A Zirconium(IV) Derivative of Bis(phthalocyaninato)neodymium(III)

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Bis(phthalocyaninato)lanthanoid(III) complexes show interesting characteristics of electrochromism [1], electroconductivity [2], and photochemistry [3]. From an X-ray diffraction analysis [4], the structure of bis(phthalocyaninato)neodymium(III) was shown to be of a sandwich type. Recently, a tridecker-type complex, Pc_3Ln_2 (Pc = phthalocyanine dianion; Ln = lanthanoid(III) cation) has also been prepared and characterized [5]. It therefore seemed appropriate to prepare stacked phthalocyanine complexes having the remarkable characteristics mentioned above. In this communication, we report on a zirconium(IV) derivative of bis(phthalocyaninato)neodymium(III).

Potassium bis(phthalocyaninato)neodymium(III), KPcNdPc, was employed as a starting material; 50 ml of *N,N*-dimethylformamide (DMF) solution containing 2.0 g of HPcNdPc was added to 100 ml of a methanol solution saturated with potassium hydroxide. After refluxing the mixture for a few hours, the potassium complex was precipitated by adding adequate amounts of water and was dried *in vacuo.* Using the potassium complex, the zirconium(IV) derivative was prepared as follows. A hot acetone solution (50 ml) containing 30 mg (1.0×10^{-4} mol) of zirconium(IV) oxychloride octahydrate was added to 300 ml of an acetone solution containing 20 mg (2.0×10^{-5} mol) of KPcNdPc, and the mixture was stirred at *ca.* 40 °C for several minutes. The bluish-green precipitates obtained were washed with acetone three times and dried *in vacuo. Anal.* Found: C, 58.68; H, 2.96; N, 15.56. Calc. for $C_{64}H_{32}N_8OCl$-NdZr·2acetone: C, 58.89; H, 3.08; N, 15.70%. The zirconium(IV) ion of the derivative was qualitatively confirmed by means of a morin method [6]. The derivative was slightly soluble in tetrahydrofuran or acetone but decomposed to a radical PcNdPc species after a few days. It also dissolved in methanol or DMF but decomposed immediately. In the electronic spectra (Fig. 1), both B and Q bands of the derivative undergo red shifts compared with those of the KPcNdPc complex, which might suggest that the zirconium(IV) ion is directly bonded to the phthalocyanine ligand. An ESR measurement also showed that the derivative is a non-radical species.

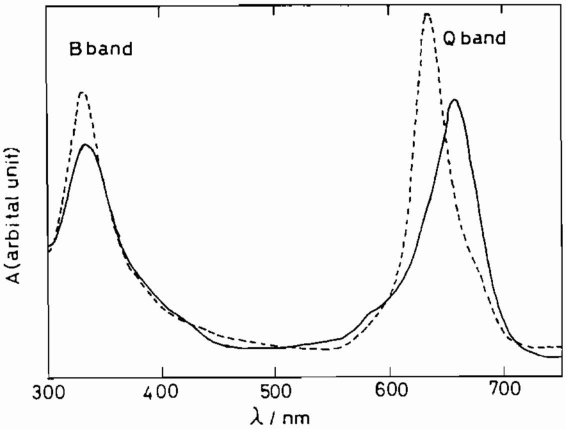

Fig. 1. Electronic spectra in tetrahydrofuran: - - -, KPcNdPc; ——, the zirconium(IV) derivative.

In a zirconium(IV) porphyrin complex, it has been reported that a metal atom is out of the porphyrin plane, and the complex takes a square-pyramidal form [7]. Recently, a binuclear (*μ*-phthalocyaninato)lanthanoid(lanthanoid(III) complex was reported; the phthalocyanine ligand bridges two samarium atoms in (*μ*-phthalocyaninato)-bis-[di(2,2,6,6-tetramethylheptane-3,5-dionato)samarium(III)] [8]. On the basis of these facts, the zirconium(IV) ion of the derivative might sit on one of the phthalocyanine ligands as proposed in Fig. 2.

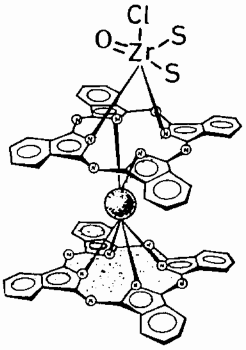

Fig. 2. The proposed structure: ● and S denote neodymium(III) and solvents, respectively.

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References

1 P. N. Moskalev and I. S. Kirin, *Russ. J. Phys. Chem., 46*, 1019 (1972); G. C. S. Collin and D. J. Schiffrin, *J. Electroanal. Chem., 139*, 335 (1982) and refs. therein.

2 L. W. terHaar, W. E. Hatfield and M. Tsutsui, *Mol. Cryst. Liq. Cryst., 107*, 181 (1984).

3 K. Kasuga, H. Morimoto and M. Ando, *Inorg. Chem.*, in press.

4 K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Von Opdenbosch, G. Pepe and E. F. Myer, Jr., *J. Am. Chem. Soc., 102*, 4836 (1980).

5 K. Kasuga, H. Morimoto, M. Ando and M. Isa, *Chem. Lett.*, in press.

6 F. Feigl and V. Anger, 'Spot Test in Inorganic Analysis', (sixth English edn.), Elsevier, Amsterdam, 1972, pp. 519–520.

7 M. Tsutsui and G. A. Taylor, in K. M. Smith (ed.), 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1975, pp. 279–312.

8 H. Sugimoto, T. Higashi, A. Maeda, M. Mori, H. Masuda and T. Taga, *J. Chem. Soc., Chem. Commun.*, 1234 (1983).