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Dichloro(triphenylmethyl)(2,2,2-cryptate)lanthanum(III), an Organolanthanide Cryptate Complex

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Although lanthanide cryptates have been the subject of recent interest [1–6] and though preparative routes, structures, chemical properties and NMR spectral properties have been investigated, no organolanthanide cryptates have apparently been previously reported. We now report the isolation of $LaCl_2(CPh_3)(2,2,2\text{-cryptate})$, where 2,2,2-cryptate = $N(CH_2CH_2OCH_2CH_2OCH_2CH_2)_3N$, as a deep red crystalline solid by the following reaction.

$$LaCl_3(2,2,2\text{-cryptate}) + LiCPh_3 \xrightarrow{THF} LaCl_2(CPh_3)(2,2,2\text{-cryptate}) + LiCl$$

Experimental

All operations were carried out under an argon atmosphere. Solvents were dried by distillation from sodium diphenylketonate. A stirred suspension of $LaCl_3(2,2,2\text{-cryptate})$ (0.212 g, 0.341 mmol) in THF (9 cm^3) at −65 °C was treated dropwise with chilled $LiCPh_3$ (−20 °C) in 2:1 THF:ether (4.70 cm^3, 0.237 *M*, 1.11 mmol). The temperature of the mixture was allowed to rise to −20 °C during 3½ hours and it was then allowed to rise to 0 °C and stirred at 0 °C for 2 hours. The red mixture was reduced to half volume by evaporation under low pressure and stored overnight at −25 °C. The extremely air-sensitive red solid product was collected by filtration (0.108 g, 38%) and dried under vacuum. *Anal.* Found: C, 53.3; H, 6.3; N, 3.2; Cl, 8.5%. $C_{37}H_{51}O_6N_2Cl_2La$ requires. C, 53.6; H, 6.2; N, 3.4; Cl, 8.5%.

The triphenylmethyl is decolourised instantly by traces of air. It is slightly soluble in THF but insoluble in benzene. The electronic spectrum showed a broad absorption, due to the CPh_3 group, with a maximum at 505 nm (reflectance spectrum as a Nujol mull). The infrared spectrum (Nujol mull) was as follows (w = weak, m = medium, s = strong, b = broad, sh = shoulder): 3080w, 3058w, 3022w, 1600m, 1562s, 1540w,sh, 1494m, 1469s, 1360w, 1352w, 1338m, 1309m, 1295m, 1274w, 1259m, 1216m, 1170m, 1120m,b,sh, 1072s,b, 1030m,b,sh, 980w, 957m, 820m,b, 755m, 736w, 700s, 693m,sh, 606w, 559w, 534w, 495w.

The $LaCl_3(2,2,2\text{-cryptate})$ used in the foregoing preparation was prepared thus. $LaCl_3 \cdot 6H_2O$ (5.5 g) was heated at 70 °C for 1 hour with Me_2SO (4 cm^3) and the viscous product was extracted with dry acetone (80 cm^3) until a white solid was obtained, which was collected by filtration and dried for 6 hours at 90 °C ($LaCl_3 \cdot 2Me_2SO$). This Me_2SO adduct was boiled for 5 hours under reflux in dry acetone with 2,2,2-cryptate (1 molar proportion) and the solution was taken to dryness under low pressure. The resulting solid was extracted with acetone five times to remove residual Me_2SO and was finally dried under low pressure.

In attempts to prepare other organolanthanide cryptate derivatives, the following reactions were carried out at low temperature, followed by warming, but without success. Products either showed evidence of decomposition or contained uncoordinated cryptate (infrared).

Lanthanide Compound	Reactant(s)	Solvent
$LaCl_3$	(i) 3MeLi (ii) 2,2,2-cryptate	THF
$LaCl_3$ (2,2,2-cryptate)	3PhCCLi	THF
$LaCl_3$ (2,2,2-cryptate)	3PhCCNa	Ether
$NdCl_3$ (2,2,2-cryptate)	6MeLi	Ether
$NdCl_3$ (2,2,2-cryptate)	4.5MeLi	THF

Discussion

As crystals of X-ray quality could not be obtained the detailed structure of this compound is unknown. It is, however, evident from the infrared spectrum that the cryptate ligand encloses and coordinates the lanthanum ion. The IR spectrum in the region 4000–400 cm^{-1} is virtually identical with the sum of the spectra of $LaCl_3(2,2,2\text{-cryptate})$ and $LiCPh_3$. In particular, the C–O absorption occurs at 1072 cm^{-1} as in $LaCl_3(2,2,2\text{-cryptate})$ and not at 1129 cm^{-1} as in the free ligand. However, many bands due to the CPh_3 entity are slightly displaced by 5–10 cm^{-1} to higher wavenumber in the complex as compared with $LiCPh_3$. The electronic absorption band at 505 nm is dissimilar to those of $Ca(CPh_3)_2(THF)_7$ [7] (314, 610, 845 nm) where the Ca^{2+} ion is likely to be entirely coordinated by THF. This spectral evidence cannot firmly indicate which of the three ligands, CPh_3 and two Cl, are coordinated to the metal ion. In spite of the 12-coordinated structure of $[La(NO_3)_2(2,2,2\text{-cryptate})]^{+2}$, an 11-coordinated

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monomeric structure [$LaCl_2(CPh_3)$(2,2,2-cryptate)] seems somewhat unlikely, due to the larger steric requirements of the chloride ions and, particularly, of the CPh_3 group when compared with the nitrate ions.

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