Structure and Magnetic Properties of a Low-spin Manganese(III) Phthalocyanine Dicyanide Complex

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A manganese(III) complex salt, TPP[$\mathrm{Mn^{III}(Pc)(CN)_2}$]•DCM was crystallized in dichloromethane solution (Pc = phthalocyaninato, $\mathrm{TPP^+}$ = tetraphenylphosphonium, and DCM = dichloromethane). In the crystal, Pc molecules form a pair of one-dimensional regular chains along the *c* axis. The magnetic susceptibility measurement revealed Mn ions in the low-spin state ($S = 1$) and a spin–orbit coupling effect due to the incomplete quenching of the angular orbital moment under the symmetrical ligand field.

Manganese phthalocyanine and porphyrin are quite useful modeling compounds for biomaterials and intermediates in biological reactions. Low-spin manganese(III) complexes with $S = 1$ state are particularly important, because they are isoelectronic with the elusive iron(IV) species. Although there have been several reports on manganese(III) porphyrins, in most of these studies the porphyrins have been in a high-spin $S = 2$ state.[1] This implies that a very strong ligand field is required to impose a low-spin $S = 1$ state on the manganese(III) ion. To the best of our knowledge, the diimidazolate and dicyanide complexes are the only cases of manganese(III) porphyrins in a low-spin state.[2–4] For phthalocyanine, only the spectroscopic properties have been reported for the dicyano complex, and there are few data on the molecular structure and few magnetic studies.[5,6] In this letter, we describe the preparation, structure, and magnetic properties of a newly synthesized manganese(III) phthalocyanine complex, TPP[$\mathrm{Mn^{III}(Pc)(CN)_2}$]•DCM (TPP = tetraphenylphosphonium, DCM = dichloromethane). This is the first report of the structural characterization and magnetic study of the low-spin manganese(III) phthalocyanine complex.

Mn(Pc) was prepared by the method of Rutter and McQueen.[7] The obtained crystals (0.5 g) were dissolved in ethanol (100 mL), and KCN (0.25 g) was added. After stirring for 72 h, a manganese(III) complex salt, K[$\mathrm{Mn(Pc)(CN)_2}$], was obtained (0.4 g). The same salt could be obtained by the similar reaction of Mn(Pc)Cl (Aldrich Products) with KCN in EtOH. The cation exchange was carried out by metathesis of K[$\mathrm{Mn(Pc)(CN)_2}$] (0.33 g) with TPPBr (0.43 g) in acetonitrile (150 mL). The TPP salt was dissolved in dichloromethane and slow evaporation was done at room temperature. Black crystals of TPP[$\mathrm{Mn^{III}(Pc)(CN)_2}$]•DCM, which were suitable for X-ray crystal structure determination, were obtained.[8]

The molecular structures of TPP and [$\mathrm{Mn^{III}(Pc)(CN)_2}$] are shown in Figure 1. There are two crystallographically independent [$\mathrm{Mn^{III}(Pc)(CN)_2}$] molecular units. The central Mn ions of each unit lie at the inversion center. The bond lengths and angles of the phthalocyaninato core are not very different from those of the Mn(Pc) molecule.[9] The cyanide ligands are coordinated in a trans configuration, and the angles of Mn–C–N for Mn1 and Mn2 are 178.6(6) and 178.0(7)°, respectively. The length between the Mn ion and cyanide ligand ($d(\mathrm{Mn1–C_{CN}}) = 2.025(7)$ Å and $d(\mathrm{Mn2–C_{CN}}) = 2.015(7)$ Å) is longer than those in the [$\mathrm{Co^{III}(Pc)(CN)_2}$] and [$\mathrm{Fe^{III}(Pc)(CN)_2}$] units,[10] reflecting the larger ionic radius of $\mathrm{Mn^{III}}$ compared with $\mathrm{Co^{III}}$ and $\mathrm{Fe^{III}}$. Since the ligand fields of CN and Pc are strong, it is considered that the Mn ion adopts the low-spin state with a d-electron configuration $(\mathrm{d}_{xy})^2$ $(\mathrm{d}_{yz})^1$ $(\mathrm{d}_{zx})^1$.

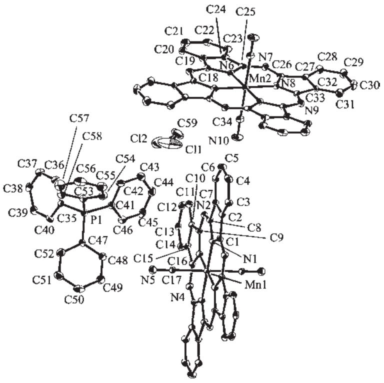

Figure 1. Molecular structures of TPP and [$\mathrm{Mn^{III}(Pc)(CN)_2}$].

Figure 2 shows the crystal structure of TPP[$\mathrm{Mn^{III}(Pc)(CN)_2}$]•DCM. The two unique [$\mathrm{Mn^{III}(Pc)(CN)_2}$] units form a one-dimensional regular chain (chain1 includes Mn1 and chain2 includes Mn2) along the *c* axis, and the chain1 is almost perpendicular to the chain2. The interplanar distances between the peripheral benzene rings are 3.32 and 3.40 Å for chain1, and 3.36 and 3.49 Å for chain2, respectively. Although these values are almost the same as the summation of the van der Waals radius of 3.4 Å, the π–π interaction between Pc molecules could not be expected, since the overlaps are insufficient. By the extended Hückel calculation,[11] the overlap integral between the Pc molecules along the *c* axis is estimated to be 2.69×10^{-3} for chain1 and 1.86×10^{-3} for chain2, and these values are less than 30% of those for TPP [$\mathrm{M^{III}(Pc)(CN)_2}$]$_2$ (M = Fe and Co).[10] This confirms the insignificance of the π–π interaction between

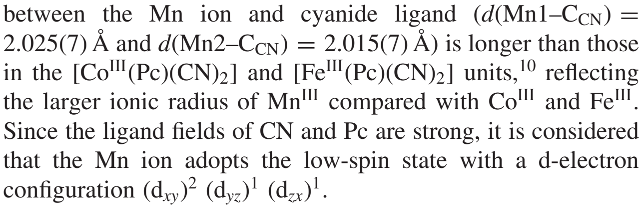

Figure 2. Crystal structure of TPP[$\mathrm{Mn^{III}(Pc)(CN)_2}$]•DCM; view along the *c* axis (a) and the *a* axis (b).

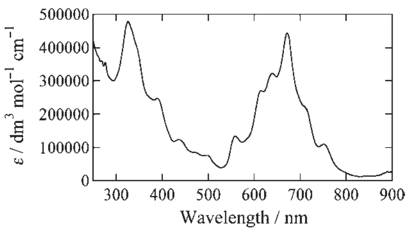

Figure 3. Absorption spectrum of TPP [Mn^{III}(Pc)(CN)$_2$].

the Pc molecules.

Figure 3 represents the UV–vis absorption spectrum for TPP[Mn^{III}(Pc)(CN)$_2$] in DCM solution. The spectrum is almost consistent with those previously reported for the analogues.[5,6] The Q band, which corresponds to the transition between HOMO (a_{1u}) and LUMO (e_g), is observed at 671 nm. The B (Soret) band is observed at 325 nm and corresponds to the excitation between NHOMO (a_{2u}) and LUMO (e_g). The peak at 614 nm may be assigned to the splitting of the Q band caused by the vibronic coupling which is characteristic for most metal phthalocyanine complexes.[6,12] The peak around 638 nm could be attributed to the LMCT (from Pc to d_{yz} or d_{zx}), since the peak is not observed for closed-shell $(d_{xy})^2(d_{yz})^2(d_{zx})^2$ complexes composed of the [Fe^{II}(Pc)(CN)$_2$] or [Co^{III}(Pc)(CN)$_2$] unit.[6,10] The peaks around 558, 498, 436, and 388 nm could be also attributed to the LMCT and/or MLCT bands.[6,13]

Figure 4a shows the temperature dependence of the magnetic susceptibility (χ) under an applied field of 1 T for polycrystallines of TPP[Mn^{III}(Pc)(CN)$_2$]•DCM. The effective moment (μ_{eff}) and the reciprocal susceptibility (χ^{-1}) are also plotted in Figure 4b. The χ^{-1} data are almost linear above 75 K and can be fitted by the Curie–Weiss expression. The Curie and Weiss constants obtained are 1.67 emu K mol^{-1} and 0.84 K, respectively. The μ_{eff} at the room temperature is 3.28 μ_B, which is considerably higher than the calculated spin-only value of 2.83 μ_B for $S = 1$. Similarly, large values are reported for the low-spin manganese(III) porphyrin dicyanide complexes, in which the μ_{eff} value is elevated by the spin–orbit coupling effect and/or magnetic anisotropy.[2,3]

The μ_{eff} value decreases remarkably below 60 K, a behavior that is remindful of an intermolecular antiferromagnetic interaction. However, the distance between the Mn ions is extremely long (8.986 Å), and there is no carrier that can mediate the spin–spin interaction. Thus the antiferromagnetic interaction should be excluded. For the [Mn(CN)$_6$]$^{3-}$ compound, which is one of the rare examples of a manganese(III) complex with a low-spin state, Kotani calculated the temperature dependence of the magnetic moment by taking account of the spin–orbit coupling effect,[14] and Buschmann et al. experimentally estimated the spin–orbit coupling with the Kotani model.[15] Although the molecular symmetry of the [Mn^{III}(Pc)(CN)$_2$] unit is lower than that of [Mn^{III}(CN)$_6$] and we can not apply the Kotani model to the [Mn^{III}(Pc)(CN)$_2$] system, the relatively highly symmetrical ligand field of D_{4h} yields degenerated d_{xz} and d_{yz} orbitals, which possess two unpaired electrons. This situation would also lead to the incomplete quenching of the angular orbital moment and the spin–orbit coupling in the [Mn^{III}(Pc)(CN)$_2$] system. Actually, the temperature dependence of χ^{-1} for TPP[Mn^{III}(Pc)(CN)$_2$]•DCM resembles that for [(Ph$_3$P)$_2$N]$_3$[Mn^{III}(CN)$_6$] reported by Buschmann et al. We, therefore, consider that the extraordinary μ_{eff} value and its temperature dependence observed for TPP[Mn^{III}(Pc)(CN)$_2$]•DCM should be caused by the spin–orbit coupling, as seen in the [Mn^{III}(CN)$_6$] system.

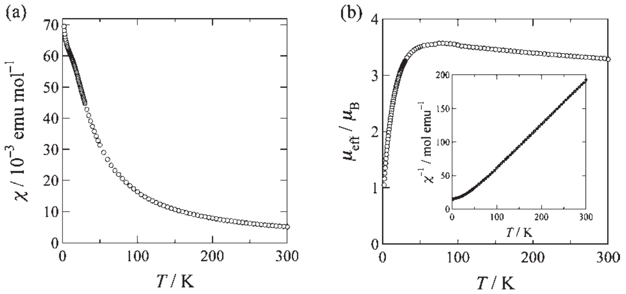

Figure 4. Temperature dependence of the magnetic susceptibility (a) and the magnetic moment (b) for TPP[Mn^{III}(Pc)(CN)$_2$]•DCM. The inset shows the reciprocal susceptibility.

In summary, we have succeeded in solving the crystal structure of the manganese phthalocyanine complex, TPP[Mn^{III}(Pc)(CN)$_2$]•DCM in the low-spin state ($S = 1$), for the first time. The temperature dependence of the magnetic susceptibility suggests the spin–orbit coupling effect due to the symmetrical ligand field in this system.

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8 Crystal data for TPP[Mn^{III}(Pc)(CN)$_2$]•DCM: C$_{59}$H$_{38}$Cl$_2$N$_{10}$MnP, triclinic, space group $P\bar{1}$, $a = 13.0468(9)$ Å, $b = 22.393(2)$ Å, $c = 8.9859(6)$ Å, $\alpha = 101.034(2)°$, $\beta = 95.391(2)°$, $\gamma = 74.430°$, $V = 2479.7(3)$ Å^3, $Z = 2$, $D_{\text{calcd}} = 1.398$ g cm^{-3}, Bruker SMART APEX system at 293 K, Mo Kα, μ(Mo Kα,) $= 4.45$ cm^{-1}, 24115 reflections measured, 12336 independent reflections, 4076 reflections with $I > 2\sigma(I)$, $R = 0.052$, $R_W = 0.086$ (12331 reflections refined with $I > 0\sigma(I)$, 662 variables). CCDC-284241
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