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PREPARATION AND CHARACTERIZATION OF SOME RARE-EARTH COMPLEXES OF THE PHTHALOCYANINE RADICAL

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The reaction of tris(2,2,6,6-tetramethyl-3,5-heptanedionato) complexes of rare-earth elements, $M^{3+}(dpm)_3$ (M = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) with lithium phthalocyanine $Li_2(Pc^{2-})$ in tetrahydrofuran gave new stable phthalocyanine radical complexes $[M^{3+}(Pc^{-\bullet})(dpm)_2]$.

The diphthalocyanine complexes of rare-earth elements were first reported eighteen years ago.1) Recently Chang and Marchon2) have reinvestigated the preparation and characterization of luthetium diphthalocyanine and concluded that the existing data are more in favor of the formula $[Lu^{3+}(Pc^{2-})(Pc^{-\bullet})]$ in which one of the phthalocyanine exists in the sta te of a free radical.3,4) In a previous paper we reported on stable mixed ligand rare-earth complexes of phthalocyanine and β-diketones formed by the reaction of tris(β-diketonato) complexes of rare-earths with lithium phthalocyanine in acetone and methanol.5) The ratio of rare-earth to phthalocyanine in these complexes is 1:1. In case the β-diketone used was 2,2,6,6-tetramethyl-3,5-heptanedione (= dipivaloylmethane, abbreviated as dpm), however, new 1:1 complexes having two β-diketonato ligands and phthalocyanine radical $[M^{3+}(Pc^{-\bullet})(dpm)_2]$ were found to be readily produced. In this communication, we wish to report the preparation and physico-chemical properties of these complexes and compared them with those of diphthalocyanine complexes and phthalocyanine radicals themselves $[H(Pc^{-\bullet})]$ and $[Li(Pc^{-\bullet})]$ recently isolated and characterized by our group.6)

A mixture of $M^{3+}(dpm)_3$ (M = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) and lithium phthalocyanine $Li_2(Pc^{2-})$ were dissolved in dried tetrahydrofuran and the solution was refluxed for 3 h. After removal of the solvent, the residual solid was recrystallized from benzene-chloroform to give dark green crystals. All complexes prepared in this way showed satisfactory elemental analyses for the formula $[M^{3+}(Pc^{-\cdot})(dpm)_2]$. These complexes are very soluble in benzene, but slightly soluble in chloroform or dichloromethane.

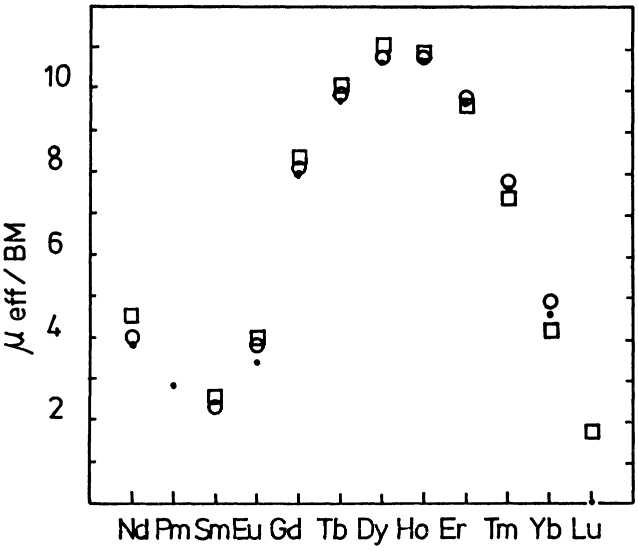

Fig. 1. Magnetic moments of $[M^{3+}(Pc^{-\cdot})(dpm)_2]$.

(☐) observed values,

(●) calculated values $\sqrt{g_J J(J+1)}$, and

(○) calculated values $\sqrt{g_J J(J+1)+4S(S+1)}$ (S=1/2).

Magnetic moments of these complexes were measured at 300 K as shown in Fig. 1. Complexes containing diamagnetic Lu^{3+} and Y^{3+} ions showed magnetic moments of 1.65 BM which is close to the free spin value. Moreover, the Lu^{3+} and Y^{3+} complexes showed characteristic ESR signals in both solid state and benzene solution. The lines are narrow and centered at the free spin values of g=2.001 (Fig. 2). These ESR spectra had very similar shapes and g-values to those of phthalocyanine radicals $[H(Pc^{-\cdot})]$ and $[Li(Pc^{-\cdot})]$.⁶⁾ Therefore, the magnetic moments and the ESR signals of the Lu^{3+} and Y^{3+} complexes are evidently attributable to the unpaired spin of the phthalocyanine radical. Other complexes having paramagnetic rare-earth elements showed no such ESR signals perhaps owing to the relaxation effect. In Fig. 1 the magnetic moments of the complexes are compared with the free ion values7) of rare-earth ions and also with the values calculated on the assumption of independent coexistence of the rare-earth ions and the phthalocyanine radical ion.

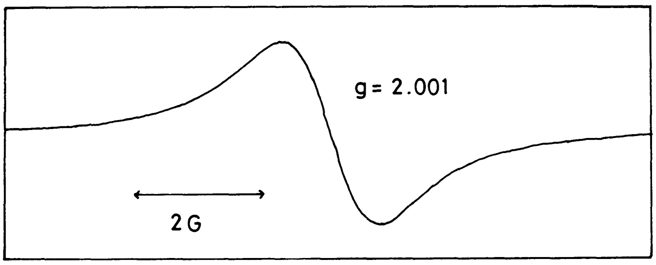

Fig. 2. ESR spectrum of $[Lu^{3+}(Pc^{-\cdot})(dpm)_2]$ in solid state at 20°C.

The magnetic moments of Nd ∿ Ho complexes have somewhat larger magnetic moments than calculated values. The Er ∿ Yb complexes had somewhat smaller values. These results indicate the existence of interactions between paramagnetic rare-earth elements and the phthalocyanine radical the extent of the interaction varying with the rare-earth ions.

All complexes showed absorption bands at about 330, 500, 620, and 680 nm as shown in Fig. 3. The molar extinction coefficient of the band at the longest wavelength is smaller than those of usual phthalocyanine complexes of rare-earth elements previously reported.5) The broad band at about 500 nm is characteristic to complexes having $(\mathrm{Pc}^{-\cdot})$ ligand8,9) and is not observed in usual complexes having (Pc^{2-}) ligand. This band was also reported to be observed in rare-earth diphthalocyanine complexes2) $[\mathrm{M}^{3+}(\mathrm{Pc}^{-\cdot})(\mathrm{Pc}^{2-})]$ and phthalocyanine radicals $[\mathrm{H}(\mathrm{Pc}^{-\cdot})]$ and $[\mathrm{Li}(\mathrm{Pc}^{-\cdot})]$.6) Upon addition of an equimolar amount of a reductant such as $\mathrm{Bu_4NBH_4}$ or 3,5-di-tert-butylcatechol, the appearance of the spectra was dramatically changed to the usual absorption spectra as shown in Fig. 3. Under the same condition, the strong ESR signal for Lu^{3+} and Y^{3+} complexes completely disappeared.

The absorption band at about 500 nm can, therefore, be regarded as evidence of the existence of the radical of phthalocyanine.

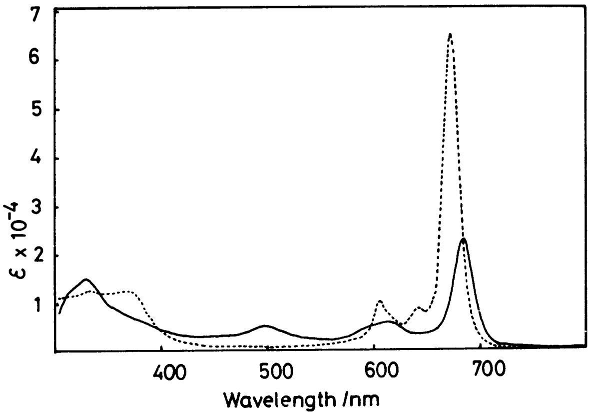

Fig. 3. Absorption spectra of (——) $[\mathrm{Tb}^{3+}(\mathrm{Pc}^{-\cdot})(\mathrm{dpm})_2]$ in benzene and (------) upon addition of an equimolar amount of $\mathrm{Bu_4NBH_4}$.

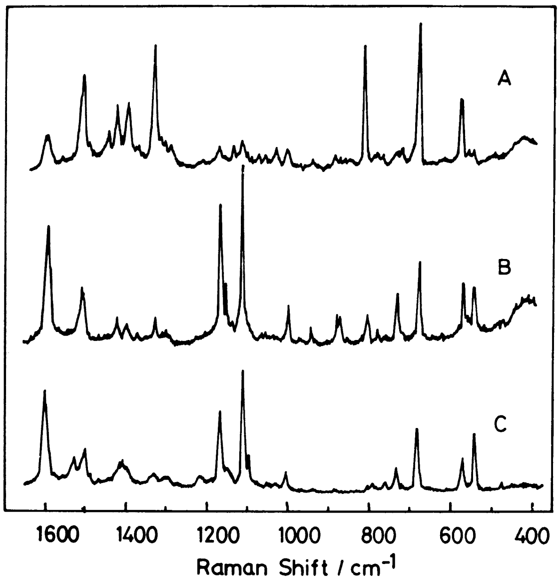

Fig. 4. Raman spectra of
(A) $[\mathrm{Er}^{3+}(\mathrm{Pc}^{2-})(\mathrm{dbm})(\mathrm{dbmH})]$,5)
(B) $[\mathrm{Er}^{3+}(\mathrm{Pc}^{-\cdot})(\mathrm{dpm})_2]$, and
(C) $[\mathrm{H}(\mathrm{Pc}^{-\cdot})]$.

Finally, the Raman spectra10) of these complexes were different from those of usual phthalocyanine complexes such as $[\mathrm{M}^{3+}(\mathrm{Pc}^{2-})(\mathrm{dbm})(\mathrm{dbmH})]$5) (dbm = dibenzoylmethane) as shown in Fig. 4. No significant dependence of Raman shifts on the rare-earth elements was observed in either series. Characteristic bands for phthalocyanine radical are strong peaks at about 1600, 1170, and 1100 cm^{-1}. These Raman spectra are similar to those of phthalocyanine radicals [H($Pc^{-\cdot}$)] and [Li($Pc^{-\cdot}$)].$^{6)}$

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10) Raman spectra were obtained with the 514.5 nm excitation line (100 mW) of the argon ion laser while the solid sample was rotated in order to minimize heating.

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