Structure and physical properties of hexacyanomanganate(iv), $[Mn^{IV}(CN)_6]^{2-}$

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Hydrolytically unstable d^3 $[Mn^{IV}(CN)_6]^{2-}$ as the $[N(PPh_3)_2]^+$ salt is crystallographically, spectroscopically, and magnetically characterized.

The observation of magnetic ordering at relatively high temperature and including ambient temperature,[1] the photo-[2a] and electro-chemical[2b] switching between magnetic states as well as the reversible binding of oxygen[3] has led to a resurgence of interest in cyanometalates. The putative mechanism of spin coupling leading to ferromagnetic behaviour for some of these materials is that of spins on adjacent spin sites residing in orthogonal orbitals in the same spatial region.[4] An example is the ferromagnet $CsNi[Cr(CN)_6]\cdot 2H_2O$ (T_c = 90 K) with the e_g^2 spins on each Ni^{II} and orthogonal t_{2g}^3 spins on adjacent Cr^{III} sites. Since Mn^{IV} is isoelectronic to Cr^{III}, we targeted the preparation of $[Mn^{IV}(CN)_6]^{2-}$.

$K_2[Mn^{IV}(CN)_6]$ has been reported to be prepared from the oxidation of $K_3[Mn^{III}(CN)_6]$ with NOCl and exhibits ν_{CN} absorptions at 2240 vs and 2150 s cm^{-1} and a room-temperature magnetic moment of 3.93 μ_B.[5a] Although $[Mn^{IV}(CN)_6]^{2-}$ is hydrolytically unstable,[5b] several $[Mn^{IV}(CN)_6]^{2-}$ salts including $K_2[Mn^{IV}(CN)_6]$[5c,d] (ν_{CN} = 2151 cm^{-1}; μ_{RT} = 3.79 μ_B) and $Mn^{II}[Mn^{IV}(CN)_6]\cdot 1.15H_2O$ have been prepared.[6] The latter is a ferrimagnet below an ordering temperature of 49 K.[5d] In order to develop non-aqueous routes to magnetic cyanometalates we prepared $[N(PPh_3)_2]_2[Mn^{IV}(CN)_6]$ the first structurally characterized simple salt which is stable in MeCN and CH_2Cl_2.§

The asymmetric unit of the unit cell‖ consists of a cation and half-anion, Fig. 1. The Mn–C and CN distances average 1.97 and 1.15 Å, respectively, and the *cis*-CNC and MnCN angles average 90.0 and 177.2°, respectively. The Mn–C and CN distances in this structure are comparable with the mean values reported for $Na_4[Mn^{II}(CN)_6]\cdot 10H_2O$ (1.95, 1.16 Å)[7] and $K_3[Mn^{III}(CN)_6]$ (1.98, 1.15 Å).[8] Within the accuracy of the crystal structure determination there is no evidence for a Jahn–Teller distortion as predicted for ^4A ground state. The cation is typical with an average PN distance of 1.579 Å and PNP angle of 139.6°. Each anion is surrounded by twelve cations in the solid state.

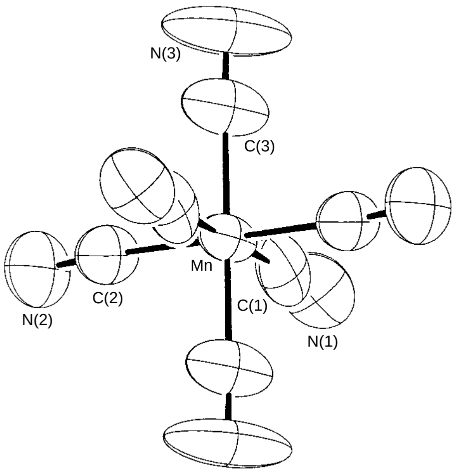

Fig. 1 ORTEP drawing depicting atom labelling for $[Mn^{IV}(CN)_6]^{2-}$ in $[N(PPh_3)_2]_2[Mn^{IV}(CN)_6]$; atoms shown as 50% probability ellipsoids. Selected bond lengths (Å) Mn–C(1) 1.970(12), Mn–C(2) 1.965(8), Mn–C(3) 1.988(8), C(1)–N(1) 1.176(12), C(2)–N(3) 1.132(9), C(3)–N(3) 1.153(9).

The 2132 cm^{-1} $\nu_{MnC\equiv N}$ absorption for $[Mn^{IV}(CN)_6]^{2-}$ is at higher energy than the 2092 and 2098 cm^{-1} values for $[N(PPh_3)_2]_3[Mn^{III}(CN)_6]$. Coordination to K^+ leads to a significant increase in the energy of the $\nu_{C\equiv N}$ absorption, although an overall similar trend is observed for $\nu_{MnC\equiv NK}$: $K_2[Mn^{IV}(CN)_6]$ (2240, 2150 cm^{-1})[5a] and $K_3[Mn^{III}(CN)_6]$ (2129, 2112 cm^{-1}).[9]

$[N(PPh_3)_2]_2[Mn^{IV}(CN)_6]$ exhibits a corrected room-temperature magnetic moment of 4.10 μ_B consistent with being a d^3 octahedral complex with isolated anions. The expected six-line hyperfine for ^{55}Mn (I = 5/2) is isotropic in the solution, frozen-solution, and even the solid-state spectra and is centred at g = 1.996. This is strong evidence for a well behaved anion which exhibits very little or no distortion in its electronic configuration. At 78 K the electron paramagnetic resonance is 340 G wide with an average hyperfine coupling constant $|A|$ = 68 G, Fig. 2. The derivative peak to peak linewidths are essentially the same for the room-temperature and 78 K spectra with a slight variation from line to line. They proceed as 33, 30, 28, 31, 32, 27 (±1) G, from low to high field. This slight inhomogeneity is expected for manganese ions.[6]

The $Mn^{III/IV}$ couples of the octahedral cyanide anions are fully reversible one-electron events. $[Mn^{IV}(CN)_6]^{2-}$ {and $[Mn^{III}(CN)_6]^{3-}$} have a reversible $Mn^{III/IV}$ couple at $E_{1/2}$ = +0.14 V in MeCN *vs.* SCE, ΔE_{pp} = 0.09 V (10 mV s^{-1} scan rate) using glassy carbon disk, Pt wire and $Ag/AgCF_3SO_3$ electrodes and ferrocene as an external standard. A reduction wave for the $Mn^{III/II}$ couple was not observed. The presence of any other metal cations affect the electrochemical response by precipitating out a cyanide complex onto the working electrode. By comparison, the $[Fe^{III/II}(CN)_6]^{3/4-}$ $E_{1/2}$ couple in MeCN is −0.42 V *vs.* SCE.[10]

The electronic spectrum of $[Mn^{IV}(CN)_6]^{2-}$ in MeCN, Fig. 3, unlike that of the isoelectronic $[Cr^{III}(CN)_6]^{3-}$,[11] possesses several charge-transfer bands. In contrast to $[Cr^{III}(CN)_6]^{3-}$ which has two d → d transitions at 26 500 (ε = 90 m^{-1} cm^{-1})

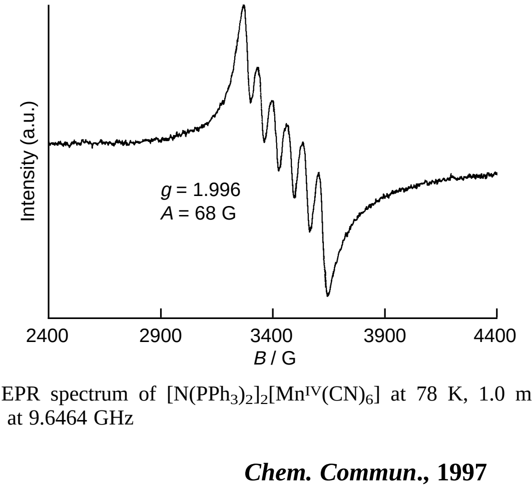

Fig. 2 EPR spectrum of $[N(PPh_3)_2]_2[Mn^{IV}(CN)_6]$ at 78 K, 1.0 mm in CH_2Cl_2 at 9.6464 GHz

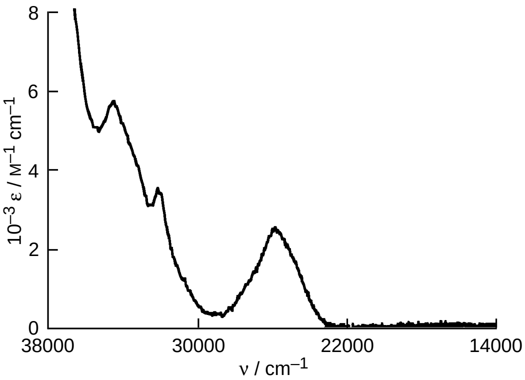

Fig. 3 Electronic spectrum of $[N(PPh_3)_2]_2[Mn^{IV}(CN)_6]$ in MeCN

and 32 400 cm^{-1} (ε = 65 m cm^{-1}) and one intense M → L charge-transfer absorption at 38 000 cm^{-1} (ε = 6240 m^{-1} cm^{-1}), $[Mn^{IV}(CN)_6]^{2-}$ possesses an intense band centred at 25 700 cm^{-1} (ε = 2500 m^{-1} cm^{-1}) which appears to be at least two overlapping bands. This band tails well into the visible region and is likely to be responsible for the extreme photosensitivity of this compound. There is a second band at 32 000 cm^{-1} (ε = 3500 m^{-1} cm^{-1}) and a third at 34 400 (ε = 5700 m^{-1} cm^{-1}) on the tail of the aromatic $\pi \rightarrow \pi^*$ transitions of the $[N(PPh_3)_2]^+$ cation which obscures the region above 36 000 cm^{-1}. This is the first electronic spectrum of a manganese cyanide taken without excess KCN[11] or perchloric acid[12] to prevent decomposition of the hydrolytically unstable anions. Reaction of $[Mn^{IV}(CN)_6]^{2-}$ to form molecule-based magnets is in progress.

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Footnotes

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§ In a typical experiment a MeCN solution (20 ml) of $[Fe(\eta\text{-}C_5H_5)_2][BF_4]$ (2.42 mmol, 1.00 g) was added to a CH_2Cl_2 solution (50 ml of $[N(PPh_3)_2]_3[Mn^{III}(CN)_6]$¶ (2.42 mmol, 4.42 g). The green colour of the $[Fe(\eta\text{-}C_5H_5)_2]^+$ gradually changed over 1.5 h to give a dark orange solution. The product was precipitated with Et_2O, isolated and recrystallized from MeCN–CH_2Cl_2–Et_2O to give small, yellow needles in 33% yield. IR: ν_{CN} (Nujol) = 2132 cm^{-1}. Raman: ν_{CN} = 2135 cm^{-1}, ν_{MC} = 365 cm^{-1}. mp 142 °C (decomp.). Anal. Calc. for $C_{78}H_{60}MnN_8P_4$: C, 72.73; H, 4.70; N, 8.40. Found: C, 72.49; H, 4.51; N, 8.58%.

¶ $K_3[Mn(CN)_6]$ (1.50 g, 4.57 mmol) was quickly added to a solution of $[N(PPh_3)_2]Cl$ (7.87 g, 13.7 mmol) disolved in 825 ml of water. The precipitated product was recovered by filtration and dried in *vacuo*. Recrystallization from a dry, oxygen-free MeCN solution layered with Et_2O gave large orange–yellow prisms in 77% yield. IR: ν_{CN}(Nujol) = 2092.2098 cm^{-1}. Raman: ν_{CN} = 2099, 2110 cm^{-1}, ν_{MC} = 359 cm^{-1}. mp 272 °C (decomp.). Anal. Calc. for $C_{114}H_{90}MnN_9P_6$: C, 74.95; H, 4.97; N, 6.90. Found: C, 74.90; H, 5.02; N, 6.96%.

‖ *Crystal data* for $C_{78}H_{60}MnN_8P_4$, M = 1288.16, monoclinic, space group $P2_1/n$, a = 10.707(2), b = 13.402(2), c = 23.662(4) Å, β = 100.41(1)°, U = 3339.5 Å^3, Z = 2, D_c = 1.281 g cm^{-3}, λ = 0.710 73 Å, crystal size 0.52 × 0.42 × 0.50 mm, T = −70 °C, $2\theta_{max}$ = 48°, R_w (on F) [R (on F)] = 0.069(0.065), for 2855 unique reflections with $I > 3\sigma(I)$. Data were collected on a Syntex $P\bar{1}$ diffractometer and the crystal structure solved using MOLEN software distributed by Enraf Nonius. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/357.

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