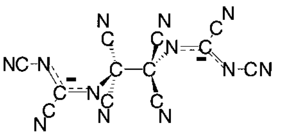
Structure and Properties of Tetracyanomanganate(II), $[Mn^{II}(CN)_4]^{2-}$, The First Paramagnetic Tetrahedral Cyanometalate Complex**

Wayne E. Buschmann, Atta M. Arif, and Joel S. Miller*

Cyanide is a well-known strong-field ligand that forms a large family of homoleptic cyanometalates.[1] Due to their small size and large stability constants these complexes have a propensity to be 18-electron complexes and coordinatively saturated. Examples include octahedral $[M(CN)_6]^{z-}$ (e.g., M = V, Cr, Mn, Fe, Co), and eight-coordinate $[M(CN)_8]^{z-}$ (e.g., M = Mo, W), as well as diamagnetic four-coordinate square-planar d^8 $[M(CN)_4]^{z-}$ (e.g., M = Ni^{II}, Pd^{II}, Pt^{II}), and tetrahedral d^{10} (e.g., M = Zn^{II}, Cd^{II}, Hg^{II}) complexes. $[Co^{II}(CN)_4]^{2-}$ also attests to the strong ligand field of CN, as such d^7 low-spin $S = 1/2$ square-planar complexes are rare.[1b] Interest in this class of compounds has recently been renewed because of the ferro- and ferrimagnetic ordering at both relatively high and ambient temperatures[2] as well as the reversible binding of oxygen.[3] Recently we prepared the $S = 3/2$ d^3 complex, $[PPN]_2[Mn^{IV}(CN)_6]$ (PPN = $[PH_3P{=}N{=}PPh_3]^+$),[4] and herein we report its photochemical degradation to 13-electron $[PPN]_2[Mn^{II}(CN)_4]$, the first member of a new class of magnetic tetrahedral coordinatively unsaturated cyanometalates.

Solutions of yellow $[Mn^{IV}(CN)_6]^{2-}$ decompose on exposure to light in a complex manner by a 10-electron process to several products including the {(1,1,2,2-tetracyano-1,2-ethanediyl)bis[imino(cyanomethylene)]}bis[cyanamide] dianion **1**[5] ($[C_{12}N_{12}]^{2-}$), and $[Mn^{II}(CN)_4]^{2-}$.[6] Crystals of $[PPN]_2$-$[Mn^{II}(CN)_4]$ were studied by single-crystal X-ray diffraction (Figure 1).[7] The MnC and CN distances average 2.159 Å and 1.133 Å, and the C-Mn-C and Mn-C-N angles average 104.2° and 177.05°, respectively. The cation is typical with an average PN distance of 1.583 Å and P-N-P angle of 136.4°. Each anion is surrounded by eight cations in the solid state.



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The 2.16 Å Mn^{II} – CN bonds are unusually long, and the CN bonds are marginally shorter than typical. The reported average Mn – CN (and CN) distances of $Na_4[Mn^{II}(CN)_6]\cdot 10H_2O$,[8a] $K_3[Mn^{III}(CN)_6]$,[8b] $Cs_2Li[Mn^{III}(CN)_6]$,[8c] and $[PPN]_2[Mn^{IV}(CN)_6]$[4] are 1.95 (1.16), 2.00 (1.14), 1.98 (1.15), and 1.97 (1.15) Å, respectively. The tetrahedral $K_2[Zn^{II}(CN)_4]$ complex has Zn – CN (and CN) bond lengths of 2.024 (1.157) Å.[9] This suggests that the CN^- ion is predominantly a σ-donor with essentially no π-backbonding, consistent with the IR and Raman data. The absence of Mn – CN multiple bond character makes $[Mn^{II}(CN)_4]^{2-}$ a good candidate to estimate the covalent radius of Mn^{II} in a similar manner used to estimate the covalent radii of $[M^0(dien)(CO)_3]$ (M = Mn, Cr).[10] Taking the average Mn – CN bond length of 2.16 Å and subtracting the radius of carbon (0.77 Å[11]) gives a value of 1.39 Å, the same as reported for $[Mn^0(dien)(CO)_3]$. This is reasonable, since the Mn^{II} – CN distance is 0.14 Å longer than the Zn^{II} – CN distance, which is consistent with the estimated difference (0.19 Å) in covalent radii of Mn^{II} and Zn^{II}.[11]

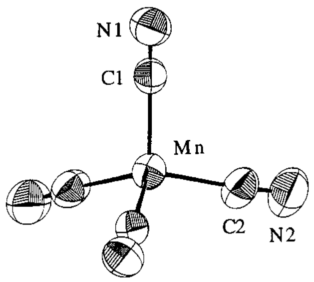

Figure 1. ORTEP drawing depicting $[Mn^{II}(CN)_4]^{2-}$ atom labeling and bond lengths; atoms shown as 30% probability ellipsoids. Selected bond lengths [Å] and angles [°]: Mn – C1 2.151 (6), Mn – C2 2.164 (5), C1 – N1 1.139 (6), C2 – N2 1.126 (5); C1-Mn-C2 104.1 (2), Mn-C1-N1 174.6 (5), Mn-C2-N2 179.5 (4).

The electronic structure can be determined from the magnetic properties. The strong-field character of the cyanide ligand, as observed for all other percyano-transition metal complexes, suggests the low-spin $^2T_2$ ground state ($S = 1/2$); however, the significantly smaller crystal-field splitting associated with T_d complexes than with O_h complexes suggests the high-spin $^6A_1$ ground state ($S = 5/2$). The high-spin $^6A_1$ ground state is confirmed by magnetic measurements with the observed moment of 5.99 μ_B in excellent agreement with the predicted spin-only value of 5.92 μ_B.

The $\tilde{\nu}_{CN}$ vibrational spectra of $[Mn^{II}(CN)_4]^{2-}$ has intense absorptions at 2202 cm^{-1} (MeCN, IR) and 2209 cm^{-1} (solid; Raman). These bands are assigned to the IR-allowed $\tilde{\nu}_5$ (F_{1u}) and Raman-allowed $\tilde{\nu}_1$ (A_{1g}) and $\tilde{\nu}_5$ (F_{2g}) modes,[12] respectively, by comparison with the assignments made for $K_2[Zn^{II}(CN)_4]$.[13] This assignment represents a pure metal-bound CN absorption without a contribution from d – π* back-bonding. Weak absorptions at approximately 298, 266, and 241 cm^{-1} are observed and assumed to be related to the $\tilde{\nu}_{MC}$ and $\tilde{\nu}_{MCN}$ (A_{1g}, E_g, and F_{2g}) modes, but assignments cannot be made without more information. These are about 50 cm^{-1} lower in energy than the three observed bands of $K_2[Zn^{II}(CN)_4]$ at 348 ($\tilde{\nu}_6$), 340 ($\tilde{\nu}_2$), 216 cm^{-1} ($\tilde{\nu}_3$).[12]

The room-temperature EPR spectrum of $[Mn^{II}(CN)_4]^{2-}$ in solution is typical of high-spin Mn^{II}.[14] At concentrations less than or equal to 1 mM the expected six-line hyperfine structure for ^{55}Mn ($I = 5/2$) is isotropic in solution and centered at $g = 2.003(1)$ with an average hyperfine coupling constant $|A| = 71 \pm 1$ G (Figure 2a).[15a] Because of the observation of isolated sites, the spectrum in frozen solution at 78 K changes to a rhombic lineshape, and there is a slight increase in the g value to 2.012(1).[15b] The temperature dependence of the lineshape has been reported previously for $Mn^{II}(ClO_4)_2$ in methanol upon cooling.[14e]

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[*] Prof. J. S. Miller, W. E. Buschmann, A. M. Arif
Department of Chemistry,
University of Utah
315 S. 1400 E. RM Dock, Salt Lake City, UT 84112-0850 (USA)
Fax: (+1) 801-581-8433
E-mail: jsmiller@chemistry.utah.edu

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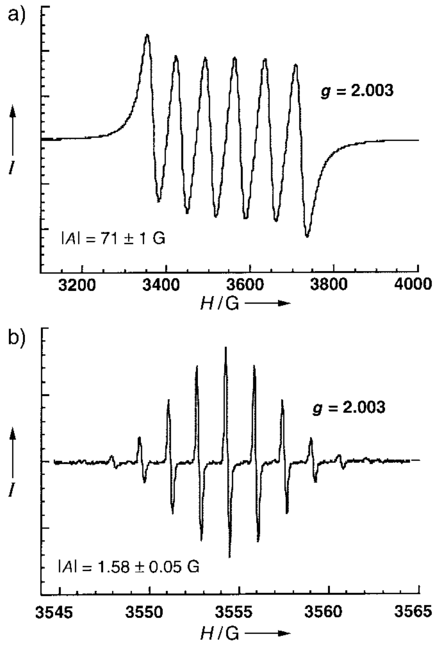

Figure 2. EPR spectrum of $[PPN]_2[Mn^{II}(CN)_4]$ at 300 K, 1.0 mM ($|A| = 71 \pm 1$ G) (a) and 1.5 mM ($|A|$ 1.58 ± 0.05 G) (b) in CH_2Cl_2 and 9.930 GHz; this is attributable to a cyanocarbon radical.

As the concentration is increased above about 1 mM, the six-line resonance pattern loses intensity, whereas a very narrow, sharp eleven-line resonance at $g = 2.003(1)$ with relative integrated peak areas of 0.026:0.063:0.23:0.51:0.83:1.00:0.83:0.51:0.23:0.063:0.026 grows (Figure 2b). The loss of signal intensity suggests some Mn^{II} nearest neighbor interactions leading to an EPR-silent integral spin system. Above 1.5 mM concentration this new resonance remains sharp and increases in intensity, while the original one is broadened into the baseline. The resonance is 16.0 G wide with an average hyperfine coupling constant $|A| = 1.58 \pm 0.05$ G, and the peak-to-peak linewidths are uniform within experimental resolution. An eleven-line pattern is characteristic of unpaired electrons delocalized between two Mn^{II} sites; however, the hyperfine splitting is unreasonably small, and the solution $\tilde{\nu}_{CN}$ shows no detectable changes even at about 10 mM. The hyperfine splitting is consistent with coupling of the unpaired electrons on $^{55}Mn^{II}$ to ^{14}N,[16] but since it lacks Mn^{II} hyperfine structure, the identity of this species is unknown, but most likely is a cyanocarbon radical.

There is a significant amount of intermolecular interactions in solution for $[Mn^{II}(CN)_4]^{2-}$ as shown by the concentration dependence of the EPR spectrum. Line broadening for aqueous Mn^{II} is not observed below 10 mM, presumably because a saturated coordination sphere inhibits intermolecular interactions, while a single broad resonance is still observed at 3.2 M.[14c] Due to the poor coordinating ability of the solvent and the ability of CN^- ions to bind to metal ions at both the C and N, the $[Mn^{II}(CN)_4]^{2-}$ ion likely distorts as it interacts with another $[Mn^{II}(CN)_4]^{2-}$ ion. This distortion could cause the CNs to twist away resulting in nonlinear MnCN bonds, which facilitate the observance of nitrogen hyperfine coupling.

The optical spectrum of $[Mn^{II}(CN)_4]^{2-}$ is atypical for a Mn^{II} ion[17] and does not obey Beer's law as its UV/Vis spectrum changes significantly with concentration, precluding assignment of the parity and spin forbidden d–d transitions. This behavior is consistent with the intermolecular interactions in solution noted from the EPR spectra.

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[6] A dry, deoxygenated solution of $[(Ph_3P)_2N]_2[Mn(CN)_6]$ (1.546 g, 0.847 mmol) in a 1:1 mixture of MeCN and CH_2Cl_2 (10 mL) was exposed to ambient sunlight until the color had changed from yellow to dark red. The solution was then layered with Et_2O to crystallize out burgundy-red prisms of $[(Ph_3P)_2N]_2[Mn(CN)_4]$ (314 mg; 30% yield). IR (Nujol): $\tilde{\nu}_{CN} = 2205 \pm 1$ cm^{-1}; Raman: $\tilde{\nu}_{CN} = 2209 \pm 1$ cm^{-1}; decomp. at 206°C. Elemental analysis calcd for $C_{76}H_{60}MnN_6P_4$: C 73.84, H 4.82, N 6.80; found: C 73.62, H 4.97, N 6.75. Thermolysis of $[(Ph_3P)_2N]_2[Mn(CN)_6]$ also led to $[(Ph_3P)_2N]_2[Mn(CN)_4]$. $(Et_4N)_2[Mn^{II}(CN)_4]$, which exhibits virtually identical spectroscopic properties, has also been prepared.

[7] Crystal data for $C_{76}H_{60}MnN_6P_4$, $M_r = 1236.20$, monoclinic, space group *C2/c*, $a = 23.001(6)$, $b = 12.810(3)$, $c = 23.820(8)$ Å, $\beta = 111.59(2)°$, $V = 6525.94$ Å^3, $Z = 4$, $\rho_{calcd} = 1.258$ g cm^{-3}, $\lambda = 0.71073$ Å, crystal size 0.48 × 0.47 × 0.38 mm, $T = 20$°C, $2\theta_{max} = 50°$, R_w (on *F*) [*R* (on *F*)] = 0.0500 [0.0425], for 3011 unique reflections with $I > 3\sigma(I)$. Data were collected on a CAD4 diffractometer, and the crystal structure solved with MOLEN software distributed by Enraf Nonius. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-179178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] A high-emission background of the $[PPN]_2[Mn^{II}(CN)_4]$ makes it difficult to obtain well-resolved Raman spectra of low-intensity absorptions even with a 764.925 nm (Ti sapphire) excitation line.

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[15] a) This resonance is about 384 G wide, and the peak-to-peak linewidths vary from 69 through 70, 71, and 72 to 73 ± 1 G from low to high field. b) This resonance is about 414 G wide with an average hyperfine coupling constant $|A| = 71 \pm 1$ G. The peak-to-peak linewidths are 56, 68, 73, 78, 80 ± 1 G from low to high field.

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$Mn^{II}[Mn^{II}(CN)_4]$—A Magnetic Interpenetrating Three-Dimensional Diamondlike Solid**

Jamie L. Manson, Wayne E. Buschmann, and Joel S. Miller*

The preparation of the first paramagnetic tetrahedral tetracyanometalate[1] enables the construction new magnetic 3-D network solids, as $[Mn^{II}(CN)_4]^{2-}$ is a building block for the preparation of four-coordinate extended network structures akin to the interpenetrating diamondlike $Zn(CN)_2$.[2] Information on the magnetic properties of this new class of materials will enable a direct comparison to the six-coordinate Prussian Blue family of ordered magnets.[3]

The reaction of equimolar amounts of $[PPN]_2[Mn^{II}(CN)_4]$ (PPN = $[Ph_3P{=}N{=}PPh_3]^+$) and $[Mn^{II}(NCMe)_6]\{B[3,5\text{-}C_6H_3(CF_3)_2]_4\}$ leads to the immediate precipitation of a solid of composition $Mn(CN)_2$, formulated as $Mn^{II}[Mn^{II}(CN)_4]$. This red solid exhibits an $\tilde{\nu}_{CN}$ absorption at 2170 cm^{-1}, shifted relative to the corresponding band of $[Mn^{II}(CN)_4]^{2-}$ by 32 cm^{-1} to lower energy, which suggests the lengthening of the CN bond upon coordination of its N atom to high-spin Mn^{II}. Based on the 2θ values and relative intensities, the powder pattern is assigned to the cubic $P\bar{4}3m$ space group with $a = 6.1229(5)$ Å (Figure 1).[4] This is consistent with an interpenetrating diamondlike (sphalerite) lattice (Figure 2), based on tetrahedral Mn^{II} sites with an $Mn^{II}\cdots Mn^{II}$ separation of 5.303 Å, which is 0.20 Å longer than the intermetallic distance found for $Zn(CN)_2$ and 0.23 Å longer than that in $K_2Mn^{II}[Mn^{II}(CN)_6]$.[7] Solvent is not evident from either IR or thermal gravimetric analyses. The interpenetrating structure would lead to a density twice the value of 0.775 g cm^{-3} (i.e., 1.550 g cm^{-3}) calculated for a noninterpenetrating structure; indeed, 1.68 g cm^{-3} is observed for a small sample.[8] Due to the inherent lability and coordinative unsaturation of the 13 e$^-$ $[Mn(CN)_4]^{2-}$ building block in polar organic solvents, the CN ligand can dissociate or bind to other $[Mn(CN)_4]^{2-}$ ions permitting the competitive formation of by-products such as octahedral complexes. Consequently, some variability in the energy of the $\tilde{\nu}_{CN}$ band and in the magnetic properties is observed.

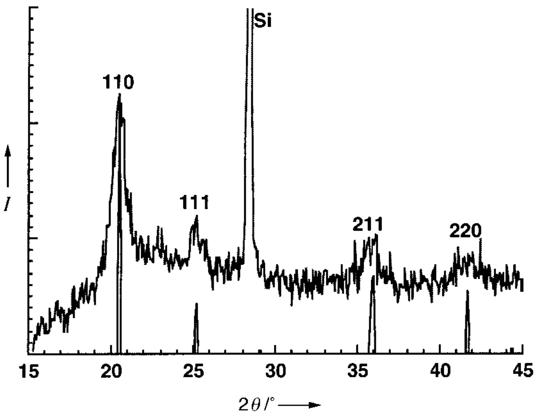

Figure 1. Observed (top) and calculated (lower) powder X-ray diffraction pattern for $Mn^{II}[Mn^{II}(CN)_4]$. The calculated pattern is for the $P\bar{4}3m$ space group with $a = 6.1229$ (5) Å. Silicon was used as an internal standard. I = intensity.

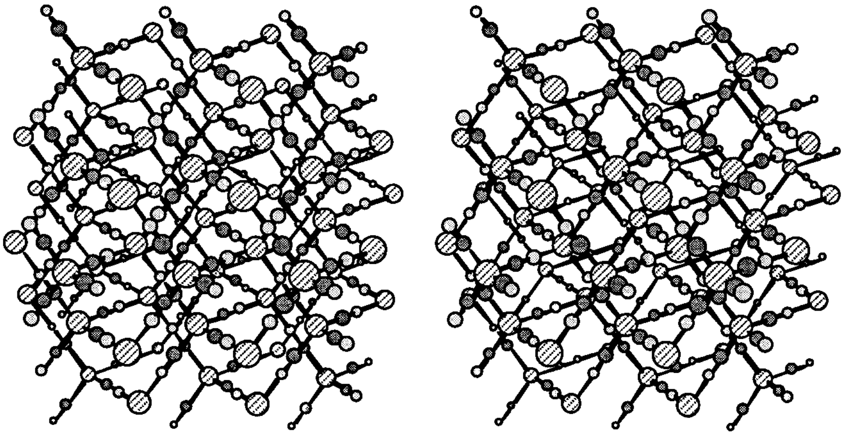

Figure 2. Stereoview of the proposed double-density interpenetrating diamondlike lattice for $Mn^{II}[Mn^{II}(CN)_4]$. The structure resembles that of sphalerite.

The room-temperature magnetic moment μ is 4.4μ_B, a value substantially lower than the predicted value (5.92μ_B) for uncoupled Mn^{II} ions with $S = 5/2$, but consistent with strong antiferromagnetic coupling. As depicted in Figure 3 the magnetic susceptibility χ gradually increases with decreasing temperature reaching a broad maximum, and then decreases rapidly upon further cooling to 2 K. The broad maximum is consistent with antiferromagnetic ordering, while the upturn at low temperature is assigned to impurities with $S = 5/2$. Mn^{II}

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[*] Prof. J. S. Miller, J. L. Manson, W. E. Buschmann
Department of Chemistry,
University of Utah
315 S. 1400 E. RM Dock
Salt Lake City, UT 84112-0850 (USA)
Fax: (+)801-581-8433
E-mail: jsmiller@chemistry.utah.edu

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