OW(3)	77.3(4)
OW(1)–Nd–OW(4)	77.3(4)
OW(2)–Nd–OW(5)	74.7(4)
OW(2)–Nd–OW(6)	74.9(4)
OW(5)–Nd–OW(6)	75.3(4)
OW(3)–OW(1)–OW(4)	60.2(4)
OW(3)–OW(1)–OW(5)	89.5(4)
OW(4)–OW(1)–OW(5)	89.2(4)
OW(4)–OW(2)–OW(5)	90.0(4)
OW(4)–OW(2)–OW(6)	89.8(4)
OW(5)–OW(2)–OW(6)	59.9(4)
Nd–O(1)–OW(1)	56.6(6)
Nd–O(1)–OW(2)	58.7(6)
Nd–O(1)–OW(4)	57.5(6)
Nd–O(1)–OW(5)	57.5(6)
Nd–O(2)–OW(1)	56.6(6)
Nd–O(2)–OW(3)	57.3(6)
Nd–O(2)–OW(5)	57.2(5)
Nd–O(2)–OW(6)	58.2(6)
Nd–O(3)–OW(2)	57.6(6)
Nd–O(3)–OW(3)	56.9(6)
Nd–O(3)–OW(4)	57.1(6)
Nd–O(3)–OW(6)	57.1(6)
Nd–O(1)–C(1)	175(1)
Nd–O(1)–N(1)	179(1)
Nd–O(2)–C(2)	176(1)
Nd–O(2)–N(2)	179(1)
Nd–O(3)–C(3)	171(1)
Nd–O(3)–N(3)	177(1)

TABLE VI. Interatomic Bond Angles (°) with Standard Deviations in Parentheses

O(1)–C(1)–N(1)	171(1)
C(1)–N(1)–C(11)	126(1)
C(1)–N(1)–C(12)	115(1)
C(11)–N(1)–C(12)	117(1)
O(2)–C(2)–N(2)	174(1)
C(2)–N(2)–C(21)	118(1)
C(2)–N(2)–C(22)	127(1)
C(21)–N(2)–C(22)	115(1)
O(3)–C(3)–N(3)	168(1)
C(3)–N(3)–C(31)	122(1)
C(3)–N(3)–C(32)	128(1)
C(31)–N(3)–C(32)	110(1)
O(11)–S(1)–O(12)	102(1)
O(11)–S(1)–O(13)	121(1)
O(12)–S(1)–O(13)	125(1)
F(11)–C(111)–F(12)	98(1)
F(11)–C(111)–F(13)	123(1)
F(12)–C(111)–F(13)	102(1)
O(21)–S(2)–O(22)	102(1)
O(21)–S(2)–O(23)	126(1)
O(22)–S(2)–O(23)	122(1)
F(21)–C(222)–F(22)	102(1)
F(21)–C(222)–F(23)	119(1)
F(22)–C(222)–F(23)	100(1)
O(31)–S(3)–O(32)	101(1)
O(31)–S(3)–O(33)	123(1)
O(32)–S(3)–O(33)	127(1)
F(31)–C(333)–F(32)	109(1)
F(31)–C(333)–F(33)	108(1)
F(32)–C(333)–F(33)	101(1)

It is interesting to note that compounds of composition $[Ln(DMA)_3(H_2O)_6](CF_3SO_3)$ have been obtained in our laboratory and present very similar spectral [23] and structural [24] properties.

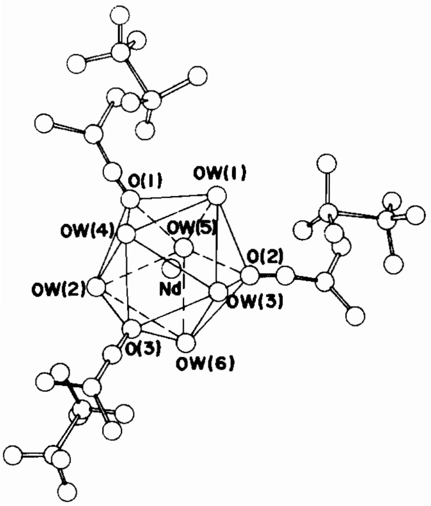

Fig. 3. A perspective view of the molecule.

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