Synthesis, Structure and Spectral Characterization of Lanthanoid Trifluoromethanesulfonate Complexes with 4-Picoline-*N*-oxide

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Fantin, C. A., Zinner, L. B., Vicentini, G., Rodellas, C. and Niinistö, L., 1987. Synthesis, Structure and Spectral Characterization of Lanthanoid Trifluoromethanesulfonate Complexes with 4-Picoline-*N*-oxide. – Acta Chem. Scand., Ser. A 41: 259–268.

Lanthanoid trifluoromethanesulfonates react in ethanol with 4-picoline-*N*-oxide (4-picNO) to form complexes of composition $Ln(4\text{-picNO})_n(CF_3SO_3)_3$ where n is 8 for the first isostructural series (Ln = La-Gd) and 7 for the second series (Ln = Tb-Lu, Y). The complexes were characterized by chemical and thermal analyses, X-ray powder diffraction and conductance measurements. Spectral studies included the recording and interpretation of infrared spectra, visible absorption spectra in the solid state and solution, and the emission spectrum of the Eu compound at 77 K. X-Ray single-crystal structural analysis of the Nd compound showed that it forms triclinic crystals with the following unit cell dimensions: a = 10.949(2), b = 15.518(3), c = 19.706(4) Å, α = 87.23(2), β = 87.57(2), and γ = 81.30(2)°. The space group is $P\bar{1}$. The Nd ions are coordinated in a square-antiprismatic arrangement by eight oxygen atoms from eight 4-picNO molecules. The Nd-O bond lengths range from 2.38 to 2.47 Å. The non-coordinated trifluoromethanesulfonate ions are distorted.

A variety of anhydrous and hydrated 4-picoline-*N*-oxide lanthanoid complexes with different counter ions have been described in the literature.[1–6] In most cases the ratio of lanthanoid to 4-picoline-*N*-oxide ligands is 1:8, suggesting octacoordination of the lanthanoid ion; however, no X-ray studies have been performed so far to corroborate this.

In this article we report the preparation and structural characterization of 4-picoline-*N*-oxide (4-picNO) complexes with the general formula $Ln(4\text{-picNO})_n(CF_3SO_3)_3$ where n is 8 for La-Gd and 7 for Tb-Lu and Y. Besides the 4-picNO ligand, the coordination of the trifluoromethanesulfonate ion is of interest in this case. $CF_3SO_3^-$ is generally considered to be an indifferent and relatively labile anion; nevertheless, several examples of its coordinating ability toward transition metals are known.[7] Especially relevant in this connection are the two recent crystallographic reports which conclusively show that $CF_3SO_3^-$ may also coordinate to the large 4*f* ions.[8,9]

Experimental

Hydrated lanthanoid trifluoromethanesulfonates were dissolved in ethanol and treated with 4-picNO (molar ratio 1:8). The compounds were precipitated by the addition of triethyl orthoformate (teof), separated by filtration, washed with teof and dried in vacuum over anhydrous calcium chloride. Single crystals of the neodymium and ytterbium compounds were obtained by recrystallization of the complexes by the diffusion method, using absolute ethanol as inner and teof as outer solvent. Ln, C, H and N analyses[§] indi-

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[§]A summary of analytical and conductance data is available upon request from one of the authors (G.V.).

cated the formula $Ln(4\text{-picNO})_n(CF_3SO_3)_3$ ($n = 8$ for Ln = La-Gd, excl. Ce, Pm; $n = 7$ for Ln = Tb-Lu, Y). The cerium complex was found to be partially oxidized. Conductance measurements in acetonitrile and nitromethane gave somewhat lower values than those expected for 1:3 electrolytes.[10]

IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer using Nujol mulls between KBr plates. The absorption spectra in acetonitrile and nitromethane solutions and in silicone mulls at 298 and 77 K were obtained using a Cary 17 spectrophotometer. Fluorescence spectra were recorded at 77 K on a Zeiss ZFM-4 spectrofluorimeter, using 394 nm excitation radiation. The refractive indexes of the solutions were determined in an Abbé-type Bausch and Lomb refractometer.

Thermogravimetric studies were made with a Perkin-Elmer TGS-1 system under nitrogen atmosphere, using samples of about 1 mg and a heating rate of 10 K min^{-1}.

Powder XRD data, recorded on a Norelco Instrument using Cu*K*α radiation, indicated the existence of two series of isomorphous compounds corresponding to the compositions with 8 and 7 molecules of 4-picNO per Ln. An irregular (approx. 0.2 × 0.2 × 0.3 mm) fragment of a large prismatic crystal of the Nd complex, belonging to the first isostructural series, was chosen for a single crystal study on a Syntex $P2_1$ four-circle diffractometer. A summary of the crystal data is given in Table 1. Intensities were recorded in the ω scan mode for $2\theta = 3-50°$, using varying scan speed ($2-29.30°$ min^{-1}) depending on the peak intensity of the reflection. 11658 reflections were measured with graphite-monochromated Mo*K*α radiation. Two test reflections were measured at regular intervals to ascertain that the crystal did not deteriorate during the data collection. 6776 reflections had intensities greater than three times their standard deviation and were used in subsequent calculations. No absorption correction was applied ($\mu = 9.8$ cm^{-1}).

The interpretation of the Patterson map gave the position of the heavy atom. Successive Fourier syntheses[11] and electron density difference maps revealed the remaining atoms of the structure. The structure was refined by full-matrix least-squares methods using anisotropic temperature factors for Nd and S atoms and isotropic temperature factors for the rest of the atoms.

Table 1. Crystal data.

Formula	$NdC_{51}H_{56}S_3N_8O_{17}F_9$
Crystal system	triclinic
a/Å	10.949(2)
b/Å	15.518(3)
c/Å	19.706(4)
α/°	87.23(2)
β/°	87.57(2)
γ/°	81.30(2)
V/Å^3	3312.01
Space group	$P\bar{1}$
Z	2
M.W.	1464.5
D_c/g cm^{-3}	1.471
μ(Mo*K*α) /cm^{-1}	9.8

Scattering factors were those given by Cromer and Mann for neutral atoms;[12] for Nd^{3+} the scattering factors and anomalous dispersion values were taken from Ref. 13.

Due to disorder in the three $CF_3SO_3^-$ ions, rigid refinement for C-F, S-O and C-S bonds was used. All hydrogen atoms were located in a difference map but they were not included in the refinement. The unweighted final R value was 0.092 and the weighted final $R_w = 0.082$ ($w = 1/\sigma^2$). The final positional parameters and temperature factors are given in Table 2. Most calculations were performed with the SHELX system of crystallographic programs.[14] Lists of observed and calculated structure factors, as well as anisotropic temperature factors for Nd and S, are obtainable from the authors (C. R. and L. N.) on request.

Spectral and thermoanalytical results

Absorption and fluorescence spectra. Fig. 1 shows the visible absorption spectra of the neodymium compound. The number of bands in the spectrum at 77 K indicate that Nd^{3+} is not located in a cubic site. From the spectrum at 298 K, the nephelauxetic parameters ($\beta = 0.988$), covalence factor[15] ($b^{1/2} = 0.078$) and Sinha's parameter[16]($\delta = 1.21$) indicate the electrostatic nature of the bonds. The parameters were determined on the basis of transitions $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ ($\nu = 17087$ cm^{-1}) and $^4I_{9/2} \rightarrow {}^2P_{1/2}$ ($\nu = 23223$ cm^{-1}) in relation to the corresponding transitions in Nd^{3+}: LaF_3.[17] The spectra in nitromethane and acetonitrile solution are very similar and show similar values of the oscillator strengths for the $^4I_{9/2} \rightarrow {}^4G_{5/2}$, $^2G_{7/2}$ tran-

Table 2. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($\times 10^2$).

$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij}\, a_i^* a_j^*\, \mathbf{a}_i \cdot \mathbf{a}_j$ for the atoms Nd and S.

Atom	x	y	z	U_{iso} or U_{eq}/Å^2
Nd	4860(1)	2467(1)	2589(1)	5.2(1)
O1	2835(9)	2126(7)	2472(5)	9.4(4)
O2	5456(9)	1174(7)	1981(5)	8.6(3)
O3	4539(8)	1347(6)	3457(5)	6.6(3)
O4	6914(8)	1837(6)	3002(4)	6.6(3)
O5	4907(8)	3126(6)	3673(5)	7.2(3)
O6	6244(8)	3506(6)	2274(5)	6.7(3)
O7	3501(9)	3884(7)	2542(5)	8.0(3)
O8	4587(8)	2787(6)	1384(5)	7.6(3)
N1	2093(10)	1576(8)	2785(6)	6.7(3)
N2	6305(11)	460(8)	2076(6)	6.9(3)
N3	5035(10)	1192(7)	4064(6)	5.6(3)
N4	7765(10)	2324(7)	3126(6)	5.9(3)
N5	4580(11)	3970(8)	3846(6)	6.9(3)
N6	6288(10)	4077(8)	1748(6)	6.8(3)
N7	2586(11)	4327(9)	2177(6)	7.5(4)
N8	4648(10)	2253(7)	860(6)	5.9(3)
C12	1769(14)	936(10)	2407(8)	7.9(5)
C13	947(16)	402(12)	2734(9)	9.8(6)
C14	537(14)	564(11)	3376(9)	8.5(5)
C141	−384(18)	−52(14)	3709(11)	13.2(7)
C15	923(14)	1202(11)	3742(8)	8.1(5)
C16	1725(13)	1729(10)	3430(8)	7.5(5)
C22	5931(13)	−201(10)	2464(7)	7.3(5)
C23	6763(15)	−985(11)	2553(8)	8.8(5)
C24	7924(17)	−1052(12)	2242(9)	10.1(6)
C241	8826(20)	−1940(16)	2304(11)	15.0(8)
C25	8234(15)	−323(12)	1843(9)	9.3(5)
C26	7433(14)	425(10)	1782(7)	7.1(4)
C32	6087(13)	617(9)	4108(7)	6.2(4)
C33	6642(12)	434(9)	4743(7)	6.5(4)
C34	6059(13)	855(10)	5327(7)	6.8(4)
C341	6650(14)	661(10)	6026(8)	8.5(5)
C35	5005(13)	1420(9)	5262(7)	6.6(4)
C36	4455(13)	1602(9)	4602(8)	6.7(4)
C42	7770(13)	2636(10)	3760(8)	7.0(4)
C43	8624(13)	3216(10)	3917(8)	7.6(5)
C44	9415(13)	3442(9)	3371(8)	6.8(4)
C441	10329(16)	4068(12)	3532(9)	11.1(6)
C45	9415(13)	3069(10)	2749(8)	7.2(4)
C46	8609(13)	2494(9)	2612(7)	6.6(4)
C52	5395(13)	4528(10)	3663(7)	6.9(4)
C53	5105(15)	5396(11)	3885(8)	8.7(5)
C54	3995(15)	5648(11)	4236(8)	8.0(5)
C541	3662(17)	6615(13)	4454(10)	12.0(7)
C55	3174(15)	5052(12)	4409(8)	9.4(5)
C56	3549(14)	4184(10)	4189(8)	7.5(5)
C62	5582(13)	4877(11)	1769(8)	7.7(5)
C63	5595(14)	5444(10)	1219(8)	8.1(5)
C64	6377(14)	5239(11)	666(8)	8.0(5)
C641	6414(17)	5894(14)	29(11)	12.6(7)
C65	7074(14)	4430(11)	625(8)	8.4(5)
C66	7035(13)	3838(10)	1199(8)	7.3(5)
C72	2312(17)	5196(13)	2295(9)	10.4(6)
C73	1330(20)	5662(14)	1966(11)	13.0(7)
C74	726(18)	5271(14)	1490(11)	11.9(7)
C741	9599(24)	5820(18)	1066(14)	18.9(10)
C75	1010(14)	4377(11)	1393(8)	8.1(5)
C76	1994(14)	3909(10)	1735(8)	7.2(4)
C82	3619(14)	1957(11)	723(8)	8.1(5)
C83	3669(15)	1419(11)	163(9)	9.1(5)
C84	4713(16)	1273(11)	−228(8)	8.6(5)
C841	4692(18)	687(14)	−868(10)	12.8(7)
C85	5785(15)	1554(11)	−53(8)	8.6(5)
C86	5702(14)	2077(10)	506(8)	7.6(5)
S1	9862(5)	1963(4)	707(3)	10.7(2)
C1	9652(20)	1773(14)	−173(4)	30.7(19)
O11	8676(6)	1935(7)	1025(5)	10.4(4)
O12	10688(16)	1171(8)	839(11)	24.4(9)
O13	10520(17)	2676(10)	784(11)	24.4(9)
F11	8906(19)	2478(14)	−354(11)	29.0(6)
F12	10755(19)	1756(14)	−456(11)	29.0(6)
F13	9220(18)	1046(13)	−250(11)	29.0(9)
S2	11219(8)	2481(6)	5434(4)	16.7(3)
C2	10758(19)	3502(9)	5841(10)	43.9(33)
O21	11720(11)	2738(8)	4789(4)	12.2(4)
O22	11874(15)	1861(10)	5899(8)	20.6(8)
O23	9977(12)	2303(16)	5400(12)	26.3(11)
F21	10183(19)	3309(14)	6409(11)	29.8(6)
F22	9944(19)	3907(14)	5425(11)	29.8(6)
F23	11838(18)	3714(15)	5958(11)	29.8(6)
S3	5632(6)	2646(4)	7585(3)	13.2(2)
C3	7076(10)	1965(10)	7760(9)	27.9(18)
O31	4890(12)	2510(10)	8184(5)	15.5(6)
O32	5271(12)	2284(9)	6985(5)	14.9(5)
O33	5925(12)	3510(5)	7473(7)	14.4(5)
F31	7848(15)	2022(11)	7243(9)	23.0(4)
F32	7516(14)	2251(11)	8298(9)	23.0(4)
F33	6874(15)	1156(11)	7832(9)	23.0(4)

sition ($P_{\text{nitrometh.}} = 41.3 \cdot 10^{-6}$ and $P_{\text{acet.}} = 39.5 \cdot 10^{-6}$ cm^{-2} mol^{-1} dm^3, respectively).

The infrared spectra of the complexes did not reveal any unexpected features and the difference between the two isostructural series was not discernible in the spectra. For the Nd complex, peaks and their interpretations in the region 1400–400 cm^{-1} were as follows: 1280s, 1258sh (ν_{as} SO_3), 1232s (ν NO), 1032s (ν_s SO_3), 640s (δ_{as} SO_3), 525m (δ_s SO_3) and 407w (ν Nd-O).

The emission spectrum of the europium complex (Fig. 2) shows an intense band with a weak shoulder due to the $^5D_0 \rightarrow {}^7F_1$ transition, indicating that the complex is nearly centrosymmetric;

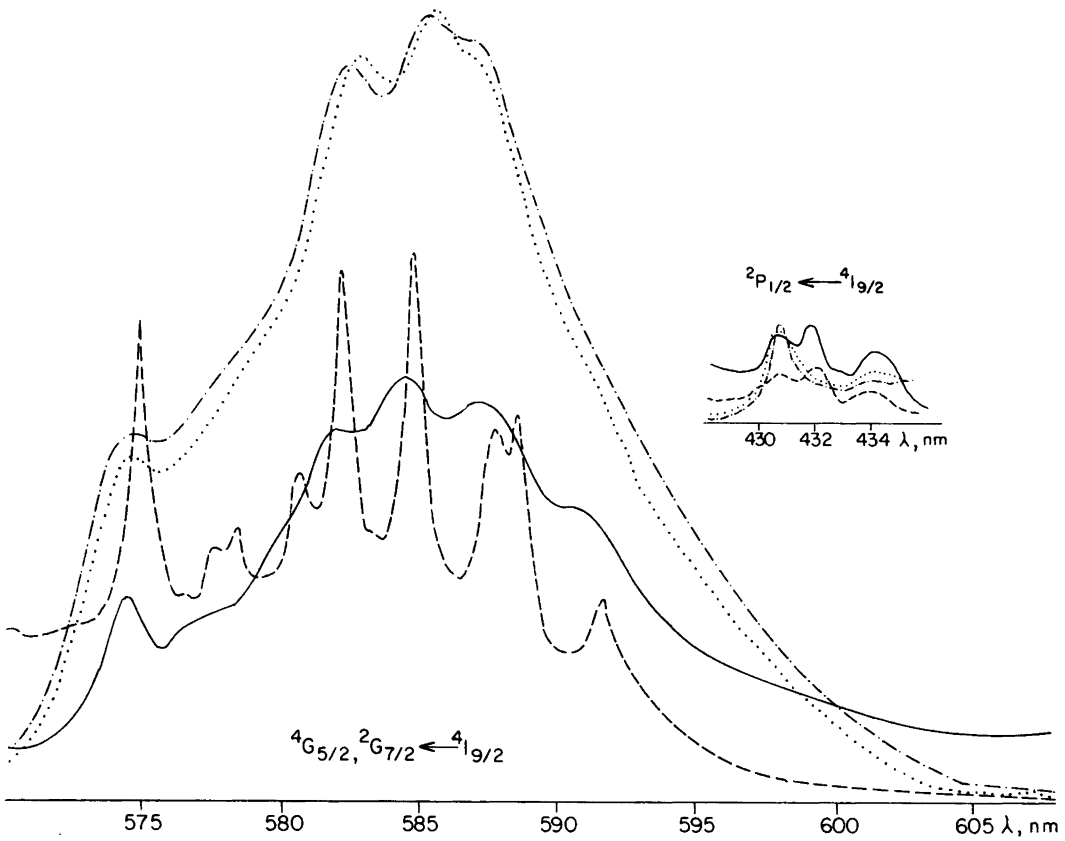

Fig. 1. Absorption spectra of the Nd compound at 298 K (solid line) and 77 K (broken line). The spectra in nitromethane (——) and acetonitrile (·····) solutions are shown above.

there are also two peaks due to $^5D_0 \rightarrow {}^7F_2$ and two peaks, one of them very strong, due to the $^5D_0 \rightarrow {}^7F_4$ transition. It is difficult, however, to derive the point group symmetry since the spectrum is not well resolved.

Thermoanalytical data. When the complexes are heated under nitrogen, melting occurs before decomposition. The melting range is 113–116 °C for the La compound and some 50 degrees higher (166–170 °C) for the Y complex.

An analysis of the TG data reveals that under the experimental conditions used, several different decomposition schemes exist, depending on the nature of the lanthanoid ion. Fig. 3 shows as representative examples the decomposition schemes for the La and Y compounds; a full analysis will be published elsewhere.[18] All decompositions yield the lanthanoid trifluoride[19] as final solid residue, indicating that a complete rearrangement of bonds takes place.

Structure of the neodymium complex

Coordination around Nd. The Nd^{3+} ion is coordinated by eight oxygen atoms belonging to the 4-picNO groups only, and the structure of the complex thus corresponds to the formula $[Nd(4\text{-picNO})_8] \cdot 3CF_3SO_3$. The Nd-O distances are in a relative narrow range of 2.38–2.47 Å (Table 3). There appear to be only a very few structures which contain a regular ML_8 chromophore,[20] and thus the present compound is an interesting case for coordination geometry calculations.

Fig. 4 shows a perspective view of the coordination around the Nd atom, indicating a square-antiprismatic configuration. The most often

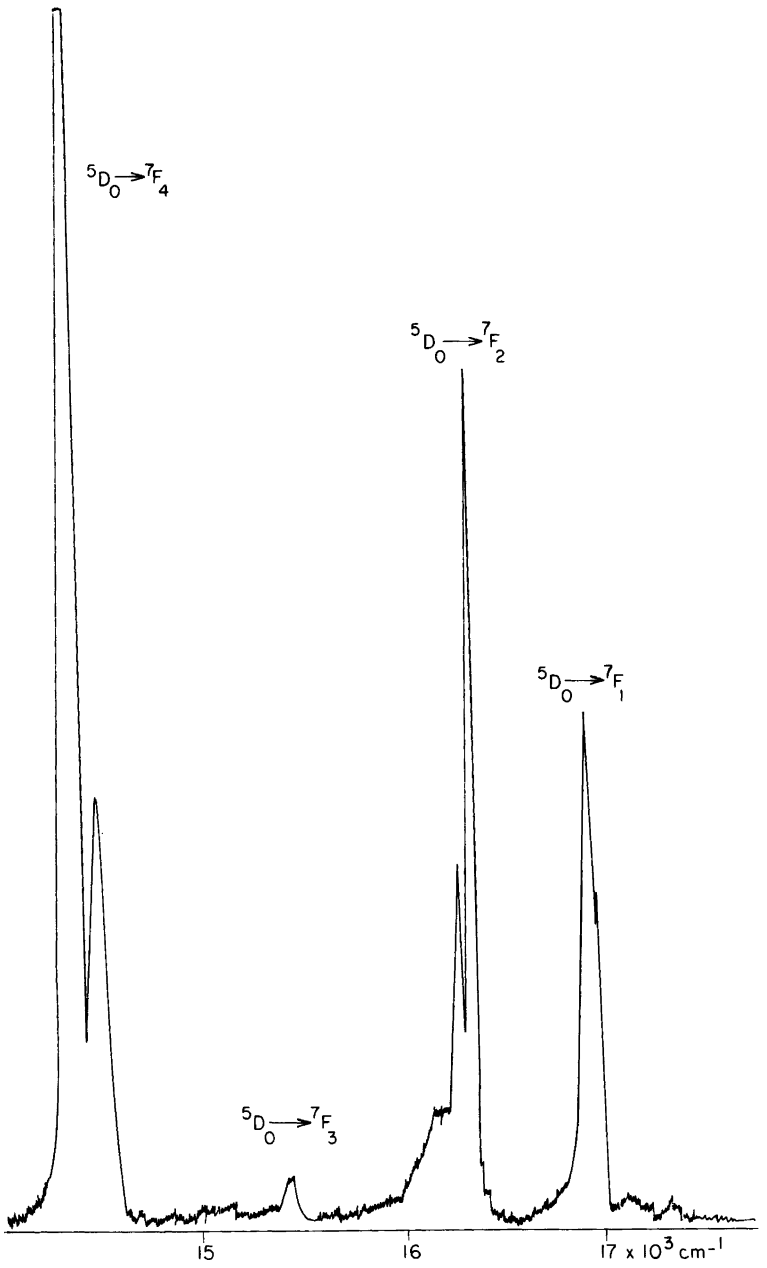

Fig. 2. Fluorescence emission spectrum of the Eu compound at 77 K.

quoted shape characteristics to define this polyhedron are the *l/s* ratio, the θ angle between the bonds and the $\bar{8}$ axis, but these are not independent since *l/s* increases when θ decreases. The two independent shape characteristics are the M-L bond length and θ. An analysis of the *l/s*, θ, and δ parameters (Table 4) describes the polyhedron as a square antiprism (SAP),[21–27] the distortions observed in this case possibly being due to packing effects. The distortion from the ideal SAP polyhedron may be rationalized by a rotation of one square face of the polyhedron, defined by O1,

Table 3. Selected distances (Å) with e.s.d.'s in parentheses.

NdO_8 coordination polyhedron			
Nd–O1	2.379(10)	Nd–O5	2.418(10)
Nd–O2	2.379(11)	Nd–O6	2.417(9)
Nd–O3	2.432(10)	Nd–O7	2.462(11)
Nd–O4	2.468(9)	Nd–O8	2.424(10)
CF_3SO_3			
C1–S1	1.803(11)	S2–O21	1.426(12)
C1–F11	1.307(30)	S2–O22	1.429(18)
C1–F12	1.306(29)	S2–O23	1.433(17)
C1–F13	1.305(29)	C3–S3	1.800(14)
S1–O11	1.423(10)	C3–F31	1.304(23)
S1–O12	1.431(17)	C3–F32	1.306(24)
S1–O13	1.426(18)	C3–F33	1.307(23)
C2–S2	1.804(18)	S3–O31	1.430(13)
C2–F21	1.305(29)	S3–O32	1.429(13)
C2–F22	1.305(28)	S3–O33	1.430(10)
C2–F23	1.307(27)		
C_6H_7NO (4-picNO)			
N1–O1	1.373(15)	N5–O5	1.360(15)
N1–C12	1.367(20)	N5–C52	1.361(19)
N1–C16	1.338(20)	N5–C56	1.298(19)
C12–C13	1.427(23)	C52–C53	1.422(23)
C13–C14	1.347(25)	C53–C54	1.385(23)
C14–C15	1.379(23)	C54–C55	1.405(24)
C14–C141	1.593(26)	C54–C541	1.566(26)
C15–C16	1.393(22)	C55–C56	1.430(24)
N2–O2	1.345(19)	N6–O6	1.335(15)
N2–C22	1.352(19)	N6–C62	1.361(20)
N2–C26	1.336(19)	N6–C66	1.360(19)
C22–C23	1.414(22)	C62–C63	1.364(22)
C23–C24	1.379(24)	C63–C64	1.376(23)
C24–C25	1.422(26)	C64–C65	1.371(22)
C24–C241	1.572(30)	C64–C641	1.580(27)
C25–C26	1.348(23)	C65–C66	1.426(22)
N3–O3	1.331(15)	N7–O7	1.341(16)
N3–C32	1.349(18)	N7–C72	1.366(24)
N3–C36	1.348(19)	N7–C76	1.352(20)
C32–C33	1.412(19)	C72–C73	1.370(28)
C33–C34	1.429(20)	C73–C74	1.384(30)
C34–C35	1.346(20)	C74–C75	1.396(27)
C34–C341	1.544(21)	C74–C741	1.627(34)
C35–C36	1.454(21)	C75–C76	1.386(22)
N4–O4	1.323(14)	N8–O8	1.348(15)
N4–C42	1.362(20)	N8–C82	1.322(19)
N4–C46	1.385(18)	N8–C86	1.322(19)
C42–C43	1.444(21)	C82–C83	1.410(24)
C43–C44	1.417(21)	C83–C84	1.347(24)
C44–C45	1.381(22)	C84–C85	1.375(24)
C44–C441	1.548(23)	C84–C841	1.593(26)
C45–C46	1.389(21)	C85–C86	1.391(22)

O3, O5 and O7, of ca. 37.6° away from the 45° projected angle characterizing the D_{4d} geometry, thus giving a coordination polyhedron of D_4 symmetry.

4-picoline-N-oxide ligands. A list of bond lengths is given in Table 3. By applying the method used for the interpretation of distances in terms of bond orders,[28,29] a π-bond order of 1.3 for the N-C bond in the 4-picoline moiety can be derived, showing that there is a delocalization of π-electrons in these rings. The N-O bond lengths in representative compounds are 1.39 Å in $(CH_3)_3NO$ (formal single bond),[30] 1.19 Å in N_2O (formal double bond)[31] and 1.06 Å in NO^+ (formal triple bond).[32] Therefore, it may be concluded that the N-O bonds (1.33–1.38 Å) in the present compound have partial double-bond character, in the same way as the N-C bond. All C-C distances are in agreement with standard values.[33]

Although the crystal structure of the free ligand 4-picoline-*N*-oxide is unknown, a number of structures of related compounds have been determined. The determination of the structure of 4-picoline has been carried out by Rose,[34] and the structure of the compound formed by 4-picoline and iodine has been solved by Hassel *et al.*[35] The bond distances in the 4-picoline-*N*-oxide ligands in the present Nd complex are also very similar to those observed in other metal complexes formed by 4- or 2-picoline-*N*-oxide.[36–40]

Trifluoromethanesulfonate ("triflate") ions. The triflate anions are uncoordinated (Fig. 5), the shortest intermolecular distances [viz. between the trifluoromethanesulfonate oxygens and 4-picNO carbons (e.g. O33–C62 is 3.1 Å)] being larger than 3 Å.

When the CF_3SO_3 ligands are involved in coordination to a metal ion,[8,9,41–48] the S-O-(M) bond is slightly stretched relative to bonds involving uncoordinated oxygens. This is also the case with lanthanoid complexes (Table 5), although the presence of disordered CF_3SO_3 groups with large temperature parameters makes accurate comparisons often difficult.

In an unstrained molecule, the F and O atoms should adopt a staggered conformation, i.e. the F-C-S-O torsion angles should be ± 60 or 180°, and in all the above cited structures containing ordered triflate groups an almost perfectly stag-

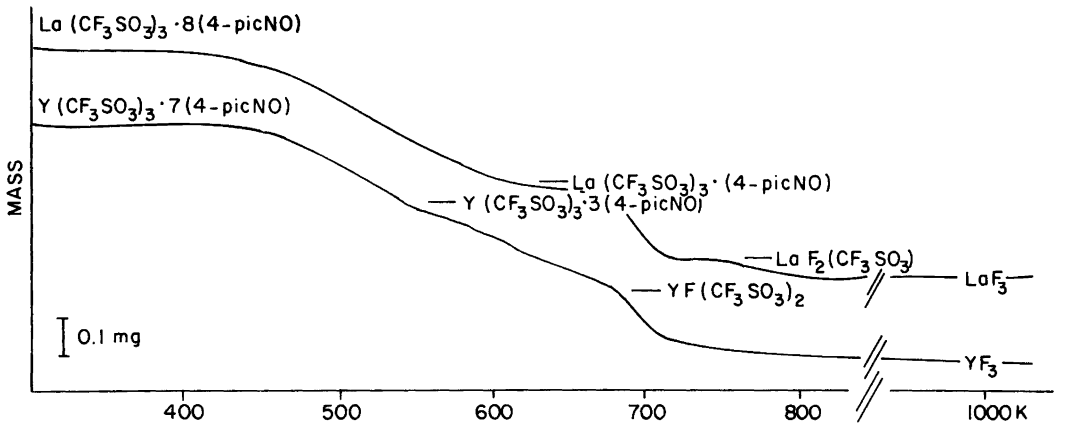

Fig. 3. Thermal decomposition of the La and Y compounds under nitrogen. The levels at right correspond to theoretical weight losses. The heating rate is 10 K min^{-1} and the sample weight 1.0 mg.

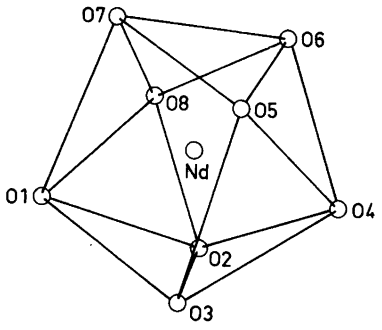

Fig. 4. Perspective view of the square antiprismatic configuration of the NdO_8 polyhedron.

gered conformation is observed. In the present structure, the values of the torsion angles in the triflate groups differ from those for the ideal configuration, as in most other disordered complexes.

The trifluoromethanesulfonate anion belongs to the group of weakly coordinating anions such as ClO_4^-, PF_6^-, FSO_3^-, BF_4^- and $B_{11}CH_{12}^-$. Especially in low dielectric media they may, however, coordinate to metal ions when there are no steric or other factors to prevent this. Two types of coordinating behaviour with the lanthanoids may be observed: outer sphere or a mixed mode (Table 5). The 4-picoline-*N*-oxide complexes of neodymium and ytterbium[51] belong to the former type, i.e. the triflate ligands are in the outer sphere. In competition with other oxygen-donor ligands, the coordination of the triflate anion in the solid lanthanoid complexes appears to be largely governed by the polarity of the solvent system used in the synthesis.

Table 4. Analysis of the eight-coordination polyhedra.

Polyhedron	δ/°				*l/s*	θ_a/°
Dodecahedron	29.5	29.5	29.5	29.5		
Square antiprism (HSM)[a]	0.0	0.0	52.5	52.5	1.000	59.2
Square antiprism (MFP)[b]	0.0	0.0	52.5	52.5	1.057	57.3
Bicapped trigonal prism	0.0	21.7	48.2	48.2		
NdO_8	9.2	12.4	45.4	45.8	1.062	54.4

[a]HSM: hard sphere model. [b]MFP: most favourable polyhedron.

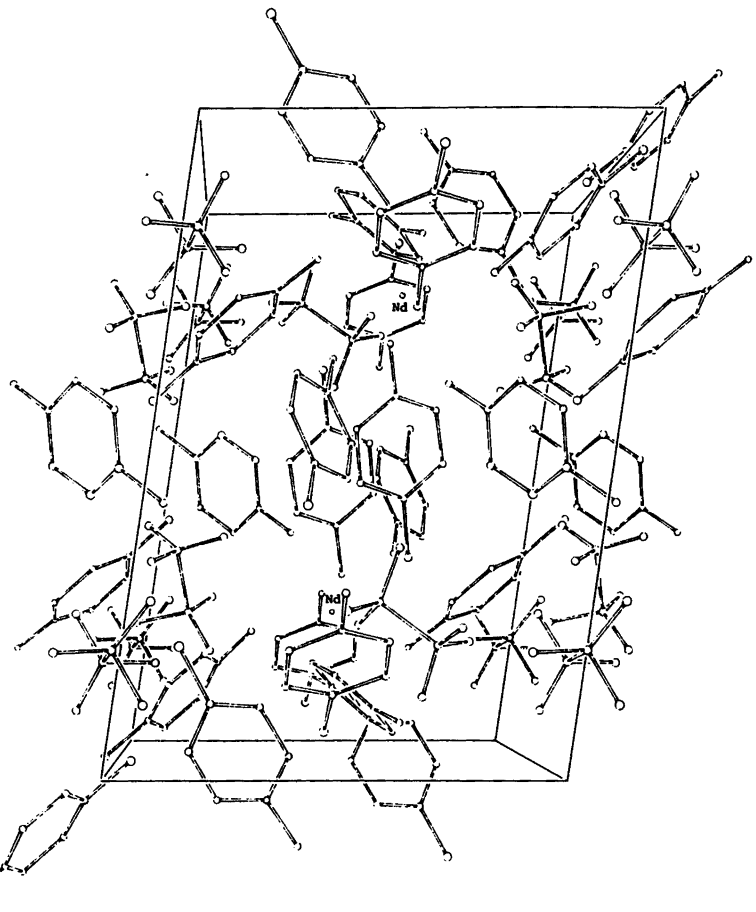

Fig. 5. A perspective view of the unit cell showing the packing of the molecules and the location of the Nd atoms. With the origin in the lower left corner the *b*-axis is pointing upwards.

Table 5. Lanthanoid trifluoromethanesulfonate compounds characterized by X-ray crystal structure analysis.

Compound[a]	Coordination number	Average S–O distance /Å			Reference
		1st coord. sphere		2nd coord. sphere	
		S–O(–M)	S–O	S–O	
$[NdL'_2(CF_3SO_3)(H_2O)_3]\cdot 2L'\cdot 2CF_3SO_3$	8	1.449	1.415	1.432	8
$[La(en)_4(CF_3SO_3)]\cdot 2CF_3SO_3\cdot CH_3CN$	9	1.442	1.424	1.423	9
$[LaL''(CF_3SO_3)_2]\cdot CF_3SO_3\cdot CH_3CN$	10	1.452	1.407	1.416	9
$[YbL''(CF_3SO_3)]\cdot 2CF_3SO_3\cdot CH_3CN$	9	1.448	1.400	1.428	9
$[NdL_8]\cdot 3CF_3SO_3$	8			1.429	This work
$[YbL_7]\cdot 3CF_3SO_3$	7			1.440	51
$[La(OH_2)_9]\cdot 3CF_3SO_3$[b]	9			1.440	49
$[Nd(OH_2)_9]\cdot 3CF_3SO_3$[b]	9			1.437	50

[a]L = 4-picNO, L′ = *trans*-1,4-dithiane-1,4-dioxide, L″ = 1,9-bis(2-aminoethyl)-1,4,6,9,12,14-hexaazacyclohexadecane. [b]Full structural data are available also for the isostructural Gd, Lu, Y and Ho compounds.[49,50]

Acknowledgements. We wish to thank Mr. Lassi Hiltunen, M.Sc., for his help during the work. One of us (C.R.) gratefully acknowledges financial support from the Kemira Foundation.

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Received February 11, 1987.