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The Mixed-Valent (μ-Nitrido)dimanganese Complex Anion $[(CN)_5Mn^{V}(\mu\text{-}N)Mn^{II}(CN)_5]^{6-}$**

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The synthesis and reactivity of complexes of the first-row transition metals with terminal and bridging nitrido ligands is a rapidly expanding area of research. Complexes with terminal nitrido ligands are known for V, Cr, and Mn,[1] whereas nitride-bridged complexes have been described for V, Cr, and Fe but not for Mn.[2] Interest in these systems derives from their unique molecular structures with very short covalent M–N bonds (1.50–1.60 Å), their electronic structures with strong axial ligand fields from the bound nitride, and from the ability of these systems to engage in N-atom transfer reactions. To date such reactions have been most thoroughly investigated for nitridomanganese(v) complexes containing tetrapyrrole or Schiff-base auxiliary ligands, where transfer of the nitrogen atom to olefins has been demonstrated.[3] N-transfer reactions between two metal ions, for example, from nitrido(porphyrinato)manganese(v) to porphyrinatochromium(III) has been demonstrated by Bottomley and Neely.[4] The homometallic N-transfer reaction from a nitridomanganese(v) complex to a different manganese(III) species has also been observed.[5] Thus, it is remarkable that no nitrido-bridged manganese complexes have been described to date. Here we report the synthesis and characterization of the (μ-nitrido)dimanganese complex $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$.

Treatment of solutions containing $[Mn^{V}(N)(salen)]$[3b] (H_2salen = bis(salicylidene)ethylenediamine) and KCN with reductants such as hydrazine or methanol produced intensely colored red-purple solutions from which the salt $K_5H[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 2H_2O$ (**1**) was isolated in low yield. The same compound was obtained in high yield from the reaction of an Mn^{II} salt with an aqueous KCN solution of $[NMe_4]_2Na[Mn^{V}(N)(CN)_5]\cdot H_2O$.[1b] The stability of aqueous solutions of **1** depends strongly on the cyanide concentration. With no added cyanide, the complex decomposes in seconds, whereas it is stable for more than 30 min in 1M NaCN. From such solutions the mixed sodium–rubidium salt $Na_2Rb_4[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 6H_2O$ (**2**) and $[Rh(tn)_3]_2[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 10H_2O$ (**3**) (tn = propane-1,3-diamine) were isolated by addition of RbCl or $[Rh(tn)_3]Cl_3$.

The structure of the anion in **2** is shown in Figure 1.[6] It consists of an eclipsed $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$ ion,[7] which possesses crystallographic 2/*m* symmetry; the center of the complex resides on an inversion center. Inspection of the thermal parameters of the atoms C(10) and N(1) (Figure 1a) reveals that these atoms are severely disordered. This disorder was successfully modeled by using a split-atom model for these atoms with isotropic thermal parameters (Figure 1b). The refinement converged smoothly to give two equally populated sites for each of these atoms. Thus, the anion in **2** is asymmetric with a short Mn≡N bond (1.58(1) Å) and a long Mn–N bond (1.84(1) Å). The shorter Mn≡N bond is only 0.05–0.08 Å longer than the Mn≡N bond in monomeric nitridocyanomanganates(v).[1b] The Mn–C bond *trans* to the short Mn≡N bond is then considered to be the long one (2.19(2) Å) due to a *trans* influence and the short Mn–C bond (1.95(2) Å) is *trans* to the longer Mn–N bond. Interestingly, the four equatorial Mn–C distances in $[Mn^{II}(CN)_6]^{4-}$ *and* $[Mn^{V}(N)(CN)_5]^{3-}$ (1.95(1) Å and 1.985(8)–2.001(8) Å,[8] respectively) are nearly equidistant despite the fact that these Mn ions differ in formal oxidation states by three.[9] In **2** the equatorial average Mn–C distance is 2.005(4) Å. This interpretation of the structure of **2** renders the anion $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$ a mixed-valent Mn^{V}–Mn^{II} species which is statistically disordered over two sites in the crystal.

The effective magnetic moment of solid **3** increases from 1.72 μ_B at 4 K to 2.03 μ_B at 300 K. The salts **1** and **2** also have magnetic moments in this range, but they are less temper-

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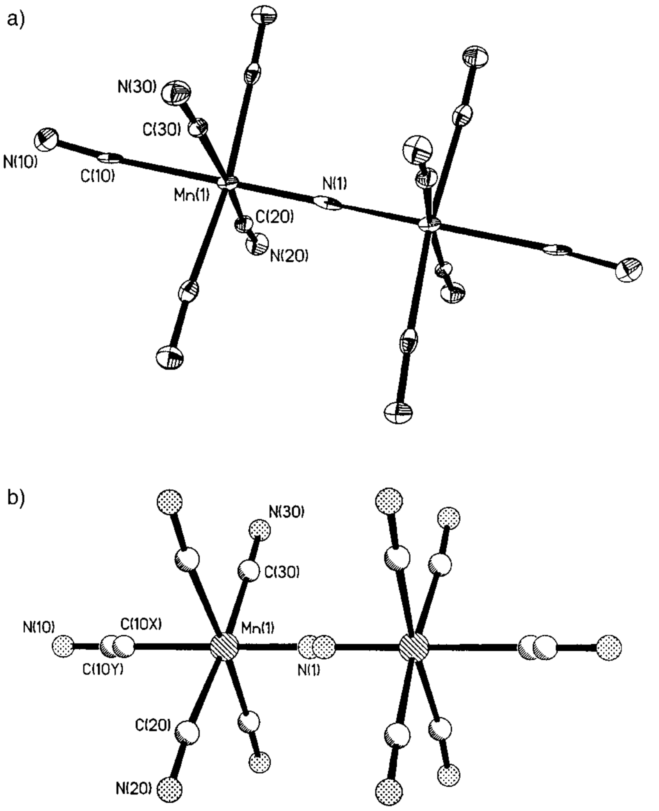

Figure 1. a) Structure of the anion in crystals of **2** (ellipsoids at the 60% probability level). Selected bond lengths [Å] and angles [°]: Mn(1)–N(1) 1.709(1), Mn(1)–C(10) 2.070(5), Mn(1)–C(20) 2.002(4), Mn(1)–C(30) 2.008(4); N(1)-Mn(1)-C(10) 179.97(9), N(1)-Mn(1)-C(20) 91.96(10), N(1)-Mn(1)-C(30) 94.07(9). b) The split-atom model described in the text.

ature-dependent. The μ_{eff} value corresponds to one unpaired electron per manganese dimer and can then be rationalized either as an antiferromagnetically coupled Mn^{III}–Mn^{IV} system or as a low-spin Mn^{II}–low-spin Mn^{V} system. In the latter formulation low-spin Mn^{V} refers to the spin-paired configuration $(d_{xy})^2$ found for all monomeric nitridomanganese(v) complexes including $[\text{Mn(N)(CN)}_5]^{3-}$.[1b]

The EPR spectra of powdered samples of **1** and **2** at 10 K show a broad axial signal with $g_{\parallel} \cong 1.96$ and $g_{\perp} \cong 2.18$ without discernible hyperfine coupling. However, a frozen solution (1M aqueous NaCN) of either compound shows an axial spectrum with a distinct ^{55}Mn hyperfine splitting of the $g_{\parallel}$ signal with coupling to *one* manganese nucleus (Figure 2). Importantly, the solid-state EPR spectrum of the magnetically more dilute salt, **3**, is almost indistinguishable from the spectrum obtained from the frozen solution of **1** or **2**. Taken in combination with the magnetism of **3**, this strongly supports that the frozen solution EPR spectrum stems from the dinuclear anion. We have also quantified the EPR signal, and could show that the signal intensity is >60% of the expected value and is thus not attributable to an impurity. The frozen solution EPR spectrum of **2** was satisfactorily fitted for an $S_t = 1/2$ system where an electron spin of 1/2 is coupled to one nuclear spin of 5/2 (see Figure 2). Thus, the EPR signal cannot originate from an antiferromagnetically coupled Mn^{III}–Mn^{IV} system. For such a system with $S_t = 1/2$, the coupling coefficients require that hyperfine coupling to both manganese centers will be observed as is experimentally borne out by numerous 11–16-line spectra observed for such dimers.[10] The axial EPR spectrum of $[\text{Mn}_2(\mu\text{-N})(\text{CN})_{10}]^{6-}$ with $g_{\parallel}$ split by ^{55}Mn-hyperfine interaction resembles that of *trans*-$[\text{Mn(pc)(NEt}_3)_2]$ (H_2pc = phthalocyanine) a low-spin manganese(II) complex.[11]

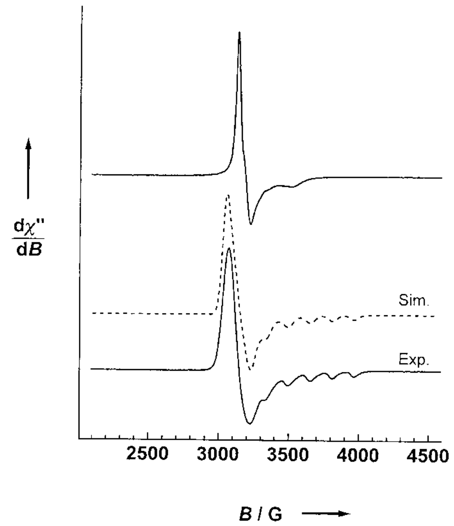

Figure 2. EPR spectra ($T = 10$ K, $\tilde{\nu} = 9.64396$ GHz) of a solid powder sample of **2** (top) and a frozen aqueous solution of **2** (bottom). The simulation of the frozen-solution spectrum (dotted) employed the following parameters: $g_{\parallel} = 1.924$, $g_{\perp} = 2.181$, $A_{\parallel} = 141 \times 10^{-4}\,\text{cm}^{-1}$, $A_{\perp} = 20(5) \times 10^{-4}\,\text{cm}^{-1}$, and Gaussian derivative lineshapes ($W = 36$ G).

The UV/Vis spectrum of $[\text{Mn}_2(\mu\text{-N})(\text{CN})_{10}]^{6-}$ in aqueous cyanide solution (Figure 3) is distinctly different from those of known cyanomanganate complexes; it is dominated by a very intense band at 345 nm ($\varepsilon = 2.25 \times 10^4\,\text{M}^{-1}\text{cm}^{-1}$), and it has an additional less intense band at 543 nm. The band at 345 nm is more intense by an order of magnitude than the CT band at similar energy found in $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5]^{3-}$ and it is also much more intense than any CT band found above 250 nm in the $[\text{Mn(CN)}_6]^{4-}/[\text{Mn(CN)}_6]^{3-}$ complexes. Therefore, we tentatively assign this band as an intervalence band. The 543 nm absorption is located at an energy similar to that of the $^1\text{A}_1(d_{xy})^2 \rightarrow {}^1\text{E}(d_{xy})^1(d_{zx},d_{yz})^1$ transition in $[\text{Mn}^{\text{V}}(\text{N})(\text{CN})_5]^{3-}$ (516 nm). Accordingly, we assign the 543 nm band to a

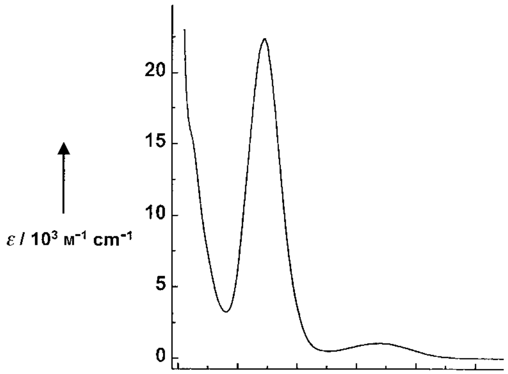

Figure 3. UV/Vis spectrum of an aqueous solution (1M NaCN) of **2**.

manganese(v)-centered d–d transition; it "borrows" intensity from the 345 nm band (neither $[\mathrm{Mn(CN)_6}]^{4-}$ nor $[\mathrm{Mn(CN)_6}]^{3-}$ have absorptions above 360 nm).

In the IR spectra of the salts **1**, **2**, and **3** the ν_{as}(Mn-N-Mn) valence stretch is observed in the range 935–976 cm^{-1}. This band, although not as sharp and intense as $\nu(\mathrm{Mn{\equiv}N})$ in Mn complexes with terminal nitrido groups, is more pronounced than the asymmetric bridge stretching frequency at 880 cm^{-1} in the genuinely symmetric oxo-bridged dimer $[\mathrm{Mn_2^{III}}(\mu\text{-O})(\mathrm{CN})_{10}]^{6-}$.[12] It is noteworthy that ν_{as}(Mn-N-Mn) band in **1**, **2**, and **3** falls only slightly below the range, 983–1043 cm^{-1}, found for $\nu(\mathrm{Mn{\equiv}N})$ in octahedral mononuclear nitridomanganese(v) complexes.[1]

In conclusion, the X-ray structure, and especially the EPR spectrum in conjunction with the magnetic data strongly suggest that $[\mathrm{Mn_2}(\mu\text{-N})(\mathrm{CN})_{10}]^{6-}$ is a Class II (Robin and Day) valence-localized $\mathrm{Mn^V}$–$\mathrm{Mn^{II}}$ system. Although examples of such large difference in oxidation states in mixed-valent homodimetallic complexes are well established when the coordination environment at the two metal sites is very asymmetric, this is to our knowledge unprecedented in systems where a single atom bridge induces the asymmetry. One related, but less extreme example is known in $[\mathrm{V^VCl_2(L)}(\mu\text{-N})\mathrm{V^{III}Cl_3(L)}]$ (L = tetramethylethylenediamine) where the coordination numbers at the two vanadium centers differ.[13]

Experimental Section

1: Method 1: To an Ar-degassed suspension of [Mn(N)(salen)] (1.3 g, 3.9 mmol) in H_2O/MeOH/DMF (1/1/1; 40 mL) an excess of KCN (3.4 g, 52 mmol) and $N_2H_4\cdot H_2O$ (0.8 g, 16 mmol) were added. The suspension was refluxed until no more solid [Mn(N)(salen)] was visible and cooled. A brown-purple crystalline precipitate was collected by filtration and washed with H_2O/MeOH (1/1) (3 ×). The product was air-stable. Yield: 0.31 g (26 %); IR (KBr) [cm^{-1}]: $\tilde{\nu}$ = 2098 (s), 2083 (s), (ν(CN)), 936 (m, br) (ν_{as}(Mn-N-Mn)); UV/Vis: (1.0 M NaCN/H_2O): λ_{max} [nm] (ε [M^{-1}cm^{-1}] = 543 (1.16×10^3), 345 (2.45×10^4), 223 sh (1.72×10^4); $\mu_{eff} = 1.65\,\mu_B$ (10 K)–$1.88\,\mu_B$ (300 K); elemental analysis (%) calcd for $C_{10}H_5K_5Mn_2N_{11}O_2$: C 19.48, H 0.82, K 31.78, Mn 17.82, N 24.99; found: C 19.29, H 0.77, K 30.08, Mn 17.72, N 24.81.

Method 2: To an Ar-degassed solution of $(NMe_4)_2Na[Mn(N)(CN)_5]\cdot H_2O$ (390 mg, 1.00 mmol) in 1 M aqueous KCN (15 mL), a solution of $Mn(CH_3COO)_2\cdot 4H_2O$ (245 mg, 1.00 mmol) in degassed water (3 mL) was added. Immediately the color changed from pink to dark red-purple. After the mixture was stirred for 10 min, solid KCN (2.5 g, 38 mmol) was added batchwise. The product was isolated as above. Yield: 0.51 g (83 %).

2: To a solution of **1** (150 mg, 0.244 mmol) in 0.5 M aqueous NaCN (3.5 mL) solid RbCl (0.5 g, 4.1 mmol) was added. Small intergrown purple rhombohedra of **2** were collected after 2 h. Yield: 116 mg (54 %); IR (KBr) [cm^{-1}]: $\tilde{\nu}$ = 2108 (s), 2084 (s) (ν(CN)), 1623 (s) ($\delta(H_2O)$), 940 (m, br.) (ν_{as}(Mn-N-Mn)); $\mu_{eff} = 1.81\,\mu_B$ (4.2 K)–$2.02\,\mu_B$ (300 K); elemental analysis (%) calcd for $C_{10}H_{12}Mn_2N_{10}Na_2O_6Rb_4$: C 13.65, H 1.37, Mn 12.41, N 17.51; found: C 13.68, H 1.48, Mn 12.00, N 17.69.

3: To a solution of **1** (120 mg, 0.195 mmol) in 0.5 M aqueous NaCN (20 mL) a solution of $[Rh(tn)_3]Cl_3$ (100 mg, 0.232 mmol) in H_2O (10 mL) was added very slowly. Flat purple needles were isolated. Yield: 125 mg (89 %). IR (KBr) [cm^{-1}]: $\tilde{\nu}$2118 (s), 2100 (s), 2083 (s) (ν(CN)), 976 (m) (ν_{as}(Mn-N-Mn)); $\mu_{eff} = 1.72\,\mu_B$ (4.2 K)–$2.03\,\mu_B$ (300 K); elemental analysis (%) calcd for $C_{28}H_{80}Mn_2N_{23}O_{10}Rh_2$: C 27.68, H 6.64, Mn 9.04, N 26.52; found: C 27.92, H 6.58, Mn 8.18, N 26.39.

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[6] Crystal data for **2** ($C_{10}H_{12}Mn_2N_{11}Na_2O_6Rb_4$): orthorhombic, *CmCa*, $a = 17.102(2)$, $b = 16.662(2)$, $c = 9.0070(8)$ Å, $V = 2566.6(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.278$ g cm^{-3}; crystal size: 0.35 × 0.24 × 0.06 mm. Of 6411 reflections with $2.38^\circ < \theta < 23.31^\circ$, 966 were independent, and 955 observed ($I > 2\sigma(I)$); 102 parameters; $R(F) = 0.0263$, $wR(F^2) = 0.0614$. The data were collected on a Siemens SMART CCD detector system with $Mo_{K\alpha}$ irradiation ($\lambda = 0.71073$ Å) at 100(2) K. Absorption correction was performed with the SADABS program (G. M. Sheldrick, Universität Göttingen, **1994**). The structure was solved by direct methods and refined by full-matrix least-squares methods against F^2 (SHELXTL program packet:, version 5.1). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410749.

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