

## X-Ray Crystal Structure of a Cryptate Complex of Lanthanum Nitrate

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*Summary* An X-ray crystal structure determination shows that the complex cations in  $[\text{La}(\text{NO}_3)_2\{\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{N}\}]_3[\text{La}(\text{NO}_3)_6]$  contain a lanthanum ion

co-ordinated to eight cryptate donor atoms together with two bidentate nitrate ions, the cryptate ligand being somewhat distorted to accommodate the latter.

THE cryptate ligands,<sup>1</sup> particularly the 8-co-ordinating  $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ , form metal complexes which are the subject of considerable interest.<sup>2,3</sup> The encapsulated metal has usually been an alkali or alkaline earth metal but a recent preliminary account<sup>4</sup> of the preparation and novel redox, n.m.r., and kinetic properties of lanthanoid cryptates makes it desirable to report our current work on the structure of  $[La(NO_3)_2(cryp)]_3 \cdot [La(NO_3)_6] \cdot 2MeOH$ , where  $cryp = 4,7,13,16,21,24$ -hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane,  $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$ .

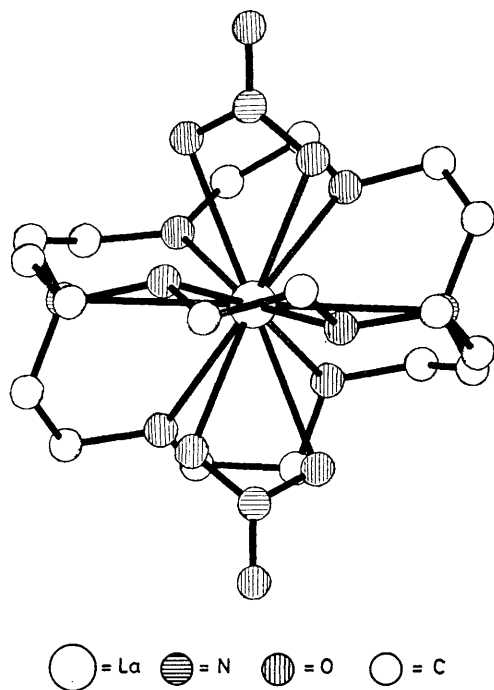


FIGURE. Structure of the  $[La(NO_3)_2(cryp)]^+$  ion lying on a general position. View along pseudo  $C_2$  axis.

Crystals of the complex were obtained by heating, in methanolic solution, lanthanum nitrate together with 1 molar proportion of the cryptate ligand, the crystals being deposited on subsequent cooling. Praseodymium nitrate treated similarly gave an immediate gelatinous basic precipitate which dissolved on digestion at 65 °C, ultimately yielding a crystalline product whose constitution is still under investigation. The heavier lanthanoids gave only intractable gelatinous precipitates.

*Crystal data:*  $[La(NO_3)_2(C_{18}H_{36}O_6N_2)]_3 [La(NO_3)_6] \cdot 2MeOH$ ,  $M = 2492.3$ , monoclinic,  $a = 32.798(6)$ ,  $b = 11.197(3)$ ,

$c = 26.763(6)$  Å,  $\beta = 109.55(3)^\circ$ ,  $U = 9261.8$  Å<sup>3</sup>, space group  $C2/c$ ,  $Z = 4$ ,  $D_m = 1.78$ ,  $D_c = 1.79$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 17.8$  cm<sup>-1</sup>,  $\lambda(Mo-K\alpha) = 0.71069$  Å.

The intensities of 8152 unique reflections ( $1.5 < \theta < 25^\circ$ ) were measured on a Nonius CAD4 diffractometer using monochromated Mo- $K\alpha$  radiation. The structure was determined by the heavy atom method and refined by blocked full-matrix least-squares<sup>5</sup> to a final  $R = 0.0373$  for 6499 reflections [ $F_o > 3\sigma(F_o)$ ]. All non-hydrogen atoms were treated anisotropically except the C and O atoms of the methanol molecule which were given isotropic temperature factors. The contributions of the H atoms were ignored.†

The structure contains three crystallographically distinct ions: (i)  $[La(NO_3)_6]^{3-}$ , lying on a centre of symmetry, (ii)  $[La(NO_3)_2(cryp)]^+$  lying on a  $C_2$  axis, and (iii)  $[La(NO_3)_2(cryp)]^+$  having no crystallographic symmetry (Figure) but having the same general arrangement of ligands as (ii). The hexanitratolanthanate ion (i) is a species of previously reported structure,<sup>6</sup> and the La-O interatomic distances in (i) lie between 2.615 and 2.709 Å. These nitrate groups are disordered over two orientations.

The ions  $[La(NO_3)_2(cryp)]^+$  have bonding interatomic distances in the following ranges: La-N, 2.813–2.848 Å; La-O(cryptate), 2.644–2.736 Å; La-O(nitrate), 2.626–2.688 Å. These distances are in or slightly (*ca.* 0.05 Å) above the range expected from previously determined structures involving co-ordination of lanthanoid ions with amines and with ether and nitrate oxygen atoms.<sup>7,8</sup> The co-ordination polyhedron shows the lanthanum atom enclosed within the cryptate ligand and co-ordinated to both nitrogen and all six oxygen atoms, as in cryptate complexes of other metals. However, two nitrate ions are co-ordinated also, each in a bidentate manner. Each nitrate ion is positioned in a gap between two  $CH_2CH_2OCH_2CH_2OCH_2CH_2$  chains of the cryptate. This has had the effect of closing the third, unoccupied, gap such that O-La-O' (where O and O' are members of adjacent chains) are 66.8–71.0°, compared with 107.9–117.3° for similar angles in the nitrate-occupied gaps. Further co-ordination by nitrate ions is thus effectively precluded. 12-co-ordination is not unusual for lanthanoid (especially lighter lanthanoid) complexes, but has apparently not previously been reported for cryptate complexes.

The methanol molecules occupy cavities in the structure, with an O(MeOH)-O(NO<sub>3</sub>) interatomic distance of 2.83 Å, corresponding to a weak hydrogen bond. A fuller account of this work will in due course be submitted for publication elsewhere.

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† 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.

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