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PREPARATION OF NEW PHTHALOCYANINE COMPLEXES OF SOME RARE-EARTH ELEMENTS

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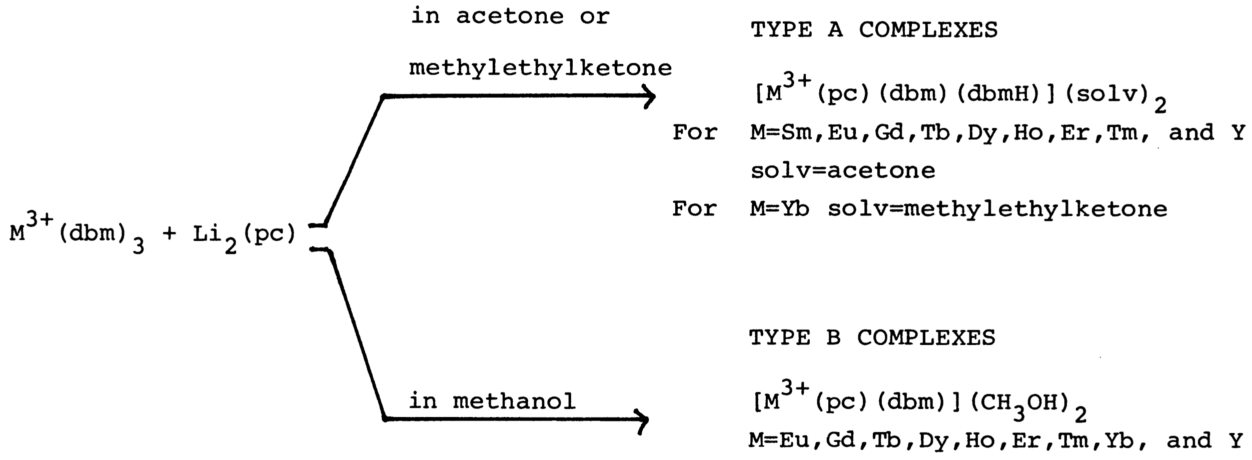
The reaction of tris(1,3-diphenyl-1,3-propanedionato) complexes of heavier rare-earth elements, $M^{3+}(dbm)_3$ and lithium phthalocyaninato(2-), $Li_2(pc)$ gave two types of new stable phthalocyanine complexes, $[M^{3+}(pc)(dbm)(dbmH)]$ and $[M^{3+}(pc)(dbm)]$ depending on the solvents used for the preparation. The structure of both types of complexes are tentatively proposed.

For the preparation of phthalocyaninatolanthanoid(III) complexes, only one method has so far been known, i.e., the thermal cyclization of phthalonitrile in the presence of $Ln^{3+}X_3 \cdot 6H_2O$.[1,2] This reaction was reported to give crude materials represented as $[Ln^{3+}(pc)_2]^-[Ln^{3+}(pc)]^+$. The 1:2 type lanthanoid phthalocyanine complexes, $[Ln^{3+}(pc)_2H]$ were later isolated as stable crystals, and well studied.[3] On the other hand, the 1:1 lanthanoid phthalocyanine complexes, $[Ln^{3+}(pc)X]$ assumedly produced at the same time in the reaction have neither been isolated nor characterized. In this communication, we wish to report the first synthesis of two types of stable 1:1 phthalocyanine complexes of heavier rare-earth elements which contain β-diketonato anions probably in the coordination sphere.


$M^{3+}(dbm)_3 + Li_2(pc)$

in acetone or methylethylketone

TYPE A COMPLEXES

$[M^{3+}(pc)(dbm)(dbmH)](solv)_2$

For M=Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm, and Y solv=acetone

For M=Yb solv=methylethylketone

in methanol

TYPE B COMPLEXES

$[M^{3+}(pc)(dbm)](CH_3OH)_2$

M=Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb, and Y

The reaction of tris(1,3-diphenyl-1,3-propanedionato) complexes of heavier rare-earth elements, $M^{3+}(dbm)_3$ (M=Sm ∿ Yb, and Y) and lithium phthalocyaninate(2-), $Li_2(pc)$ gave type A complexes in acetone or methylethylketone, and type B complexes in methanol, respectively. All new compounds gave satisfactory elemental analyses. However, type A and B complexes contained the solvent molecules used in the preparation; acetone or methylethylketone for the former and methanol for the latter, which were also confirmed by their IR spectra. These complexes are stable both in solid state and in aprotic solvents such as $CHCl_3$, acetone, and DMF, while in protic solvents such as methanol the complexes are gradually decomposed to give phthalocyanine. It is noted that whereas the 1:2 complexes of phthalocyanine were reported for the whole members of the lanthanoids, the 1:1 complexes obtained as stable forms in this research are those of heavier rare-earth elements including Sm and Eu, except Lu.

The paper electrophoresis in $DMF-NH_4Cl$ revealed that these chromophores are cationic in the solvent. The existence of coordinated dbm ligand molecule was confirmed by the IR spectra, which were little dependent on the metal.

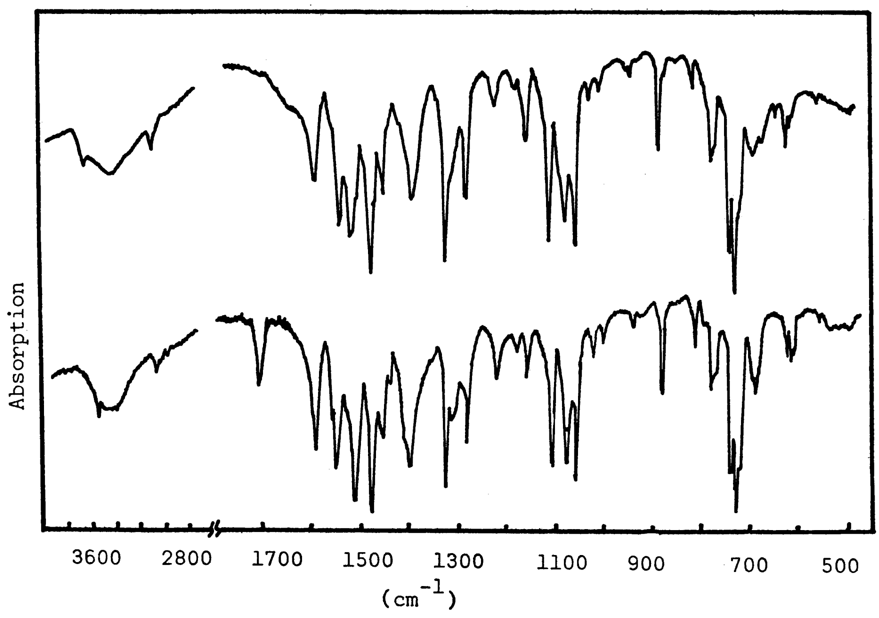


Figure 1. IR spectra of $[Er^{3+}(pc)(dbm)(dbmH)]$ (lower), and $[Er^{3+}(pc)(dbm)]$ (upper).

As shown in Fig 1, the IR bands characterized for the dbm ligand molecule appeared at 1500∿1600 cm^{-1} as three strong bands, and also at ∿1400, ∿1300, 1060, and ∿670 cm^{-1}. These strong bands around 1500∿1600 cm^{-1} could be easily assigned to the $\nu_{C-C}+\nu_{C-O}$.⁶⁾ Moreover, a sharp band at 3560 cm^{-1} of type A complexes means that the neutral dbmH ligand coordinates in the enol form. The band at 3600 cm^{-1} of type B complexes are assignable to ν_{O-H} of methanols. The visible spectra of type B complexes are somewhat different from those of type A complexes in nonpolar solvents such as $CHCl_3$, while in polar solvents such as DMF or acetone, the absorption spectra of these two types of complexes are similar to each other, The absorption maxima of UV-VIS bands appeared at about 336 and 679 nm, respectively. The maxima were not sensitive to the metal (Fig 2). The magnetic moments of these complexes at room temperature were quite consistent with those caluculated by Van-Vleck-Frank theory⁷⁾ (Fig 3).

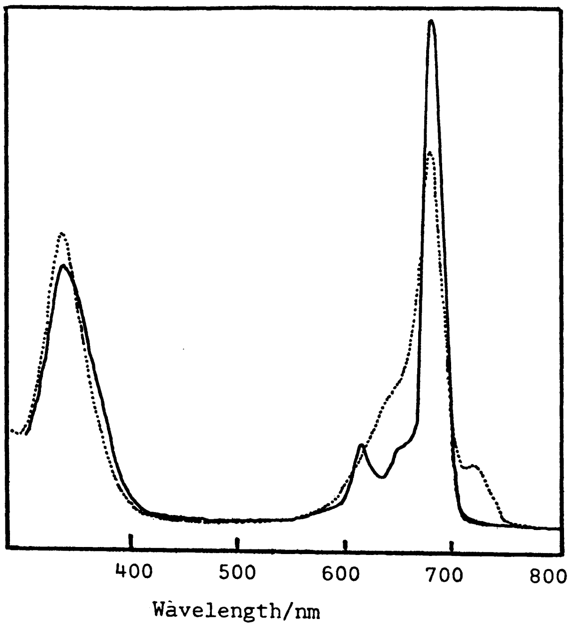


Figure 2. UV-VIS spectra of (——) [Er^{3+}(pc)(dbm)(dbmH)] and (-----) [Er^{3+}(pc)(dbm)] in $CHCl_3$.

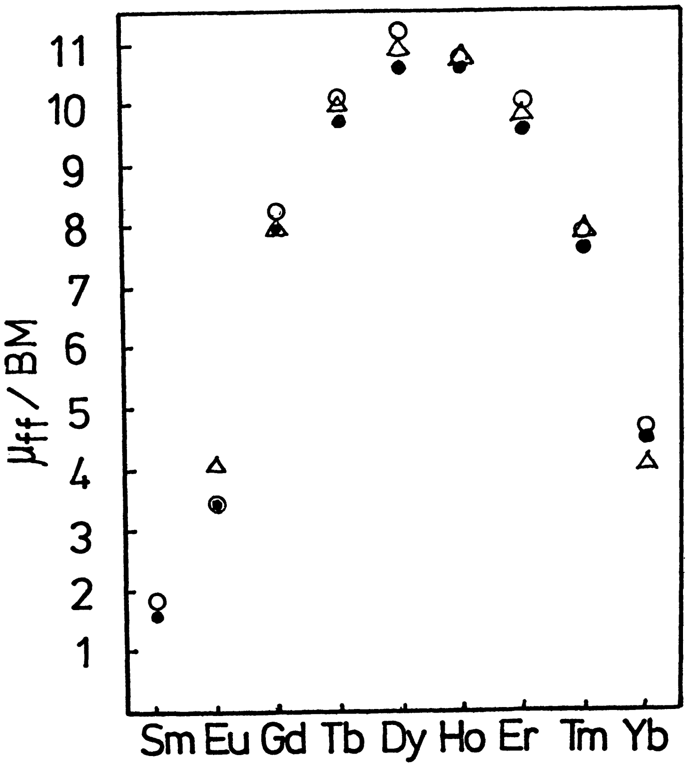


Figure 3. Magnetic moments of some lanthanide complexes. (○) type A complexes, (△) type B complexes, and (●) caluculated values by Van-Vleck-Frank theory.

Fig 4 shows the ^1H-NMR spectra for both type A and type B complexes of diamagnetic yttrium complexes in $CDCl_3$-acetone-d_6 (10:1 vol/vol). In type A complex, four phenyl protons of two dbm molecules resonated at 7.27 and 7.26 ppm as two peaks. On the other hand, in type B complex two phenyl protons of one dbm ligand molecule shifted to up-field compared with those in type A complex by about 0.5 ppm and splitted into three signals at 6.29 (triplet, 2H, p-H), 6.64 (triplet, 4H, m-H), and 6.24 ppm (doublet, 4H, o-H), respectively. These characteristic features observed in ^1H-NMR spectra suggest the different mode of the coordination of dbm ligand to the metal atom between these two types of complexes.

From the results obtained above, we can tentatively assign to type A and B complexes the structure (A) and (B), respectively as illustrated below. X-Ray crystallographic studies for these complexes are now in progress.

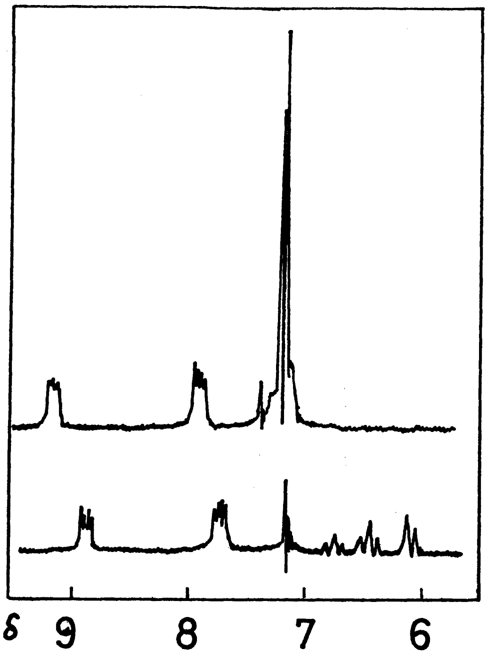
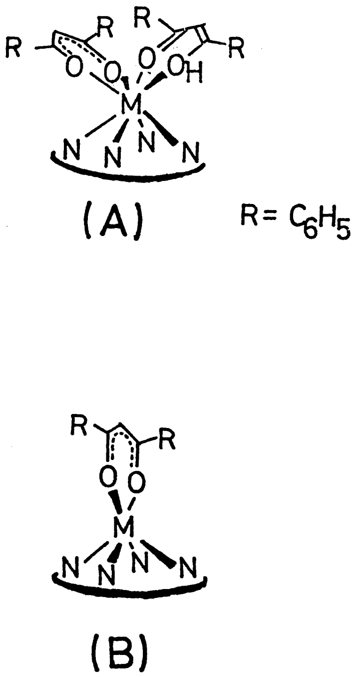


Figure 4. ^{1}H-NMR spectra in low field region of [Y^{3+}(pc)(dbm)(dbmH)] (upper) and [Y^{3+}(pc)(dbm)] (lower) in $CDCl_3$-acetone-d_6.



Proposed structure for type A and type B complexes.

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