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Mixed Valence State of Cerium in Bis(phthalocyaninato)cerium Complex

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Spectroscopic properties of the titled complex are reported compared to the other radical bis(phthalocyaninato)lanthanoid(III) complexes. Electronic, infrared, and Ce 3d XPS spectra show that the cerium in the titled complex is neither tri- nor tetravalent and Ce 4f electron delocalizes in a phthalocyanine π orbital.

The compounds containing lanthanoid elements in mixed valence state have been attractive subjects in the field of solid state physics.1) In particular, some kinds of cerium compounds have attracted much attention in recent years because every cerium ion has an intermediate number of 4f electron of between 0 and 1 in quantum-mechanical ground state. In these phenomena, hybridization of the most extended Ce 4f orbital in the lanthanoid series with other orbitals plays an important role.2) Meanwhile, bis(phthalocyaninato)lanthanoid(III), $Ln(pc)_2^{\bullet}$ (Ln = lanthanoid(III), $pc^{2-} = C_{32}H_{16}N_8{}^{2-}$ and one of the two phthalocyanine chromophores is one-electron oxidized form, $pc^{-\bullet}$), have been intensively studied as electrochromic materials 3) and organic semiconductors. 4) Among a series of $Ln(pc)_2^{\bullet}$, the titled complex (abbreviated as $Ce(pc)_2$) shows an exceptional electronic absorption spectrum. 5) In this work, anomalous spectroscopic properties of $Ce(pc)_2$ and mixed valence state of cerium in the complex will be described.

$Ce(pc)_2$ was prepared from cerium(III) acetate and 1,2-dicyanobenzene according to the literature6) and purified as follows: Crude product was dissolved into $CHCl_3$ and the solution was chromatographed over silica-gel column (Merck Silica Gel 60). A blue chromatographic band containing $Ce(pc)_2$ was eluted out with CH_2Cl_2. Removal of solvent yielded violet needle crystals. Yield; 35% vs. cerium acetate. Anal. Found: C, 65.79; H, 2.82; N, 18.96%. Calcd for $CeC_{64}H_{32}N_{16}$: C, 65.97, H, 2.77, N, 19.24%. $Ln(pc)_2^{\bullet}$ complexes (Ln = La, Pr, Sm, Eu, Tb, Ho, and Yb) were prepared in a similar way and characterized by electronic and infrared spectra. Infrared spectra of solid samples were recorded on a JEOL JIR-100 spectrometer by diffuse reflectance method. Measurements of XPS were carried out using a VG Scientific ESCA LAB Mk II (Mg Kα) spectrometer on the sample which was powdered and fixed on a piece of adhesive tape. All the measurements were carried out at room temperature unless noted.

An electronic spectrum of Ce(pc)$_2$ in CH_2Cl_2 solution showed an intense Q-band at 635 nm which is considerably blue-shifted compared to those of Ln(pc)$_2^{\bullet}$ complexes (660—680 nm) and an additional less intense absorption band at 685 nm (Fig. 1). Absorption band around 460 nm, which is characteristic of radical Ln(pc)$_2^{\bullet}$,[7)] was not observed. No other absorption band was observed in 750—1100 nm region. Therefore, the spectrum is rather close to those of Ln(pc)$_2^-$ (one-electron reduced form of Ln(pc)$_2^{\bullet}$)[8)] than those of Ln(pc)$_2^{\bullet}$. Ce(pc)$_2$ was ESR silent in solid state over the range 77 K—room temperature. On the contrary, an intense signal around g = 2.00, which is characteristic of organic free radicals, was observed for Lu(pc)$_2^{\bullet}$.[6)] An infrared spectrum of Ce(pc)$_2$ was similar to those of Ln(pc)$_2^{\bullet}$ complexes (Fig. 2). On the basis of similarity of the infrared spectrum and result of elemental analysis, molecular structure of Ce(pc)$_2$ is similar to those of Ln(pc)$_2^{\bullet}$ complexes, i.e., sandwich structure.[9-10)] The asterisked bands around 880 cm^{-1} were metal-sensitive. Figure 3 shows wave numbers of the asterisked bands as a function of ionic radii,[11)] r_i, of trivalent lanthanoids (coordination number = 8). A linear correlation is observed except for Ce(pc)$_2$. These bands are considered to be related to metal-nitrogen(pyrrole) bond (M-Np) distances because an average M-Np distance in bis(phthalocyaninato) complex increases with an increase in r_i of central metal of the complex; 2.347 Å[12)] for Sn(pc)$_2$ (r_i = 0.81 Å[13)]), 2.38 Å[9)] for Lu(pc)$_2^{\bullet}$ (0.97 Å), 2.43 Å[14)] for U(pc)$_2$ (1.00 Å), and 2.44 Å[10)] for Nd(pc)$_2^{\bullet}$ (1.12 Å), respec-

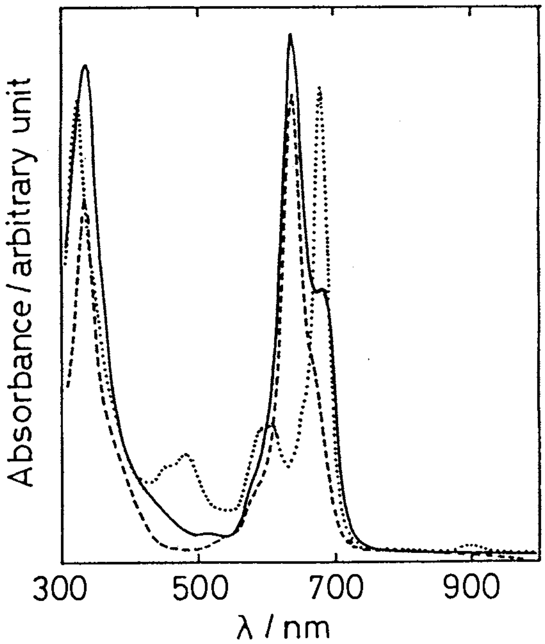

Fig. 1. Electronic absorption spectra of Ce(pc)$_2$ (——), Pr(pc)$_2^-$ (---), and Pr(pc)$_2^{\bullet}$ (·····) in CH_2Cl_2.

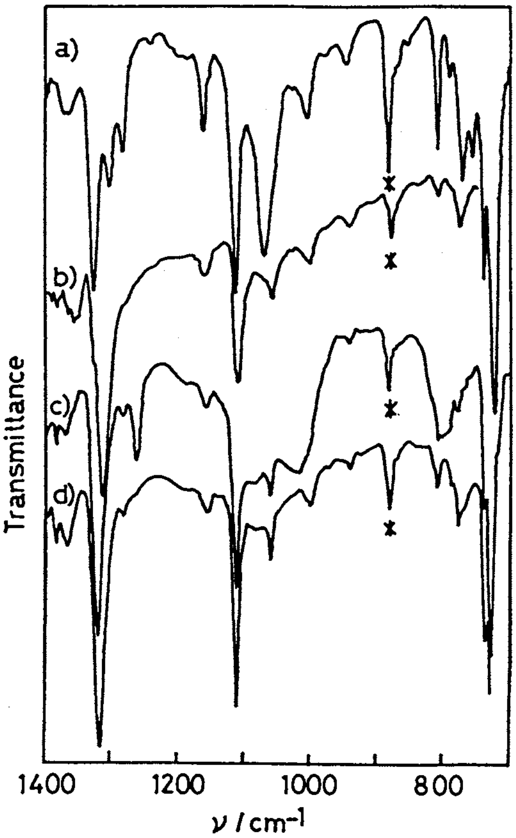

Fig. 2. Infrared spectra of a) Ce(pc)$_2$, b) Pr(pc)$_2^{\bullet}$, c) Ho(pc)$_2^{\bullet}$, and d) Tb(pc)$_2^{\bullet}$ complexes.

tively. Keen and Malerbi assigned the metal-sensitive bands around 900 cm^{-1} of some M(pc) complexes (M = Pt(II), Pd(II), etc.) as M-Np rocking vibration.15) Since the asterisked bands of $Ln(pc)_2^{\bullet}$ complexes in this study shifted to lower frequency with an increase in r_i and the rocking vibration is directly related to the strength of the M-Np bonds, our experimental result supports their assignment. $Ce(pc)_2$, considerably deviates from the straight line and shifts to higher frequency, and hence the M-Np distance in $Ce(pc)_2$ would be too short assuming that the cerium would be trivalent. From the linear $\nu_{max}-r_i$ correlation, an apparent ionic radius of the cerium in $Ce(pc)_2$ is evaluated to be 1.01 Å, which is an intermediate value between those of trivalent (1.14 Å) and tetravalent ions (0.96 Å).11) Indeed, Ce 3d XPS spectrum of $Ce(pc)_2$ showed a complicated feature which is peculiar to the compounds containing cerium in mixed valence state.2a) Namely, each spin-orbit component showed a splitting due to the following three different final states; $4f^0$, $4f^1$, and $4f^2$, and intensity of the f^0 and f^1 components were comparable with each other (Fig. 4). There have been a few debates on valence of the cerium in $Ce(pc)_2$; the cerium was characterized as trivalent by Misumi and Kasuga16) whereas tetravalent by Luk'yanets and coworkers.5) However, it is found that the cerium is in neither tri- nor tetravalent state but in mixed valence state of them.

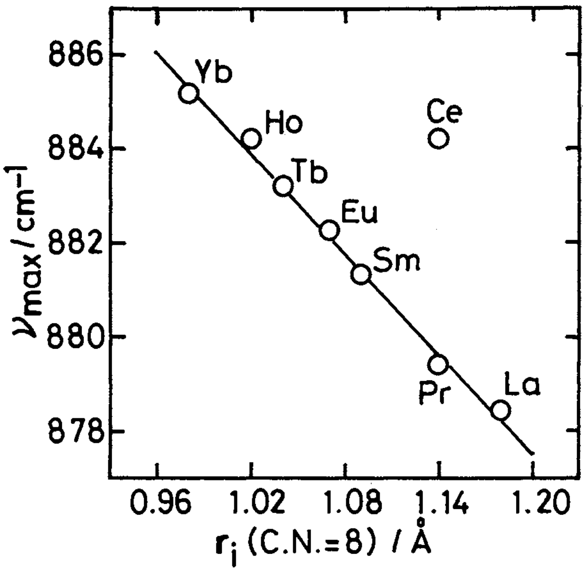

Fig. 3. Wave numbers of the metal-sensitive infrared band as a function of r_i.

In order to satisfy both the chemical composition and the electrical neutrality of the whole molecule of the bis-(phthalocyaninato)lanthanoid(III), its formula must be either $H^+Ln^{3+}(pc^{2-})_2$ or $Ln^{3+}(pc^{2-})(pc^{-\bullet})$. In case of complex except for $Ce(pc)_2$, the latter formula is preferred to the former by recent studies,6) and hence a hole is created in the molecule. Moreover, the Ce 4f orbital, which is most extended in the lanthanoid series, is known to be hybridized with other orbitals, for example, those of ligands.2) Since the chromophore of

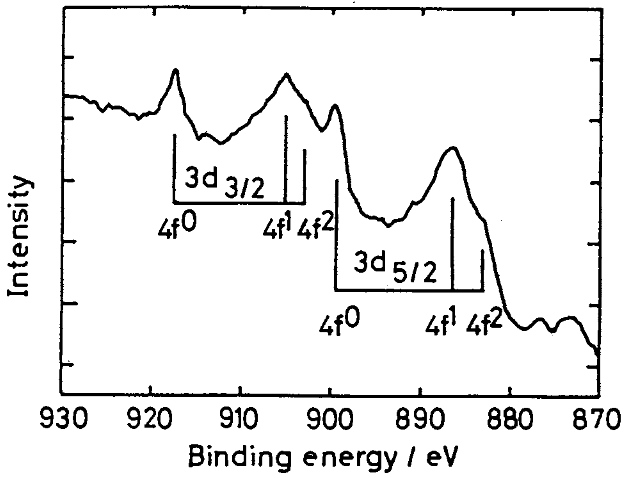

Fig. 4. Ce 3d XPS spectrum of $Ce(pc)_2$.

phthalocyaninato complex lies in a π system of the phthalocyaninate and anomaly of Ce(pc)$_2$ is also observed in its electronic spectrum, it is considered that the Ce 4f electron delocalizes in the phthalocyanine π system of the complex. Therefore, the experimental results mentioned above can be interpreted by postulating the mixing of the following two local configurations; Ce^{3+}(pc^{2-})(pc$^{-\bullet}$) and Ce^{4+}(pc^{2-})$_2$. That is, the mixed valence state of the cerium in this complex seems to be caused by delocalization of the Ce 4f electron in the phthalocyanine π orbital.

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