Isolation and structural determination of octacyanobutanediide, $[C_4(CN)_8]^{2-}$; precursors to $M(TCNE)_x$ magnets‡

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The reaction of $MI_2 \cdot xMe_3CN$ (M = Mn, Fe) and TCNE (tetracyanoethylene) leads to unprecedented $[C_4(CN)_8]^{2-}$ μ_4-metal complexes which have been crystallographically characterized and are precursors to $M(TCNE)_x \cdot yS$ magnets.

The study of cyanocarbons has led to the discovery of both molecule-based conductors[1] and magnets[2] as well as several new classes of compounds based upon reduction of the nitrile triple bond.[3,4] While generalizing the room-temperature molecule-based magnet $V(TCNE)_x \cdot yCH_2Cl_2$[5] to magnetic systems based upon other metals, we discovered several new magnets in this class: $M(TCNE)_2 \cdot xS$ (M = Mn, Fe, Co, Ni; S = MeCN, CH_2Cl_2).[6] In contrast to the V magnet, the Fe and Mn magnets exhibit X-ray powder diffraction. Therefore, we attempted to grow single crystals of these magnets *via* slow diffusion of $MI_2 \cdot xMeCN$ (M = Mn, Fe) and TCNE in a H-tube using either MeCN–CH_2Cl_2 (M = Mn) or pure MeCN (M = Fe). Crystals of new compounds (light yellow for M = Mn; dark brown for M = Fe) were isolated with ν_{CN} IR absorptions at 2304m, 2275m, 2212s, 2205s, 2153s, and 2096m (sh) cm^{-1} for M = Mn and 2307m, 2280m, 2213s, 2154s, and 2108w cm^{-1} for M = Fe. These ν_{CN} absorptions are similar to, but distinguishable from, those observed for the $M(TCNE)_2 \cdot xCH_2Cl_2$.[6] magnets. The absorptions above 2230 cm^{-1} are assigned to coordinated MeCN, while the latter are assigned to reduced nitriles and were initially thought to be associated with a metal-bound reduced form of TCNE.

Single crystal X-ray diffraction studies‡ of $Mn[C_4(CN)_8](NCMe)_2 \cdot CH_2Cl_2$ **1** and $Fe[C_4(CN)_8](NCMe)_2 \cdot MeCN$ **2** each revealed the unprecedented octacyanobutane-diide dianion, $[C_4(CN)_8]^{2-}$ **3**. This dianion is bound to four

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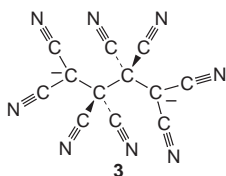
octahedral M^{II} centres (M = Mn, Fe) in a plane with the MeCN molecules filling the axial coordination sites, and the non-coordinated CH_2Cl_2 (**1**) and MeCN (**2**) lying in diamond-shaped holes in the structure, Figs. 1 and 2. Adjacent planes are eclipsed. The interlayer M···M separaions are 7.626(2) and 9.356(4) Å, respectively, for **1**, and, **2**, while the intralayer M···M separations are 7.581(2) and 9.344(2) Å for **1**, 7.562(4) and 9.368(4) for **2**.

Compound **3** is disordered about the midpoint of the C(5)–C(5′) bond for M = Mn and ordered for M = Fe. The chemically equivalent M–N, C≡N, NC–C and $(MNC)_2C–C$ distances average 2.218(4), 1.151(6), 1.389(7) and 1.615(10) Å, respectively, for Me = Mn, and average 2.221(7), 1.151(10),

1.398(11) and 1.508(9) Å, respectively, for M = Fe. The central C–C bond is 1.59(2) (M = Mn) and 1.627(14) Å (M = Fe). The terminal C_4-backbone carbon atoms are sp^2 hybridized as indicated by the average angle of 119.0° (M = Mn) and 119.8° (M = Fe) while the central carbon atoms are sp^3 hybridized [average angles are 109.5° (M = Mn) and 109.4° (M = Fe)].

This is the first example of a σ-dimer of [TCNE]$^{\cdot-}$, however, several examples of a structurally related σ-dimer of [TCNQ]$^{\cdot-}$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) have been reported.[7] The backbone C–C bonds are significantly longer[8] than the conventionally accepted value of 1.54 Å for an sp^3–sp^3 C–C bond length and are comparable to the central C–C bond for the σ-dimers of [TCNQ]$^{\cdot-}$ (1.630–1.659 Å).

For **1** thermogravimetric analysis–mass spectrometry (TGA–MS) reveals a one-step mass loss between 100 and 120 °C, during which both MeCN and CH_2Cl_2 are simultaneously observed in the effluent gas. The 34.3% mass loss is in good agreement with the formula $Mn[C_4(CN)_8](NCME)_2 \cdot CH_2Cl_2$ (34.9%). At *ca.* 250 °C a second mass loss occurs which is accompanied by the generation of C_2N_2 and HCN. An exothermic event is also observed in the DSC data at this temperature. This mass loss is only 4%, corresponding to *ca.* 0.7 CN per Mn. The observation of C_2N_2 and HCN is consistent with the formation of CN$^{\cdot}$ radicals which either combine or
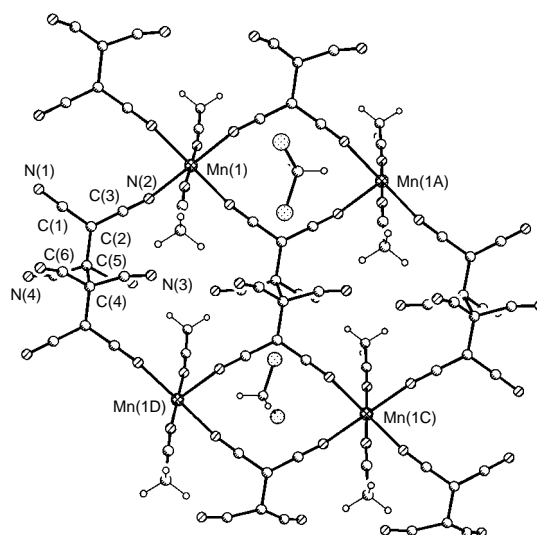
Fig. 1 Structure and labeling diagram of $Mn[C_4(CN)_8](NCMe)_2 \cdot CH_2Cl_2$. Selected bond lengths (Å) and angles (°): Mn(1)–N(2) 2.206(3) Å, N(2)–C(3) 1.154(5), C(3)–C(2) 1.389(7), C(2)–C(1) 1.389(7), C(1)–N(1) 1.148(6), N(1)–Mn(1^a) 2.230(4), C(2)–C(5) 1.615(10), C(5)–C(5^b) 1.59(2); N(2)–Mn(1)–(N1^a) 86.08(13), Mn(1)–N(1^a)–C(1^a) 154.4(4), N(1)–C(1)–C(2) 179.0(5), C(1)–C(2)–C(3) 118.7(4), C(2)–C(3)–N(2) 178.0(5), C(3)–N(2)–Mn(1) 165.7(3), N(1^b)–Mn(1)–N(2) 93.92(13), C(3)–C(2)–C(5) 116.6(4), C(2)–C(5)–C(5^b) 105.2(7), C(5^b):C(2^b)–C(1^b) 121.8(4). ^{a} −x, −y, −z; ^{b} x − 1, y, z.
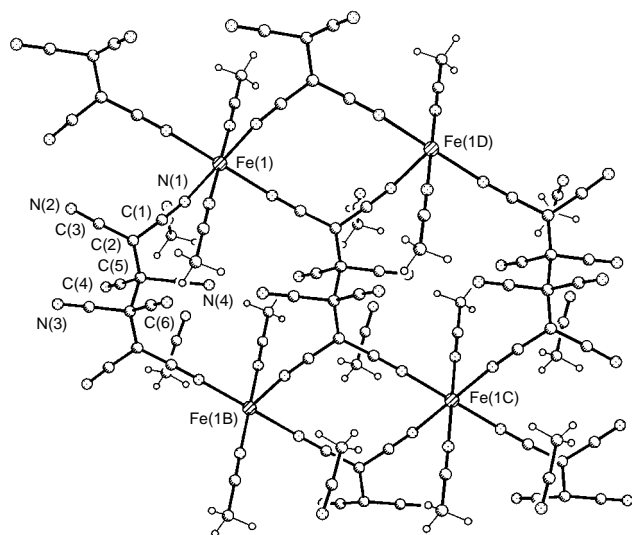
Fig. 2 Structure and labeling diagram of Fe[C₄(CN)₈](NCMe)₂·MeCN. Selected bond lengths (Å) and angles (°): Fe(1)–N(1) 2.218(7), N(1)–C(1) 1.147(10), C(1)–C(2) 1.395(12), C(2)–C(3) 1.401(11), C(3)–N(2) 1.144(9), N(2)–Fe(1ᶜ) 2.224(6), C(2)–C(5) 1.508(9), C(2ᵇ)–C(5ᵇ) 1.508(9), C(5ᵇ)–C(5ᵇ)–C(5ᵃ) 1.627(14); N(1)–Fe(1)–N(2ᵈ) 86.4(2), C(1ᵈ)–N(1ᵈ)–Fe(1ᶜ) 163.0(6), Fe(1ᶜ)–N(2)–C(3) 165.3(6), N(2)–C(3)–C(2) 177.4(7), C(3)–C(2)–C(1) 118.2(6), N(2ᵃ)–Fe(1)–N(1) 93.6(2), Fe(1)–N(1)–C(1) 163.0(6), N(1)–C(1)–C(2) 177.9(7), C(1)–C(2)–C(5) 120.3(6), C(2ᵇ)–(C5ᵇ)–C(5ᵃ) 113.2(7), C(5ᵃ)–C(2ᵃ)–C(3ᵃ) 120.9(6). ᵃ *x* − 1, *y*, *z*; ᵇ −*x* + 1, −*y* + 1, −*z* + 1; ᶜ *x* + 1, *y*, *z*; ᵈ −*x* + 1, −*y* + 1, −*z* + 2.

abstract hydrogen. Despite the lower volatility of MeCN as compared to CH_2Cl_2, **2** loses solvent very rapidly when removed from the mother-liquor and cannot be isolated with all three MeCN molecules present. A sample with 1.7 MeCN per Fe was obtained after drying *in vacuo* at room temperature. TGA–MS on this material shows that it loses the remaining solvent at 100 °C and formation of C_2N_2 begins at *ca.* 150 °C and peaks at 320 °C. We have observed similar thermal decomposition processes in other compounds containing [TCNE]·⁻ such as [NBu₄][TCNE] and K[TCNE]. Thus, we believed that desolvation leads to cleavage of the long central C–C bond of [C₄(CN)₈]²⁻ to reform [TCNE]·⁻ which subsequently decomposes to form the observed byproducts, HCN and C_2N_2.

Compound **1** is a paramagnet with a room temperature effective moment of 6.7 μ_B and obeys the Curie–Weiss law above 5 K. This is consistent with a diamagnetic [C₄(CN)₈]²⁻ which weakly couples the metal spin sites ($S = 5/2$ Mnᴵᴵ), albeit with a larger than expected room temperature moment. The magnetic properties of **2** are as yet undetermined since it cannot be isolated without loss of solvent.

Upon desolvation of **1** at 100 °C the ν_{CN} absorptions disappear and new ν_{CN} bands characteristic of the Mn(TCNE)₂·xCH₂Cl₂ magnet (2225, 2182, and 2170 cm⁻¹)[6] appear. In addition the room temperature moment increases. The desolvated sample magnetically orders at a T_c of 95 K, in reasonable agreement with the value previously reported (107 K) for Mn(TCNE)₂·xCH₂Cl₂ prepared directly in CH_2Cl_2.[6] **2** behaves in a similar fashion upon desolvation. The desolvated material has ν_{CN} IR absorptions characteristic of the Fe(TC-

NE)₂·xMeCN (x = 1.7) magnet (2280, 2220, 2164 and 2117 cm⁻¹) and orders magnetically at *ca.* 6 K [Fe(TCNE)₂·xMeCN orders at *ca.* 8 K].[6] These observations are consistent with the TGA–MS data and indicate that desolvation leads to formation of $S = 1/2$ [TCNE]·⁻ which can bind to additional metal centers and provide strong spin coupling leading to the observed magnetic ordering. Evidence for this bond breaking has been reported for σ-dimers of [TCNQ]·⁻.[7a]

Notes and References

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‡ Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday.
§ *Crystal data*: Mn[C₄(CN)₈](NCMe)₂·CH₂Cl₂, **1**: C₁₇H₈C₁₂MnN₁₀, triclinic, space group P1̄, *a* = 7.5805(6), *b* = 7.6259(6), *c* = 9.3443(7) Å, α = 89.1436(12), β = 88.8320(20), γ = 87.2979(14)°, *V* = 538.85(7) Å³, *Z* = 1, *T* = 223(2) K, D_c = 1.472 g cm⁻¹, $R(F)$ = 0.0501, $R(wF^2)$ = 0.1512 for 1103 independent observed reflections (3 ≤ 2θ ≤ 58°).
  Fe[C₄(CN)₈](NCMe)₂·MeCN, **2**: C₂₀H₁₂FeN₁₂, monoclinic, space group P2₁/c, *a* = 7.5623(5), *b* = 16.1971(11), *c* = 9.3682(6) Å, β = 90.8167(9)°, *V* = 1147.37(13) Å³, *Z* = 2, *T* = 233(2) K, D_c = 1.379 g cm⁻¹, $R(F)$ = 0.0796, $R(wF^2)$ = 0.2149 for 1324 independent observed reflections (3 ≤ 2θ ≤ 58°). Further details of either crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting depository number CSD-407730 and 407731, respectively. CCDC 182/887.

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