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LETTER

Preparation of Bis(tetra-2,3-pyradinoporphyrazinato)ytterbium(III)

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Lanthanoid(III) phthalocyanine complexes have three types of composition: a ratio of metal to ligand = 1:1, 1:2 and 2:3 [1–3]. A 1:1 type complex is known to exhibit a photocatalytic activity for reduction of methylviologen in methanol [4]. The structure of a 1:2 type complex was revealed to be a sandwich-type configuration by an X-ray diffraction analysis; in the case of a neodymium(III) complex, it has an exactly staggered orientation and the distance between the N_4 plane of the two macrocycles is 2.96 Å [5]. It has been reported that the sandwich-type complex exhibits many characterisitic properties such as electrochromism, electroconductivity and photochemical reaction [6–8]. For example, application of the sandwich-type lutetium(III) complex to an electrochromic display has been extensively investigated in the past decade [9]. It is also reported that a radical species of the sandwich-type complex is an intrinsic semiconductor [10], and its long alkyl-chain derivative shows a unique conductivity behavior [11].

Recently, metallophthalocyanine analogs with annelated electron-withdrawing pyridine have been noted for their increased solubilities in common organic solvents and also by interesting properties such as photocatalysis and electroconductivity [12]. We report here the preparation of a sandwich-type phthalocyanine analog with annelated pyridine of ytterbium(III) and some of its properties (Fig. 1).

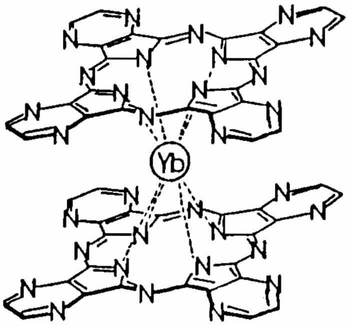

Fig. 1. Proposed structure of $(T\text{-}2,3\text{-}P,P)_2Yb$.

Bis(tetra-2,3-pyradinoporphyrazinato)ytterbium(III) (abbrev. $(T\text{-}2,3\text{-}P,P)_2Yb$) was prepared as follows. The mixture of 2,3-dicyanopyradine (5.0 g, 3.7×10^{-2} mol) and ytterbium(III) acetate trihydrate (1.5 g, 3.7×10^{-2} mol) was heated to *c.* 170 °C. Then the molten mixture was left to stand for 5 h at that temperature. After cooling to room temperature, the crude clusters were grinded and dissolved in 20 ml of DMF. After filtering the residues, the solution was poured on to a silica gel column, and the objective was eluted out with DMF. After concentration of the eluent, the green compound was obtained by the addition of adequate amounts of methanol. *Anal.* Found: C, 46.90; H, 2.17; N, 34.41. Calc. for $(T\text{-}2,3\text{-}P,P)_2Yb \cdot 3MeOH$: C, 46.75; H, 2.15; N, 34.21%. The other lanthanoid(III) complexes were also prepared and purified by a similar method to that described above.

An ESR spectrum of the ytterbium(III) complex shows an intense signal at $g = 2.0023$ with a band width of *c.* 2 G at room temperature, which is typical of a radical species of an extended π conjugated-ring system [13].

Mass spectrometric measurements were performed by evaporating the sample at 380–400 °C under 10^{-6} to 10^{-7} torr; a m/e value of 1246 was obtained for singly charged species, in agreement with the formula shown in Fig. 1.

In electronic spectra, the ytterbium(III) complex shows the Q band at 680 nm in a DMF solution (Fig. 2). On addition of adequate amounts of sodium dithionite to the solution, the intensity of the band decreased and a new band appeared around 480 nm. On bubbling air through the solution, the original spectrum of the ytterbium(III) complex was recovered, showing that the ring can be reduced reversibly. On the other hand, it could not be oxidized by oxidants such as iodine and nitrosonium tetrafluoroborate. This might be explained similarly to the phthalocyanine analog with annelated pyridine

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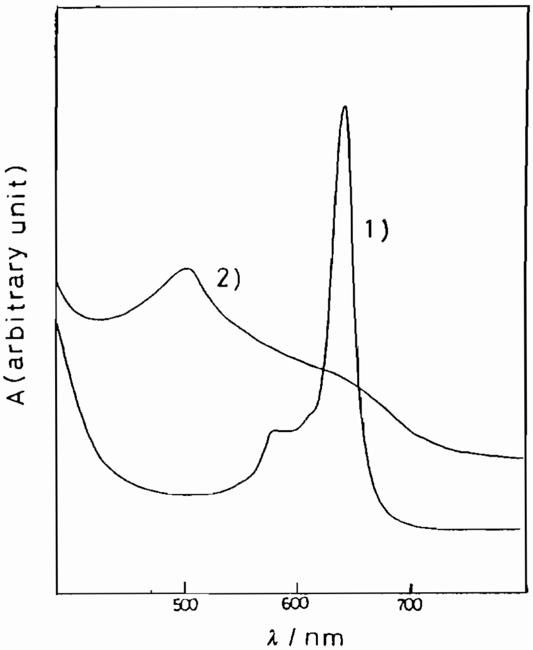

Fig. 2. Optical spectra of (T-2,3-P,P)$_2$Yb and its reduced species in DMF. 1, (T-2,3-P,P)$_2$Yb; 2, the reduced species with sodium dithionite.

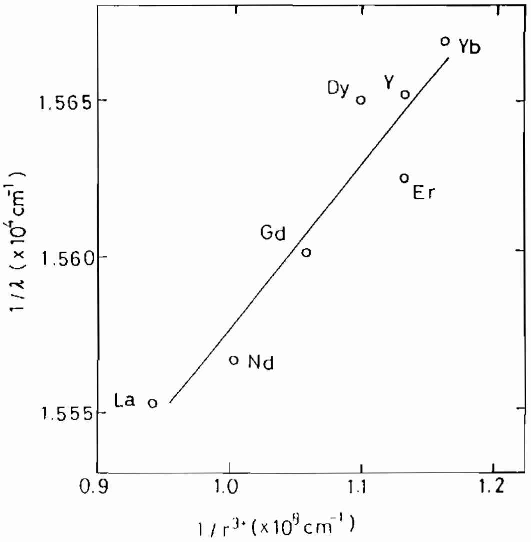

Fig. 3. Q band vs. inverse ionic radius of the lanthanoid(III) ion.

which was easily reduced by the presence of electron-withdrawing pyridine [14].

The Q band of the complex is shifted to the shorter wavelength with a decrease in the ionic radius of the lanthanoid(III) ion (Fig. 3). It has been found that a decrease in the ionic radius shifts the Q band to the shorter wavelength in the sandwich-type phthalocyanine complex, but scarcely shifts it in the usual 1:1 type complex [15]. Thus, the present complexes are identified to be the sandwich-type species. This shift might occur because the distance between the macrocycles in the complex is shortened by the decrease in the ionic radius, resulting in an increase in the π–π interaction [8]. In addition, the ytterbium(III) complex did not exhibit fluorescence in accord with the bis(phthalocyaninato)lanthanoid(III) complex, which also suggests the ytterbium(III) complex is a sandwich-type species.

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