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Complexes of Lanthanoid Salts with Macrocyclic Ligands. Part 32.* Synthesis and Characterization of the Complexes between Lanthanoid Nitrates and a Tetraoxadiaza Macrocycle

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Abstract

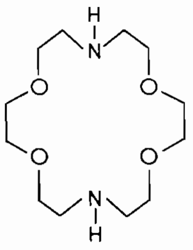
Lanthanoid nitrates react with 1,7,10,16-tetraoxa-4,13-diaza-*N*,*N*′-dimethylcyclooctadecane, $Me_2(2,2)$, to give complexes with two different metal:ligand ratios, 1:1 (Ln = La, Ce, Tb) and 4:3 (Ln = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho). The complexes were isolated from anhydrous solutions in acetonitrile and characterized by elemental analysis, X-ray diffraction, magnetic susceptibility measurements and vibrational analysis.

The La and Ce 1:1 complexes are non-ionic and probably 12-coordinated, with the metal ion bound to the six donor atoms of the ligand and to three bidentate nitrate ions. The 4:3 complexes are ionic; they contain three bis(nitrato) complex cations $[Ln(NO_3)_2 \cdot Me_2(2,2)]^+$ and one hexakis(nitrato) anion $[Ln(NO_3)_6]^{3-}$. Spectroscopic data, including luminescence spectra, point to the 1:1 Tb-complex as being a 4:3 complex with an additional outer-sphere coordinated molecule of ligand.

In solution, the 1:1 complexes remain essentially non-ionic, although some dissociation cannot be ruled out, whereas the 4:3 complexes behave as 2:1 (or even 3:1) electrolytes.

Introduction

Cyclic polyethers, e.g. 15-crown-5 or 18-crown-6 ethers, are known to form coordination compounds with rare earth ions [2, 3]. When ether functions are replaced by amine groups, such as in ligand (2,2), the stability of the complexes increases by approximately three orders of magnitude [4]. In a previous communication, we have shown that the 1:1 complex between europium nitrate and the tetraoxadiaza macrocycle (2,2) is comprised of bis(nitrato) complex cations $[Eu(NO_3)_2(2,2)]^+$ and of free nitrate ions NO_3^- [5]. In order to determine the effect of alkyl substitution on the amine function, we have synthesized the ligand 1,7,10,16-tetraoxa-4,13-diaza-*N*,*N*′-dimethylcyclooctadecane, $Me_2(2,2)$, together with its complexes with lanthanoid nitrates. In this paper, we report the synthetic procedures used as well as the characterization of the complexes.



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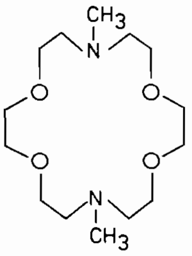

$Me_2(2,2)$

Experimental

Synthesis of the Ligand

The ligand $Me_2(2,2)$ was synthesized from ligand (2,2) by slightly modifying the procedures described in refs. 6–8. A solution of 1 g of (2,2) (Merck, Kryptofix® 22) in 0.88 g 100% formic acid (Merck, p.a.) was cooled to 0 °C; 0.7 g of formaldehyde (36% solution, Fluka puriss) was added and the resulting mixture was heated for 15 h under reflux at 100 °C. The yellow solution was cooled to room temperature, acidified by 1.1 ml 25% HCl, heated again under reflux at 110 °C for 4 h, and concentrated to almost dryness on a rotatory evaporator. The product was dissolved in 5 ml H_2O, neutralized with 10 ml 25% NaOH and extracted twice with 20 ml benzene (Merck, p.a.). An additional 5 ml 25% NaOH were added to the aqueous phase, which was further extracted by 20 ml benzene. The organic extract was dried with NaOH pellets, filtered and evaporated to dryness. The oily product was dried for 3 h under vacuum (10^{-1} mm Hg) and purified by chromatography and recrystallization as follows.

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*For Part 31, see ref. 1; for Part 30, see ref. 3.

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TABLE I. Elemental Analyses of the Complexes Between $Ln(NO_3)_3$ and Ligand L = $Me_2(2,2)$

Ln	Ln:L	Molecular weight	C (%)		H (%)		N (%)		Ln (%)	
			Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
La	1:1	615.3	27.33	27.43	4.91	4.90	11.38	11.32	22.57	22.52
Ce	1:1	616.5	27.27	27.12	4.90	4.83	11.36	11.31	22.73	22.71
Pr	4:3	2178.9	23.15	23.05	4.16	4.11	11.57	11.27	25.87	25.92
Nd	4:3	2192.2	23.01	23.11	4.14	4.06	11.50	11.35	26.32	26.22
Sm	4:3	2216.7	22.76	22.93	4.09	4.11	11.37	11.27	27.13	27.27
Eu	4:3	2223.1	22.69	22.71	4.08	4.18	11.34	11.27	27.34	26.99
Gd	4:3	2244.3	22.48	23.07	4.04	4.00	11.23	10.78	28.03	27.73
Tb	1:1	635.3	26.47	26.42	4.76	4.74	11.02	10.91	25.01	24.96
	4:3	2251.0	22.41	22.55	4.03	4.22	11.20	11.01	28.24	27.43
Dy	4:3	2265.3	22.27	22.32	4.00	4.09	11.13	11.12	28.69	28.68
Ho	4:3	2275.0	22.17	22.64	3.99	4.29	11.08	10.78	28.99	28.84

A 30-cm long column with a 2.5-cm O.D. was packed with 20 g basic Al_2O_3 suspended in CH_2Cl_2 (Fluka, puriss). The oily product was added and eluted (1 ml/mn) with CH_2Cl_2/CH_3OH (99:1). The purity of the collected fractions (3 ml) was checked by thin layer chromatography: $R_f = 0.34$ and 0.69 for (2,2) and $Me_2(2,2)$, respectively (Al_2O_3 plates and CH_2Cl_2/CH_3OH (95:5) mixed solvent). The five purest fractions were combined, evaporated to dryness and dried under vacuum (10^{-1} mm Hg). Dry acetonitrile (1–2 ml) was then added and the solution cooled to −22 °C. White crystals were deposited with a fusion point of *ca.* 20 °C. The ligand was characterized by its IR and NMR spectra. Yield: 0.89 g (80%).

Synthesis of the Complexes

Lanthanoid nitrates were synthesized from pure oxides (99.9%) and nitric acid as previously described [9]. All the reactions were performed under strictly anhydrous conditions and Ar atmosphere. Acetonitrile (Merck, p.a.) was distilled three times over P_4O_{10} prior to use. A solution of 1 mmol $Ln(NO_3)_3 \cdot xH_2O$ ($1 \leqslant x \leqslant 3$) in 20 ml CH_3CN and 2 ml freshly distilled $HC(OEt)_3$ (Fluka, purum) was stirred and heated for 3 h under reflux. If necessary, the solution was filtered while hot to eliminate insoluble material. After cooling, a solution of 1 mmol $Me_2(2,2)$ in 15 ml CH_3CN was added and the resulting mixture was heated for 3 h under reflux. In most cases microcrystals deposited upon cooling. For Ln = Dy or Ho, dry Et_2O was added dropwise to the cooled solution (4 °C) in order to initiate precipitation. The microcrystalline powders were recrystallized several times in dry CH_3CN. They are very hygroscopic and exhibit the characteristic colours of Ln(III) ions. The results of C, H, N elemental analyses (Ilse Beetz Mikroanal. Lab., Kronach) and complexometric analyses of Ln(III) ions by EDTA are given in Table I.

Spectroscopic and Physicochemical Measurements

IR spectra were measured as KBr pellets on a Mattson Alpha Centauri or Bruker IFS 113V FT IR spectrometer. Raman spectra were recorded with a Spex Ramalog-4 instrument. X-ray diffraction data were collected with a Philips PW 1279 generator equipped with a PW 1050 diffractometer and a PW 1710 microprocessor (Cu Kα, 35 kV, 30 mA). Samples were protected by thin polyethylene films. Effective magnetic moments were calculated from the measured mass susceptibilities at 20 ± 1 °C (Faraday method, Bruker BE-10 magnet, Mettler ME-21 microbalance). Corrections for diamagnetic contributions were made [10] and $HgCo(NCS)_4$ was used as calibration standard [11]. Conductometric measurements were carried out at 25.0 ± 0.1 °C, with 0.001 M solutions in dry CH_3CN, using a Metrohm E-365 conductometer (cell constant = 0.073).

Results and Discussion

Provided the syntheses are performed under strictly anhydrous conditions, ligand $Me_2(2,2)$ forms complexes with both the lighter and the heavier lanthanoid ions. Pure compounds are usually obtained only after several recrystallizations so that the yield of the syntheses is low. In the presence of hydration water, hydroxides tend to coprecipitate and non-stoichiometric compounds are isolated. The complexes appear to undergo hydrolytic decomposition if exposed to air. The metal:ligand ratio is 1:1 for La and Ce, and 4:3 for Pr–Dy and Ho. A 1:1 complex has also been isolated for Tb but, as will be discussed below, most of its properties resemble those of the 4:3 complexes.

According to X-ray diffraction powder patterns, the La and Ce complexes are isostructural and so are the 4:3 complexes with Pr, Nd, Gd–Dy, and Ho.

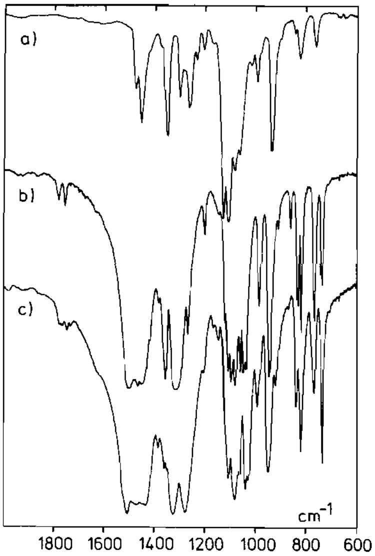

Fig. 1. Part of the IR spectra (film or KBr pellets) of (a) ligand $Me_2(2,2)$; (b) $La(NO_3)_3 \cdot Me_2(2,2)$; and (c) $[Nd(NO_3)_3]_4[Me_2(2,2)]_3$.

TABLE II. Nitrate Vibrations in 1:1 and 4:3 Complexes with $Me_2(2,2)$[a]

La (1:1)		Eu (4:3)		Assignment[b]
IR	Raman	IR	Raman	
	712	705vw	703	$\nu_5(B_2)$
733				
737	737		737	$\nu_3(A_1)$
741	742	740	743	
816		815sh		
818	824	819	821	$\nu_6(B_1)$
828[c]		826sh[c]		
		1029sh	1028	
1038	1035sh	1038		
1045				$\nu_2(A_1)$
1048[c]	1049		1044	
		1280	1272	$[Eu(NO_3)_6]^{3-}$
1315br	1317	1326		$\nu_4(B_2)$[c]
1497br	1503	1497		
1502br		1509	1511	$\nu_1(A_1)$

[a] Key: br = broad, sh = shoulder, vw = very weak. [b] On the basis of bidentate nitrates with local C_{2v} symmetry [13]. [c] Possible interference from ligand modes.

Patterns for Sm and Eu are more difficult to assign to this latter series because many lines have an intensity quite different from that of the Pr or Dy lines. However, a single-crystal X-ray diffraction study has shown that the Nd and Eu complexes belong to the same crystallographic space group [12]. All the 4:3 complexes may then be considered as being isostructural. The diffraction pattern of the 1:1 Tb complex is almost identical to those of the 4:3 complexes.

Vibrational spectra are in agreement with the X-ray data. They fall into two series: (i) La and Ce 1:1 complexes; and (ii) all the 4:3 complexes (*cf.* Fig. 1). Despite interferences from the ligand vibrations, the nitrate modes could be assigned (Table II). In the case of the 1:1 complexes, six vibrations are found in spectral ranges corresponding to absorptions by bidentate nitrate ions. The observed separation of the ν_1 and ν_4 modes (*ca.* 180–190 cm^{-1}) is in agreement with this conclusion and corresponds to data reported for similar complexes with 18-membered macrocyclic ligands [2, 3, 14]. Moreover, the separation of the two combination bands ($\nu_2 + \nu_3$) found at 1756 and 1781 cm^{-1} lies at the lower end of the 20–66 cm^{-1} range proposed by Lever *et al.* [15] as indicative of bidentate nitrate groups. In view of the many interferences between ligand and anion vibrations, however, one cannot completely rule out the presence of one monodentate nitrate. Several absorption bands, for instance ν_3, ν_6 and ν_2, are split into two or three components, pointing to slightly non-equivalent nitrates. Despite this, no IR absorption could be unambiguously assigned to ionic nitrate groups, as was the case for $[Eu(NO_3)_2(2,2)]NO_3$ [5]. This is confirmed by the Raman spectra in which the nitrate emissions are quite intense: in particular, a single, large band appears for ν_2, the frequency of which is similar to that observed for the 1:1 molecular complexes $[Ln(NO_3)_3(2,2)]$ with Ln = La–Sm [14].

The vibrational spectra of the 4:3 complexes are similar to each other except for small systematic shifts in the position of the absorption bands when the atomic number increases. They display somewhat simpler nitrate vibrations than the 1:1 complexes, several modes being dominated by an intense component. This may be traced back to the presence of an hexakis(nitrato) anion [12] characterized by a large ν_4 absorption around 1280 cm^{-1}. A similar band has been observed for other 4:3 nitrato complexes [16] and the corresponding absorption for $M_2Ce(NO_3)_6$ occurs at 1275 cm^{-1} ($M = NH_4^+$) and 1290 cm^{-1} ($M = K^+$) [17]. Combination bands appear at 1730–35 (weak), 1743–48, 1767–73 (weak) and 1773–81 cm^{-1}, indicating the presence of two types of bidentate nitrates.

Ligand vibrations are shifted upon complexation and are often split into several components. This, along with interferences from nitrate vibrations, makes any precise assignment difficult. For both 1:1 and 4:3 complexes, the most noticeable changes occur for vibrations at 782 cm^{-1} ($r(CH_2)$, displaced -15 to -17 cm^{-1} towards lower wave-numbers) and *ca.* 1110 cm^{-1} (ν(C–C–O) and ν(C–C–N), shifted by *ca.* -30 cm^{-1}). Bands at 833, 946, 993, 1430–1480 and 2750–2950 cm^{-1} experience much

TABLE III. Corrected Magnetic Moments (21 ± 1 °C, ± 2%, Bohr Magneton) of the Isolated Complexes and of the Corresponding Complexes with 18-Crown-6 Ether

Ln	Ln:L	L	
		$Me_2(2,2)$	18C6[a]
Ce	1:1	2.64	2.38
Pr	4:3	3.33	3.35
Nd	4:3	3.39	3.32
Sm	4:3	1.58	1.59
Eu	4:3	3.34	3.30
Gd	4:3	7.87	7.89
Tb	4:3	9.65	
Dy	4:3	10.67	
Ho	4:3	10.65	

[a] Data from ref. 2.

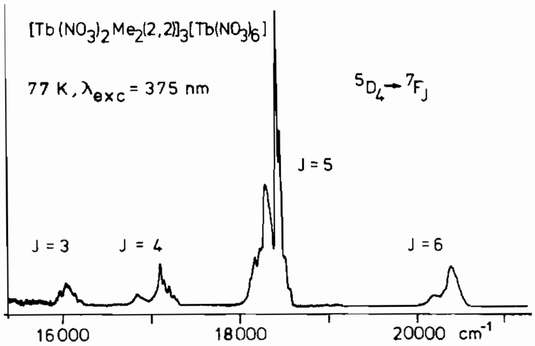

Fig. 2. Part of the luminescence spectrum of $[Tb(NO_3)_3]_4$-$[Me_2(2,2)]_3$ at 77 K. Excitation: 375 nm ($^5L_{10}$ level); analysing bandpass: 0.5 nm. The weak transitions to the $^7F_0$, $^7F_1$ and $^7F_2$ levels (15 600–14 500 cm^{-1}) are not shown. Vertical scale: arbitrary units.

smaller shifts, *ca.* ±5 cm^{-1}. Small differences between the 1:1 and 4:3 complexes can be detected in the intensity distribution of the vibrations around 1050–1120, 1430–1480 and 2750–2950 cm^{-1}, but the most characteristic change is seen in the region of the 'ring-breathing' mode. This vibration appears at *ca.* 860 cm^{-1} both in the IR and Raman spectra of the 1:1 complexes. For the 4:3 complexes, it appears as a very weak shoulder in the IR spectrum (870 cm^{-1}), but is clearly present in the Raman spectrum (866 cm^{-1}). A similar situation has been reported for 1:1 and 4:3 nitrato complexes with 18-crown-6 ether [16].

The IR spectra of the Tb 1:1 and 4:3 complexes are almost identical. A close scrutiny, however, reveals vibrational bands in the spectrum of the 1:1 complex that can be assigned to the uncomplexed ligand (e.g. 835, 948, 1110 and 1440–1470 cm^{-1}). It therefore appears that the 1:1 complex contains chemical species analogous to those found in the 4:3 complexes with, in addition, an extra molecule of uncomplexed ligand. This latter is probably held in the crystalline lattice by hydrogen bonding, as has been observed in other macrocyclic complexes [3, 18–20]. Three other properties of the 1:1 Tb complex are in line with this interpretation. The first pertains to magnetic susceptibility measurements: the effective magnetic moments of the Tb(III) ions in the 1:1 complex are, within experimental error, the same as the value reported in Table III for the 4:3 complex. All the magnetic moments determined for $Me_2(2,2)$ complexes are close to the values previously reported for 1:1 and 4:3 complexes with 18-crown-6 ether [2] and are only a few percent smaller than the free ion values. The second property is the luminescence of the 1:1 complex which, again, is identical to that of the 4:3 complex, even when the spectra are compared under high-resolution conditions, e.g. under laser-excitation to the $^5D_4$ level. This means that the Tb(III) ions experience very similar crystal-field effects in both complexes. The luminescence spectrum of the 4:3 complex is presented in Fig. 2. All the transitions arise from the $^5D_4$ level. The relative, corrected and integrated intensities of the $^5D_4 \rightarrow {^7F_J}$ transitions are: 21 (barycentre 20 355 cm^{-1}), 100 (18 345 cm^{-1}), 20 (17 062 cm^{-1}), 10 (16 057 cm^{-1}), 0.9 (15 378 cm^{-1}), 0.6 (14 984 cm^{-1}) and 0.2 (14 714 cm^{-1}) for J = 6, 5, 4, 3, 2, 1 and 0, respectively. This intensity distribution is close to that observed for $Tb(NO_3)_3$ solutions in a strong donor solvent, e.g. DMSO [21]. Finally, the thermal behaviour of the 1:1 complex was studied by thermogravimetry: a loss of weight occurs between 130 and 250 °C corresponding to the transformation into the 4:3 complex with loss of ligand. The enthalpy of this reaction is almost zero (*cf.* ref. 2). From 250 °C on, the compound decomposes completely in a strongly exothermic process.

The molar conductivities at 25 °C of 10^{-3} M solutions of the 1:1 and 4:3 complexes have been determined in dry acetonitrile. The 1:1 complexes are non-electrolytes: $\Lambda_M = 48$ (La) and 65 (Ce) Ω^{-1} cm^2 mol^{-1}. Under similar conditions, the molar conductivities of 18-crown-6 complexes with a 1:1 metal:ligand ratio were found to be 28 (Pr) and 57 (Nd) Ω^{-1} cm^2 mol^{-1} [16], and that of $[Eu(NO_3)_2$-$(2,2)]NO_3$ was 135 Ω^{-1} cm^2 mol^{-1} [5]. This latter value is clearly in the range accepted for 1:1 electrolytes (120–160 Ω^{-1} cm^2 mol^{-1} [22]). There is evidence that many lanthanide complexes with 18-membered macrocycles form $[LnX_2 \cdot L]^+$ species, both in the solid state [3] and in solution [3, 23]. The La and Ce 1:1 complexes could therefore undergo some dissociation

$$[Ln(NO_3)_3 \cdot Me_2(2,2)] \rightleftharpoons [Ln(NO_3)_2 \cdot Me_2(2,2)]^+ + NO_3^-$$

in solution, which would explain their somewhat large Λ_M values: non-ionic complexes with smaller macrocycles have molar conductivities in the range 10–15 Ω^{-1} cm^2 mol^{-1}. The 4:3 complexes have much larger molar conductivities, e.g. 313 (Sm) and 279 (Eu) Ω^{-1} cm^2 mol^{-1}, which means they are between 2:1 (accepted range 220–300 Ω^{-1} cm^2 mol^{-1} [22]) and 3:1 electrolytes (accepted range 340–420 Ω^{-1} cm^2 mol^{-1} [22]). The spectroscopic properties presented above for these 4:3 complexes, as well as the preliminary results of a crystal structure determination [12], point to compounds comprised of bis(nitrato) complex cations and of an hexakis(nitrato) anion. The observed conductivities would then correspond to the following equilibria taking place into solution:

$$[Ln(NO_3)_2\cdot Me_2(2,2)]_3[Ln(NO_3)_6] \rightleftharpoons 3[Ln(NO_3)_2\cdot Me_2(2,2)]^+ + [Ln(NO_3)_6]^{3-}$$

$$[Ln(NO_3)_6]^{3-} \rightleftharpoons [Ln(NO_3)_5]^{2+} + NO_3^-$$

Indeed, Walker and Weeden [24] have shown the hexakis(nitrato) anions to be unstable in solution.

Conclusions

Ligand $Me_2(2,2)$ forms non-ionic 1:1 complexes with lanthanum and cerium nitrates, in which all the three nitrate groups are coordinated, most probably in a bidentate fashion, suggesting a coordination number of twelve for La(III) and Ce(III). The other lanthanoid nitrates (Pr–Dy, Ho) form 4:3 ionic complexes that may be formulated as $[Ln(NO_3)_2\cdot Me_2(2,2)]_3[Ln(NO_3)_6]$. The coordination number of the Ln(III) ions in the complex cations is therefore ten. A complex having a 1:1 metal:ligand ratio has also been isolated for an intermediate lanthanoid ion, *i.e.* Tb(III), but it turned out to be a 4:3 complex with an additional outer-sphere coordinated molecule of ligand held in the crystalline lattice. Upon recrystallization, this 1:1 complex yields its ligand-free 4:3 analogue.

A different situation has been reported for the unsubstituted (2,2) ligand. Indeed, 1:1 complexes are isolated for the entire series La–Yb. The nitrate ions are bonded differently in the lighter (La–Sm) and heavier (Gd–Yb) lanthanoid series [14]. A subsequent crystal structure determination has shown the Eu complex as being ionic, $[Eu(NO_3)_2\cdot(2,2)]^+\cdot NO_3^-$, with a coordination number of ten [5]. It is reasonable to think that the complexes of the other heavier ions with ligand (2,2) display a similar structure. Hence, substitution of the amine functions by methyl groups shifts the coordination change to the beginning of the lanthanoid series. This may be understood as follows. To keep the 1:1 metal:ligand ratio along the lanthanide series, the ligand would have to adopt a more and more puckered boat conformation with decreasing ionic radius of the metal ion. With $Me_2(2,2)$, the presence of the methyl groups creates a steric hindrance preventing this conformational change to occur from praseodymium onwards.

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