Three-co-ordination in Lanthanide Chemistry: Tris[bis(trimethylsilyl)amido]lanthanide(III) Compounds

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Summary The new compounds $M[N(SiMe_3)_2]_3$ (M = La, Pr, Sm, Eu, Gd, Lu) have been isolated and shown to be the first examples of 3-co-ordinated lanthanides.

THE occurrence of lanthanide compounds which show the co-ordination numbers 6, 7, 8, 9, 10, and 12 has been established.[1] Among these, 8-, 9-, and 10-co-ordination are most common, while a co-ordination number even as low as 6 is unusual in the case of these large ions.

We now report the synthesis of some new lanthanide compounds $M[N(SiMe_3)_2]_3$ which are monomeric and 3-co-ordinate.

Reaction of $LiN(SiMe_3)_2$ with $LaCl_3$ in tetrahydrofuran–n-pentane or in ether solution ultimately afforded tris[bis(trimethylsilyl)amino]lanthanum(III), obtained as colourless needles from n-pentane. Similarly were obtained the corresponding Pr (pale yellow-green), Sm (pale yellow), Eu (orange), Gd, and Lu (colourless) compounds. All of these compounds are decomposed by traces of moisture and were handled under strictly anaerobic conditions. Satisfactory analytical values were obtained. The compounds are volatile, subliming at 75—100° and 10^{-4} mm. They are monomeric in solution in boiling benzene (experimental values being independent of concentration over the range employed: 0·025—0·1 M). Thus, for La[N(SiMe$_3$)$_2$]$_3$, $M_{\text{expt}} = 612$; $M_{\text{calc}} = 620$; the samarium and europium compounds gave strictly comparable results. Preliminary *X*-ray data[2] indicate that the crystalline europium compound is isostructural with Fe[N(SiMe$_3$)$_2$]$_3$, which has a monomeric structure of D_3 symmetry.[3]

In deuteriobenzene solution, ^{1}H n.m.r. absorption was at τ 9·75 (La), 18·64 (Pr), 11·58 (Sm), 3·57 (Eu), and 9·70 (Lu). The paramagnetic shifts of the methyl protons of the Pr, Sm, and Eu compounds with respect to the absorptions for the diamagnetic La and Lu compounds are of opposite sign to, but of approximately the same relative magnitude as, those reported[4] for the methyl signals of the lanthanide shift reagents [M(Me$_3$CCOCHCOCMe$_3$)$_3$].

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