

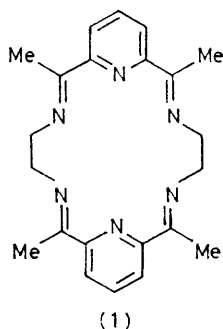
Preparation and Properties of Complexes of Lanthanides with a Hexadentate Nitrogen-donor Macrocyclic: X-Ray Crystal Structure of the Complex $[\text{La}(\text{NO}_3)_3\text{L}]$

By J. D. JULIUS BACKER-DIRKS, COLIN J. GRAY, F. ALAN HART,* MICHAEL B. HURSTHOUSE, and BARBARA C. SCHOOP
(Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS)

Summary The template condensation of 2,6-diacetylpyridine with ethylenediamine gives complexes $[\text{M}(\text{NO}_3)_3\text{L}]$ ($\text{M} = \text{La}$ or Ce) of the hexadentate nitrogen donor macrocycle L; the structure of $[\text{La}(\text{NO}_3)_3\text{L}]$ has been determined by X-ray diffraction, and the complexes, whose ^1H n.m.r. spectra are described, are kinetically stable in water with respect to dissociation of the macrocycle.

A RECENT report¹ has described the template synthesis of Ca^{2+} , Sr^{2+} , Ba^{2+} , and Pb^{2+} complexes of the macrocyclic ligand L (1). We now report similar syntheses of lanthanide complexes of L. Hydrated lanthanum nitrate (0.75 mmol), ethylenediamine (1.5 mmol), and 2,6-diacetylpyridine (1.5 mmol) were boiled under reflux in methanol (30 cm³) for 4 h, giving pale pink-brown crystals of $[\text{La}(\text{NO}_3)_3\text{L}]$ [61%, m.p. 240–245 °C (decomp.)]. The reaction proceeded similarly with cerous nitrate hexahydrate, giving deep yellow $[\text{Ce}(\text{NO}_3)_3\text{L}]$. Satisfactory analytical results were obtained from these compounds. The heavier lanthanides do not give analogous complexes $[\text{M}(\text{NO}_3)_3\text{L}]$ under these conditions. The structure of $[\text{La}(\text{NO}_3)_3\text{L}]$ has been determined by X-ray crystallography.

Crystal data: $\text{C}_{22}\text{H}_{26}\text{LaN}_9\text{O}_9$, $M = 699.4$, monoclinic, $a = 8.623(1)$, $b = 18.221(2)$, $c = 17.039(2)$ Å, $\beta = 99.01(2)^\circ$, $U = 2644.2$ Å³, space group $P2_1/c$, $D_m = 1.73$, $D_c = 1.75$ g cm⁻³, $Z = 4$, $F(000) = 1400$, $\mu(\text{Mo-K}\alpha) = 15.55$ cm⁻¹. Intensity data (5114 reflections) were recorded on a Nonius CAD4 diffractometer and the structure solved and refined by standard methods. The current R value is 0.036 for 3453 data with $I > 3\sigma(I)$.†



The crystal structure of $[\text{La}(\text{NO}_3)_3\text{L}]$ (Figure) shows 12-co-ordination of the metal ion to the six macrocyclic nitrogen atoms and to three bidentate nitrate ions. La–N(pyridine) internuclear distances are 2.746 and 2.764 Å while La–N(imine) distances are slightly shorter at 2.672–2.729 Å. La–O distances lie in the range 2.689–2.767 Å.

These distances are best compared with those in $[\text{Gd}(\text{NO}_3)_3(\text{dpae})]^{2+}$ [dpae = 1,2-di(pyridine-2-aldimino)ethane, $\text{C}_5\text{H}_4\text{N}-\text{CH}:\text{NCH}_2\text{CH}_2\text{N}:\text{CH}-\text{C}_5\text{H}_4\text{N}$], where Gd–N = 2.50–2.60 and Gd–O = 2.45–2.51 Å. After allowing for the lanthanide contraction, the La–N distances are ca. 0.05 Å greater and the La–O distances are ca. 0.12 Å greater than expected, and these increases may well arise from the change in co-ordination number from 10 to 12.

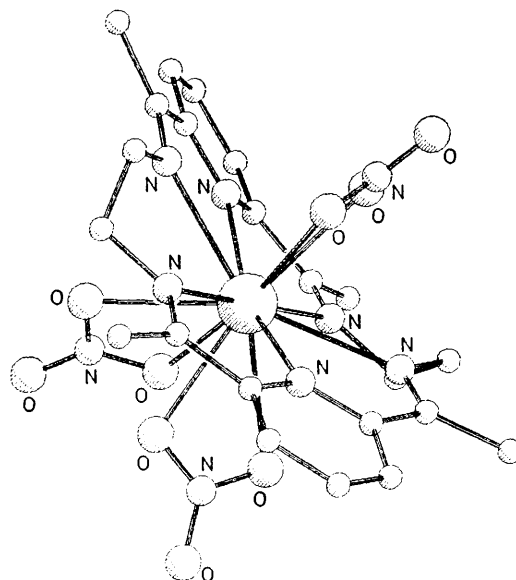


FIGURE. The molecular structure of $[\text{La}(\text{NO}_3)_3\text{L}]$

The complexes exist in water solution mainly as $[\text{ML}(\text{H}_2\text{O})_n]^{3+}$, as shown by conductivity measurements. The macrocyclic ligand remains undissociated in water and is kinetically stable to dissociation, as shown by the ^1H n.m.r. spectra in D_2O solution [$\text{M} = \text{La}$: τ 1.86 (C_5NH_3), 6.08 (CH_2), and 7.58 (Me); $\text{M} = \text{Ce}$: τ 2.80 ($\beta\text{-C}_5\text{NH}_3$) and -1.92 ($\gamma\text{-C}_5\text{NH}_3$), 9.56 (CH_2), and 6.47 (Me)]. These spectra (which indicate that the cerium compound has a biaxial susceptibility tensor) remain unaltered for 24 h after addition of Ce^{3+} ion to $[\text{LaL}(\text{H}_2\text{O})_n]^{3+}$, or of La^{3+} ion to $[\text{CeL}(\text{H}_2\text{O})_n]^{3+}$. Furthermore, the complexes give no precipitate when treated in aqueous solution with KF or KOH. Apart from 3-dimensionally enclosed lanthanide complexes of ethylenediaminetetra-acetic acid or cryptate^{3,4} ligands these are the first lanthanide complexes to be demonstrated to be kinetically stable in aqueous solution. They thus contrast

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

with lanthanide crown ether complexes, which immediately dissociate in water, as shown, for example, by precipitation of the ligand on addition of water to a methanol-acetone solution of the dibenzo-18-crown-6 complex of NdCl_3 .

The ^1H n.m.r. signal of acetate ion (0.092 M) in a D_2O solution of $[\text{Ce}(\text{NO}_3)_3\text{L}]$ (0.043 M) is shifted 2.51 p.p.m.

upfield relative to the position in the absence of the cerium complex. This type of complex might therefore be of use as an aqueous n.m.r. shift reagent.

We thank the S.R.C. for support.

(Received, 1st June 1979; Com. 575.)

¹ J. de O. Cabral, M. F. Cabral, W. J. Cummins, M. G. B. Drew, A. Rodgers, and S. M. Nelson, *Inorg. Chim. Acta*, 1978, **30**, L313.

² G. D. Smith, C. N. Caughlan, Mazhar-ul-Haque, and F. A. Hart, *Inorg. Chem.*, 1973, **12**, 2654.

³ O. A. Gansow, A. R. Kausar, K. M. Triplett, M. J. Weaver, and E. L. Yee, *J. Amer. Chem. Soc.*, 1977, **99**, 7087.

⁴ F. A. Hart, M. B. Hursthouse, K. M. Abdul Malik, and S. Moorhouse, *J.C.S. Chem. Comm.*, 1978, 549.