Exchange Interaction in Hybrid Spin Systems: Chloro-*meso*-tetraphenylporphyrinatochromium(III) Derivatives ligated with 3- and 4-(*N*-Oxy-*N*-*tert*-butylamino)pyridines

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The 3d electrons of chromium(III) and the unpaired electron of the nitroxide radical interact ferro- and antiferro-magnetically in chloro-*meso*-tetraphenylporphyrinatochromium(III) ligated with 3- and 4-(*N*-oxy-*N*-*tert*-butylamino)pyridines to produce quintet and triplet ground states, respectively.

Hybrid-type spin systems in metal complexes consisting of transition metals and ligands carrying organic unpaired electrons are of great interest to scientists aiming at construction of molecular magnetic materials.[1] A number of such successful examples use the ligands in which the radical centres also serve as the ligating centres. We have prepared a pair of ligands that have a radical centre remote from but in conjugation with the ligating centre and studied the sign and magnetic interactions of their electron spins with the 3d electrons of a transition metal to see if the spin polarization mechanism[2] is operative in these hybrid-type spin systems.

Isomeric 3- and 4-(*N*-oxy-*N*-*tert*-butylamino)pyridines (3-NOPy and 4-NOPy) were prepared and purified by a procedure employed for analogous phenyl derivatives.[3] They were stable in solution under a nitrogen atmosphere [EPR spectra in $CHCl_3$: $a_N = 11.0, 2.1$ and $a_H = 1.35$ (3- and 5-H), 0.61 (2, and 6-H) G for 4-NOPy and $a_N = 12.6, 0.97$ and $a_H = 1.63$ (2-, 4- and 6-H), 0.87 (5-H) G for 3-NOPy][4] but unstable in the solid state, and therefore used for spectral and magnetic measurements immediately after the preparation.

Their complexes (CrTPP/3- and 4-NOPy) with chloro-*meso*-tetraphenylporphyrinatochromium(III) (CrTPP)[5] were precipitated by addition of *n*-hexane to a mixture of the latter and a slight excess of the corresponding NOPy in CH_2Cl_2, washed with *n*-hexane to remove excess nitroxide radicals, and then dried under reduced pressure. The binding constants ($\log K = 4.0$ and 4.4 for 3-NOPy and 4-NOPy, respectively) were measured by using absorptions at $\lambda_{max} = 611.2$ nm ($\log \varepsilon = 4.11$) in CH_2Cl_2 to find that they were in good agreement with that of CrTPP with pyridine reported in the literature.[5]

CrTPP and a slight excess of 3- and 4-NOPy in frozen toluene at 10 K showed contrasting EPR spectra together with signals at $g = 2$ due to the excess free nitroxide radicals. The two spectra were quite different from that of CrTPP ligated with pyridine and 3- or 4-(*N*-hydroxy-*N*-*tert*-butylamino)pyridines under similar conditions, indicating that magnetic interaction between the Cr^{III} and the nitroxide radical took place through the coordination with the pyridine ring nitrogen of NOPy in two different fashions. From 10 to 115 K, the EPR signal intensities of CrTPP/3-NOPy decreased in accordance with the Curie law, while new signals at 259, 279, 376 and 421 mT appeared at *ca.* 75 K at the expense of the decreasing signals in CrTPP/4-NOPy. The observed thermal behaviours of the EPR spectra were reversible and reproducible, suggesting that a quintet and triplet ground states might be produced by ferro- and antiferro-magnetic interaction between Cr^{III} ($S = 3/2$) and the nitroxide radicals ($S = 1/2$) on the sixth ligand in CrTPP/3- and 4-NOPy, respectively. The new signals observed for CrTPP/4-NOPy above 75 K were assigned to the thermally populated quintet state lying at least 50 cm^{-1} ($\Delta E_{Q\text{-}T} = -4J$) above the triplet ground state.

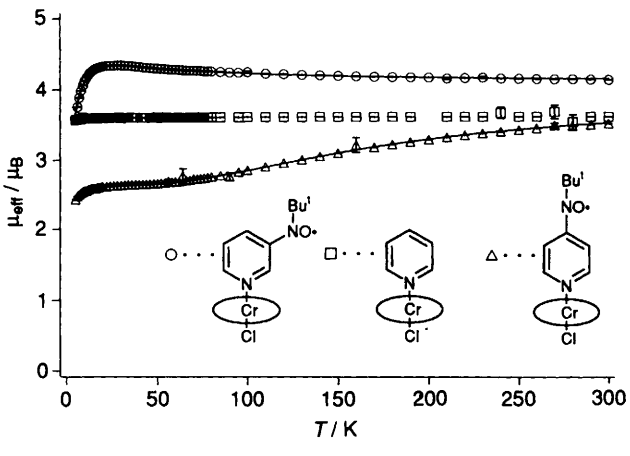

Fig. 1 Temperature dependence of the effective magnetic moments μ_{eff}/μ_B of CrTPP/3-NOPy (○), CrTPP/4-NOPy (△), and CrTPP/Py (□). Solid curves are theoretical ones calculated on the basis of eqn. (1) with the optimized parameters given in text.

To understand the magnetic interactions between CrTPP and two isomeric NOPys on the ligated pyridines in more detail, magnetic moments of the powder samples were measured between 5 and 300 K at a constant magnetic field of 0.2 T on a SQUID susceptometer. The temperature dependence of the effective magnetic moment (μ_{eff}) of CrTPP/3- and 4-NOPy together with CrTPP/Py as a reference are shown in Fig. 1. The μ_{eff}/μ_B values at 300 K were 3.95 and 3.41 for CrTPP/3 and 4-NOPy, respectively. As the temperature was decreased, the μ_{eff}/μ_B value for CrTPP/3-NOPy gradually increased between 24 and 300 K and reached a maximum ($\mu_{eff}/\mu_B = 4.34$) at 24 K, while that of CrTPP/4-NOPy decreased monotonically from 70 to 300 K and became nearly constant at 13 to 70 K. The μ_{eff}/μ_B values for CrTPP/Py were almost constant in all the temperature range studied. Sharp decreases of the μ_{eff}/μ_B values below 24 and 13 K for CrTPP/3- and 4-NOPy, respectively, suggest the presence of intermolecular antiferromagnetic interaction. The observed temperature dependencies of μ_{eff}/μ_B values for CrTPP/3- and 4-NOPy were analysed in terms of eqn. (1) representing equilibria between the triplet and quintet states and refined by means of a least-squares method.

$$\mu_{eff}/\mu_B = \left[\frac{3fg^2T}{(T-\theta)}\cdot\frac{2+10e^{-(-4J))/k_BT}}{3+5e^{-(-4J)/k_BT}}\right]^{\frac{1}{2}} \qquad (1)$$

where g is assumed to be 2, *f* is a purity factor and the other symbols have their usual meaning. From the best fitted theoretical curves, $J/k_B(\Delta E_{T\text{-}Q} = 4J)$, θ and *f* were found to be 8.5 ± 0.2 cm^{-1} (34.1 ± 0.9 cm^{-1}), -2.23 ± 0.03 cm^{-1}, and 0.933 ± 0.003 for CrTPP/3-NOPy and -53.6 ± 0.5 cm^{-1} (-214 ± 2 cm^{-1}), -0.76 ± 0.04 cm^{-1}, and 0.898 ± 0.003 for CrTPP/4-NOPy, respectively. The J/k_B values thus obtained clearly show that CrTPP/3-NOPy has a quintet ground state and is a mixture of quintet and thermally populated triplet states in equilibrium between 5 and 300 K, while CrTPP/4-NOPy has a triplet ground state and a thermally accessible quintet state begins to contribute at temperatures above *ca.* 70 K. The latter results from SQUID are consistent with the thermal behaviour of EPR spectra of CrTPP/4-NOPy.

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