The Peroxo-group as a Doubly Bidentate Bridging Ligand in Five-co-ordinate Lanthanide Complexes

By Donald C. Bradley, Joginder S. Ghotra, F. Alan Hart, Michael B. Hursthouse, and Paul R. Raithby
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary Reaction of $OPPh_3$ with $M\{N(SiMe_3)_2\}_3$ (M = a lanthanide) yields complexes $M_2O_2\{N(SiMe_3)_2\}_4(OPPh_3)_2$ which contain a doubly bidentate peroxo-group and 5-co-ordinate lanthanide ions.

In an attempt to prepare $La(btsa)_3(OPPh_3)_n$, where btsa = $N(SiMe_3)_2$, $La(btsa)_3$[1] was treated in benzene solution with $OPPh_3$† under N_2. Two products were obtained. When $La(btsa)_3$ was treated with 1 mol $OPPh_3$, the expected

† Prepared by hydrolysis of Ph_3PBr_2 and not from $PPh_3 + H_2O_2$.

adduct La(btsa)$_3$OPPh$_3$ was obtained as colourless crystals. When, however, an excess of OPPh$_3$ (2—5 mol) was used, a colourless peroxo-compound La$_2$O$_2$(btsa)$_4$(OPPh$_3$)$_2$ was obtained in good yield as were its colourless Pr, cream Sm, and orange Eu analogues by similar means.‡ All these compounds are air-sensitive. Satisfactory analytical results were obtained for all products. P–O stretching frequencies fall within the range 1135—1140 cm^{-1}. Since air was rigorously excluded from the preparation, it seems that the peroxo-group is derived from the phosphoryl oxygen of the excess of OPPh$_3$ in an unusual reaction whose full stoicheiometry is still under investigation. In addition to the *X*-ray data given below, evidence for the presence of the peroxo-group was obtained from iodine liberation on treatment of the complex with dilute H$_2$SO$_4$/KI. La(btsa)$_3$OPPh$_3$ treated similarly as a blank gave no iodine.

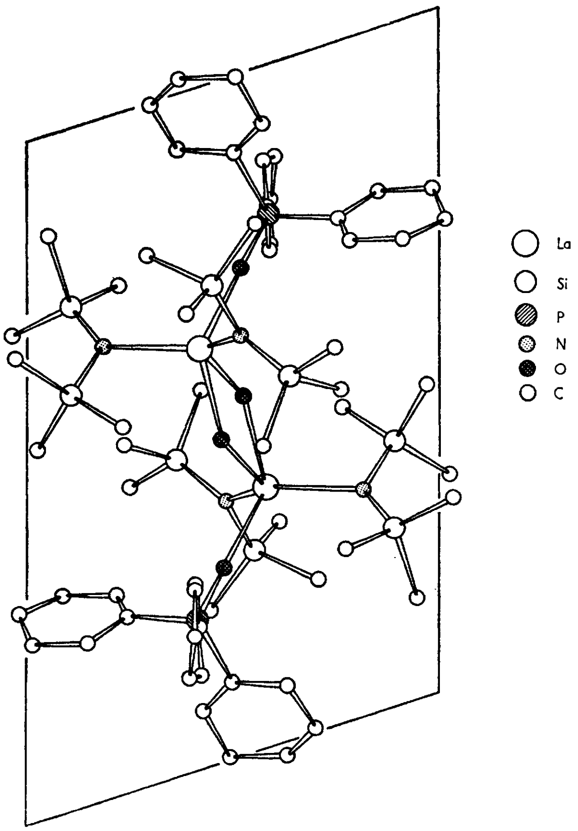

FIGURE. Some of the important distances are: La–O (peroxide) 2·33 and 2·35, La–O (phosphine oxide) 2·44, La–N (silylamide) 2·39 and 2·40, O–O (peroxide) 1·70 Å.

Crystal data: $C_{60}H_{102}O_4N_4P_2Si_8La_2$, triclinic, $a = 13{\cdot}551$, $b = 18{\cdot}54$, $c = 12{\cdot}541$ Å, $\alpha = 90{\cdot}80$, $\beta = 121{\cdot}74$, $\gamma = 115{\cdot}32°$, $Z = 1$, $D_c = 1{\cdot}06$, space group = $P\bar{1}$. Intensity data were recorded on a G.E. XRD6 diffractometer in a manner described previously.[2] Of the 2887 intensities measured ($2\theta_{max} = 80°$), 2050 had significant values ($I > 3\sigma$). The structure was solved by Patterson and Fourier methods and refined to an R value of 0·10 (C atoms isotropic, others anisotropic). The geometry of the molecule is shown in the Figure, which also includes some of the more important bond parameters.

Though known as a doubly monodentate bridging ligand, *e.g.* in $[(NH_3)_5Co–O–O–Co(NH_3)_5]^{4+}$,[3] and in bidentate non-bridging situations, *e.g.* in $CrO(O_2)_2(C_5H_5N)$,[4] a doubly bidentate bridging peroxo-group has apparently not previously been reported. Its formation is probably to be attributed to a minimisation of electrostatic potential energy in the $La^{3+}–O_2^{2-}–La^{3+}$ system. The compounds described are apparently the first lanthanide peroxo-compounds to be characterised. Until more examples are known, it will not be clear whether lanthanide ions as a class particularly favour the unusual doubly bidentate configuration of the peroxo-ligand.

Lanthanide ions usually show co-ordination numbers of 6—9, though 10 and 12 appear with small bidentate ligands such as the nitrato-group. Bulky ligands yield complexes with co-ordination numbers of 3[1] and 4[5], but the described peroxides are the first examples of lanthanides having 5-co-ordination (the peroxo-group being considered to occupy two co-ordination positions of each metal ion).

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‡ The peroxo-compound can be more directly obtained by the reaction of La(btsa)$_3$ with 0·5 mol (Ph$_3$PO)$_2$H$_2$O$_2$. [Care is needed—preparations of (Ph$_3$PO)$_2$H$_2$O$_2$ can explode.]

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