

12-Co-ordinated Crown Ether Complex of Lanthanum; X-Ray Crystal Structure

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Summary A single-crystal X-ray study of trinitrato-*cis*, *syn*, *cis*-2,5,8,15,18,21-hexaoxatricyclo[20,4,0,0⁹,14]hexacosanelanthanum shows the metal ion to be co-ordinated to six polyether oxygen atoms and three bidentate nitrate ions; structural parameters are discussed.

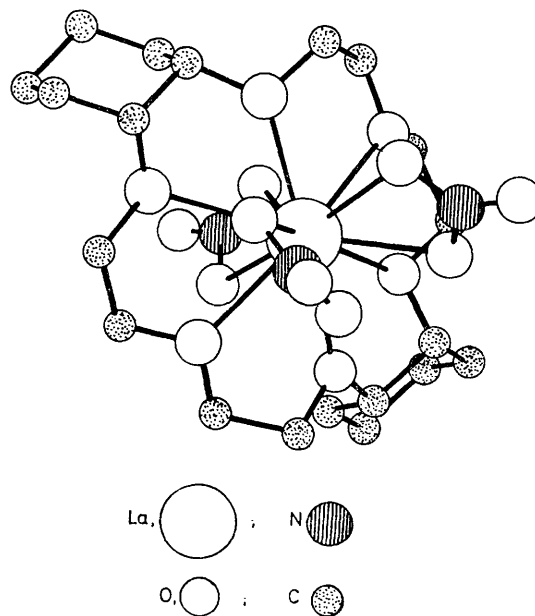
Fourier techniques and refined by least-squares to a present R of 0.108. The molecular structure is shown in the Figure.

ANNULAR polydentate ligands, particularly the crown ethers,¹ have attracted attention because of their ability to complex with metal ions such as sodium² or barium³ which are often reluctant to combine with other types of ligand. The lanthanides, which are Class A acceptors of suitable ionic radii for combination with 5- or 6-oxygen crown ethers, form complexes with the dibenzo-18-crown-6 and benzo-15-crown-5 ligands.⁴

We find that *syn*-di-(*cis*-cyclohexyl)-18-crown-6† complexes with lanthanum nitrate, depositing a well-crystallised product from ether-ethanol, and we present the first X-ray structural data concerning a lanthanide crown ether complex. This complex is also apparently the first uncharged molecular 12-co-ordinated complex to be described. Where other examples of 12-co-ordination are known, for example in $[\text{Ce}(\text{NO}_3)_6]^{n-}$ ($n = 2, 3$) or CaTiO_3 , the metal is co-ordinated entirely by anions.

Crystal data: $[\text{La}(\text{NO}_3)_3(\text{sdcc } 18,6)]$; M 697.44, monoclinic, $a = 11.440$, $b = 22.995$, $c = 11.892$ Å, $\beta = 118.74^\circ$, $U = 2743$ Å³, $Z = 4$, $D_c = 1.689$ g cm⁻³, space group Cc , $\mu(\text{Mo-K}\alpha) = 15.1$ cm⁻¹. Intensity data were recorded on a Nonius CAD4 automatic diffractometer using an ω - 2θ scan technique. A total of 2424 unique reflections were recorded, of which 2209 were considered significant, $2\theta_{\text{max}}$ being 50° . The structure was solved by Patterson and

† Systematic name as in Summary, henceforward called (sdcc 18,6).



FIGURE

The lanthanum atom is co-ordinated by the six oxygen atoms of the crown ether ring, by one bidentate nitrate ion on the more sterically hindered side of the ring, and by two

bidentate nitrate ions on the less hindered side. There is a two-fold pseudo-axis normal to the polyether ring. The six ether oxygen atoms are not quite coplanar, two diametrically opposed atoms being displaced 0.81 Å below the mean plane of the other four. The direction of displacement is away from the paired nitrate ions and thus tends to equalise the distances between the twelve ligand atoms. The shortest inter-ligand atom distance and smallest O-La-O angles of each type are (a) 2.06 Å and 44.9° in the same nitrate ion, (b) 2.78 Å and 63.0° between different nitrate

ions, (c) 2.82 Å and 62.0° between a nitrate oxygen and a polyether oxygen, and (d) 2.70 Å and 58.7° between two polyether oxygen atoms. Metal-ligand interatomic distances fall within the limits 2.63–2.71 Å (La-O_{nitrate}) and 2.61–2.92 Å (La-O_{ether}). These bonding distances are as expected except for two distances of 2.89 and 2.92 Å, unusually long for La-O, which relate to the two polyether oxygen atoms which have been displaced as noted above.

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