Syntheses and Properties of Complexes of a Conjugated Macrocyclic Hexamine with Lanthanide Nitrates

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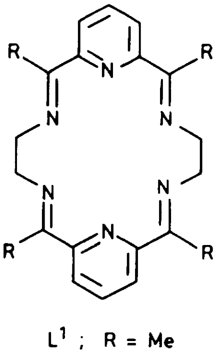
Complexes $[M(NO_3)_3L^3]$, where M = La, Ce, Pr, or Nd, and L^3 is the fully conjugated hexaimine 3,10,18,25,31,32-hexa-azapentacyclo$[25.3.1.1^{12,16}0^{4,9}0^{19,24}]$dotriaconta-1(31),2,4,6,8,10,12,14,16(32),17,19,21,23,25,27,29-hexadecaene, have been synthesised by ligand exchange. Properties, including n.m.r. paramagnetic shifts, are described and possible structures are discussed.

Following earlier investigations of lanthanide complexes of macrocyclic polyethers, there has recently been considerable interest in the rather analogous but more stable lanthanide complexes of macrocyclic polyamines.[1–5] Thus in previous reports[1,2] we have described the template or ligand-transfer syntheses and *X*-ray structure determinations of some complexes of lanthanide ions with the macrocyclic hexamine L^1. The synthesis of $La(ClO_4)_3L^1(H_2O)_2$ has also been reported,[3] as have the template syntheses of lanthanide complexes of the analogous ligand L^2 together with the crystal structure of the Sm derivative.[4] In this last instance there was evidence that in the cases of the heavier lanthanides Nd, Sm, and Gd—Lu, some of the –CH=N– linkages in the initial products had been hydrolysed to the –CH(OH)–NH– form.

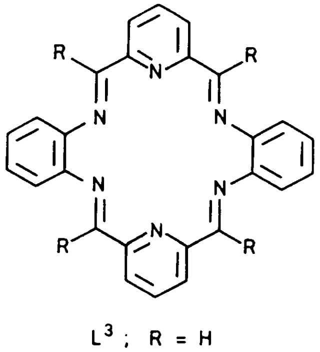
We now report the syntheses and properties of complexes of the fully conjugated ligand L^3, which would be expected to remain planar when co-ordinated, in contrast to complexes of L^1 or L^2 where the hexamine adopts a folded conformation. While this work was in progress, the template synthesis and properties of complexes of Ce, Pr, and Nd nitrates with the related ligand L^4 were reported,[5] and the free ligand L^3 has also been obtained.[6]

Experimental

2,6-Diformylpyridine.—As this compound is not readily available it was synthesised from 2,6-dimethylpyridine, and the synthetic path is summarised here for convenience of other workers. 2,6-Dimethylpyridine was oxidised by potassium permanganate to the diacid, which was converted by thionyl chloride into the double acid chloride (not isolated). The latter on treatment with butanol in carbon tetrachloride gave the diester which on reduction with diethyl ether–$LiAlH_4$ and hydrolysis afforded the diol. Finally, the diol was selectively oxidised by freshly prepared active MnO_2[7] to give 2,6-diformylpyridine (yield 10% based on 2,6-dimethylpyridine).



L^1 ; R = Me
L^2 ; R = H



L^3 ; R = H
L^4 ; R = Me

Preparation of Complexes.—(a) *Template condensation experiments.* Preliminary experiments in which methanolic solutions of equimolar amounts of 2,6-diformylpyridine, *o*-phenylenediamine, and hydrated lanthanum nitrate were mixed at room temperature produced a yellow solution from which a bright yellow solid precipitated after a few seconds. Although the i.r. spectrum of the product showed no absorption attributable to C=O or N–H stretching modes but showed absorption near 1 630 cm^{-1} due to co-ordinated imine groups, analysis of the material was unsatisfactory, being over 2% low in carbon compared with the theoretical value for a 1:1 complex between lanthanum nitrate and L^3. Similar results were obtained using hydrated cerium or praseodymium nitrates, these products being brown in contrast to the pure complexes obtained as described below.

(b) *Ligand-transfer reactions.* Bright orange $[BaL^3{}_2][ClO_4]_2$ was prepared[8] and gave satisfactory analyses. Hydrated neodymium nitrate, $Nd(NO_3)_3\cdot6H_2O$ (0.15 g, 0.34 mmol) dissolved in a mixture of methanol (12.5 cm^3) and water (2.5 cm^3) was added to the barium complex (0.030 g, 0.026 mmol) and heated at 50 °C in a stoppered flask for 24 h. The orange crystalline product was collected by filtration, washed with a little methanol, and air dried. Yield: 0.028 g (73%). The corresponding yellow lanthanum, orange cerium, and pale orange praseodymium compounds were prepared similarly in 70—80% yields. Analytical data are given in Table 1.

Table 1. Analytical data for $[M(NO_3)_3L^3]$, $C_{26}H_{18}MN_9O_9$ (M = La, Ce, Pr, or Nd)

	Analysis* (%)		
M	C	H	N
La	41.8 (42.2)	3.0 (2.45)	16.5 (17.05)
Ce	41.9 (42.2)	2.5 (2.45)	16.7 (17.0)
Pr	41.9 (42.1)	2.6 (2.45)	16.75 (17.0)
Nd	41.8 (41.9)	2.55 (2.4)	16.7 (16.9)

* Calculated values are given in parentheses.

Results and Discussion

Properties of the Complexes.—As the crystals were unsuitable for single-crystal *X*-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate, and acetonitrile, investigations into the structure and properties of the compounds were restricted to i.r. spectra, thermogravimetric analysis, and ^{1}H n.m.r. in Me_2SO, in which the complexes are slightly soluble. The compounds are also involatile and mass spectra could not be obtained by electron impact.

Infrared spectra. These were obtained from Nujol or hexachlorobutadiene mulls. Assignments were aided by comparison with $[BaL^3{}_2][ClO_4]_2$. No stretching bands assignable to NH, OH, or CO were present, so that condensation is known to be complete, in contrast to observations[4] relating to the preparation of lanthanide complexes of L^2, when –NH–CH(OH)– groups were present in some circumstances.

The nitrate groups seem certain to be co-ordinated to the metal because the E' band of unco-ordinated nitrate is split into bands at 1 445, 1 426 cm^{-1} (La) and 1 455, 1 425 cm^{-1} (Nd) (B_1), and at 1 340, 1 300, 1 290 cm^{-1} (La) and 1 344, 1 311, 1 292 cm^{-1} (Nd) (A_1), while the symmetrical stretch A_1 is observed at 1 013 cm^{-1} (La and Nd). These values show rather less splitting of the E' mode than those of $[La(NO_3)_3(bipy)_2]$ (bipy = 2,2′-bipyridyl), shown by *X*-ray diffraction[9] to be 10-co-ordinated and to contain bidentate nitrate ions, which has bands at 1 497, 1 489, 1 458; 1 296; and 1 032, 1 024 cm^{-1}. This effect is likely to be caused by the difference in co-ordination number, if the structure of the presently described complexes is, as is extremely likely, 12-co-ordinated and similar to that of $[La(NO_3)_3L^2]$.[2] However the presence of monodentate nitrate certainly cannot be ruled out, particularly as L^3 is likely to be unable to flex in the same way as L^2 is found to do,[2] apparently in order better to accommodate an uneven 2:1 co-ordination of the three bidentate nitrate ions in the two co-ordination hemispheres.*

The hexamine frequencies are very similar to those observed for $[BaL^3{}_2][ClO_4]_2$, where there is good evidence that the Ba ion co-ordinates both macrocycles with the perchlorate groups free. Observed bands include the aldimine CN stretch at 1 633 (La) and 1 634 cm^{-1} (Nd) and the pyridine stretch at 1 593 (La) and 1 594 cm^{-1} (Nd). These data suggest a further possibility of an alternative formulation, namely as $[ML^3{}_2][M(NO_3)_6]$ where M = La, Ce, Pr, or Nd, in which case the cation would be analogous to the presumed sandwich cation in $[BaL^3{}_2][ClO_4]_2$.

Thermal measurements. The La and Nd compounds were heated in a thermogravimetic analysis apparatus in air; they decomposed rapidly in the range 375—395 °C, leaving a black residue. A sample of the La compound was removed after being heated to 360 °C from 20 °C during 100 min. Its i.r. spectrum was identical with that of the original material, which clearly has considerable thermal stability.

N.m.r. measurements. Although insoluble in most solvents, the complexes are slightly soluble in Me_2SO, and ^{1}H n.m.r. spectra were obtained at 400 MHz (La) or 80 MHz (Ce, Pr, or Nd) in this medium (Bruker WH-400 or WP-80 spectrometers respectively). Results are shown in Table 2. All resonances are observed for the paramagnetic and the diamagnetic compounds. Assignments are straightforward on the basis of shift, coupling, and integration except for the relative assignments of the two *o*-phenylene resonances which in the case of the La complex might just possibly be interchanged, and which in the cases of the paramagnetic complexes have been assigned on the basis that the 3,6 protons, which are nearer the metal ion than the 4,5, should have the larger paramagnetic shift. The spectra further substantiate the co-ordination of the macrocycle in the fully condensed form L^3 after ligand transfer.

Table 2. ^{1}H N.m.r. data of $[M(NO_3)_3L^3]$*

		Pyridine		Phenylene	
M	CH=N	β	γ	3,6	4,5
La	9.35	8.35	8.58	7.70	7.94
Ce	8.90	7.85	8.52	4.77	6.24
	0.45	0.50	0.06	2.93	1.70
Pr	10.27	8.24	9.10	0.65	4.21
	−0.92	0.11	−0.52	7.05	3.73
Nd	19.28	10.19	9.84	6.28	7.03
	−9.93	−1.84	−1.26	1.42	0.91

* Spectra were obtained at 80 MHz (Ce, Pr, or Nd) or 400 MHz (La) in Me_2SO at ambient temperature. Upper values are positions of observed resonances in p.p.m. relative to Me_2SO at $\delta = 2.52$. Lower values are the shifts relative to the La complex (shifts to high field taken as positive). The 3,6- and 4,5-phenylene assignments, as explained in the main text, might possibly be interchanged. Linewidths at half height ranged from 1—2 Hz (La) to 5—15 Hz (Nd).

The paramagnetic shifts vary from 7.05 p.p.m. upfield to 9.93 p.p.m. downfield according to proton and lanthanide. It is evident from comparison of the paramagnetic shifts with the values of the Bleaney constants[10] for Ce—Nd that these shifts cannot arise from an isostructural series of compounds experiencing dipolar shifts only, and the contact contribution might be expected to be considerable in the case of a fully conjugated macrocyclic amine. Although the structure of the metal–macrocycle moiety probably remains the same along the series La—Nd, co-ordination by anions or Me_2SO ligands may well vary in stoicheiometry or geometry, thus altering the magnetic anisotropy tensor and perhaps the contact contribution also. In these circumstances, and particularly because of the absence of *X*-ray structural data, it seems unsound to attempt to apportion the shifts as between dipolar and contact.

Acknowledgements

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* It has been suggested by a Referee, whose contribution we acknowledge, that some or all of the nitrate groups may be bidentate bridging, leading to a dimeric or higher polymeric structure; this is entirely possible.