

Preparation and X-Ray Crystal Structure (for Ln = Sm) of (μ -Phthalocyaninato)bis[di(2,2,6,6-tetramethylheptane-3,5-dionato)Ln^{III}] (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y)

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The reaction of dilithium phthalocyanine with tris(2,2,6,6-tetramethylheptane-3,5-dionato)Ln^{III} (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y) affords a series of (μ -phthalocyaninato)(diketonato)₄Ln₂ complexes; the X-ray crystal structure of the samarium compound shows that the phthalocyanine ligand bridges two samarium atoms each co-ordinated by two β -diketonato ligands, and important molecular parameters include Sm—O_{av} 2.284(17), Sm—N_{av} 2.656(16), and Sm—Sm_{av} 3.627(3) Å.

The diphtalocyanine complexes of rare-earth elements were first reported eighteen years ago by Kirin *et al.*¹ Recently we have reported on some types of mixed ligand rare-earth metal complexes containing phthalocyaninato and β -diketonato ligands with a metal to phthalocyanine ratio of 1:1.² The composition of the complexes obtained was dependent on the solvent and the β -diketone used in the synthesis. Here we report the preparation and structure of novel dinuclear rare-earth metal complexes with a bridging phthalocyanine ligand.

A mixture of dilithium phthalocyanine Li₂(Pc²⁻)³ and tris(2,2,6,6-tetramethylheptane-3,5-dionato)Ln^{III} (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y) in dry tetrahydro-

furan was refluxed for 2 h under an argon atmosphere.[†] After removal of the solvent, the solid residue was recrystallized from benzene. In this way the title complexes were obtained for Sm—Yb and Y as green crystals.[‡] The complexes of the lighter lanthanoids such as Nd were too un-

[†] In the presence of oxygen the reaction gives 1:1 complexes of the rare-earth elements and the phthalocyanine radical (Pc^{•-}), [Ln^{III}(Pc^{•-})(2,2,6,6-tetramethylheptane-3,5-dionato)₂] (Ln = Nd, Sm—Lu, and Y). H. Sugimoto, T. Higashi, and M. Mori, *Chem. Lett.*, 1983, 1167.

[‡] All new complexes showed satisfactory elemental analyses.

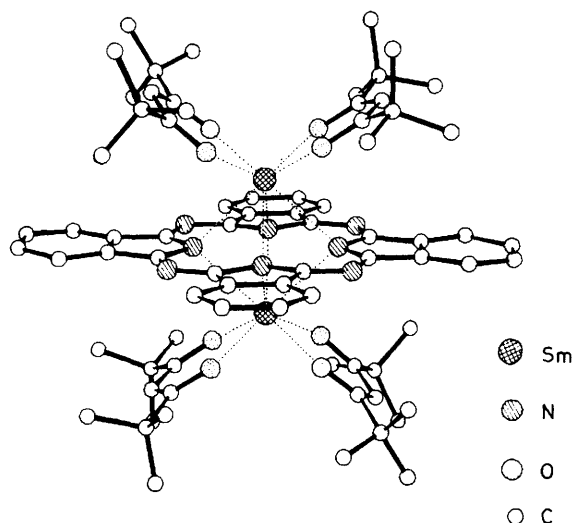


Figure 1

stable to be isolated as analytically pure crystals. In the case of lutetium, the heaviest rare-earth metal, the reaction gave only a 1:1 complex $(\text{Pc}^{2-})(2,2,6,6\text{-tetramethylheptane-3,5-dionato})\text{Lu}^{\text{III}}$.§ Elemental analysis and preliminary X-ray data suggested that all these complexes were isostructural. Single crystals of the samarium compound suitable for X-ray analysis were obtained from benzene.

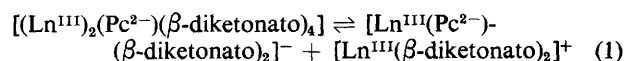
Crystal data: $\text{C}_{76}\text{H}_{92}\text{N}_8\text{O}_8\text{Sm}_2$, $M = 1546.32$, space group $P\bar{1}$, triclinic, $a = 12.941(6)$, $b = 14.680(4)$, $c = 21.205(4)$ Å, $\alpha = 88.22(2)$, $\beta = 86.54(3)$, $\gamma = 71.32(3)^\circ$, $Z = 2$, $D_m = 1.35$, $D_c = 1.348$ g cm $^{-3}$, $U = 3808.9$ Å 3 , $\mu = 124.2$ cm $^{-1}$. 5948 Reflections measured (with $2\theta < 200^\circ$) on a Rigaku AFC-S diffractometer had $F_0 > 3\sigma(F_0)$ and were used in the refinement of the structure. The hydrogen atom positions were calculated (for C-H 1.00 Å).¶

§ The structure of the Lu compound was supported by its elemental analysis and spectral data.

¶ 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.

In the crystal structure of the samarium compound shown in Figure 1 the planar phthalocyanine ligand bridges two samarium atoms, each of which is co-ordinated by the four nitrogen atoms of the phthalocyaninato ligand and by four oxygen atoms of two β -diketonato ligands. There are a few dinuclear (μ -porphyrinato) complexes such as $[\text{M}(\text{CO})_3]_2$ -(tetraphenylporphyrin) ($M = \text{Re}$ and Tc),⁴ $[\text{Rh}(\text{CO})_2]_2$ -(octaethylporphyrin),⁵ or $[\text{Ir}(\text{CO})_3]_2$ -(octaethylporphyrin).⁶ In these the central atom is co-ordinated by three of the four nitrogen atoms of the porphyrin in contrast to the present case of equivalent co-ordination of all four nitrogen atoms of the phthalocyanine group to each of the lanthanoid atoms.

These dinuclear rare-earth metal complexes have their longest absorption band (Q-band)⁷ at about 700 nm in non-polar solvents such as CH_2Cl_2 or benzene, the position of the band being dependent on the nature of the ions in solution. In polar solvents such as dimethylformamide or Me_2SO the absorption maxima are at ca. 670 nm, a typical value for the 1:1 rare-earth metal-phthalocyanine complexes previously reported.² Together with the n.m.r. data for the diamagnetic ytterbium derivative, these results suggest a dissociation [equation (1)] of the complexes owing to solvation by a polar solvent of the rare-earth atoms.



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