

# Isolation and structural determination of octacyanobutane diide, $[C_4(CN)_8]^{2-}$ ; precursors to $M(TCNE)_x$ magnets $\ddagger$

Jie Zhang,<sup>a</sup> Louise M. Liable-Sands,<sup>b</sup> Arnold L. Rheingold,<sup>\*b</sup> Rico E. Del Sesto,<sup>a</sup> Douglas C. Gordon,<sup>a</sup> Brian M. Burkhart<sup>c</sup> and Joel S. Miller<sup>\*a†</sup>

<sup>a</sup> Department of Chemistry, University of Utah, Salt Lake City, UT 84112-0850, USA

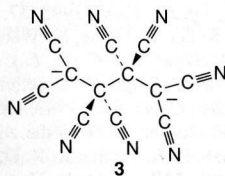
<sup>b</sup> Department of Chemistry, University of Delaware, Newark, DE 19716, USA

<sup>c</sup> Hauptman-Woodward Medical Research Institute, Buffalo, NY 14203, USA

The reaction of  $Ml_2 \cdot xMe_3CN$  ( $M = Mn, Fe$ ) and TCNE (tetracyanoethylene) leads to unprecedented  $[C_4(CN)_8]^{2-}$   $\mu_4$ -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<sup>1</sup> and magnets<sup>2</sup> as well as several new classes of compounds based upon reduction of the nitrile triple bond.<sup>3,4</sup> While generalizing the room-temperature molecule-based magnet  $V(TCNE)_x \cdot yCH_2Cl_2$ <sup>5</sup> to magnetic systems based upon other metals, we discovered several new magnets in this class:  $M(TCNE)_2 \cdot xS$  ( $M = Mn, Fe, Co, Ni$ ;  $S = MeCN, CH_2Cl_2$ ).<sup>6</sup> 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  $Ml_2 \cdot xMe_3CN$  ( $M = Mn, Fe$ ) 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  $\nu_{CN}$  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  $\nu_{CN}$  absorptions are similar to, but distinguishable from, those observed for the  $M(TCNE)_2 \cdot xCH_2Cl_2$ <sup>6</sup> 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 $\ddagger$  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



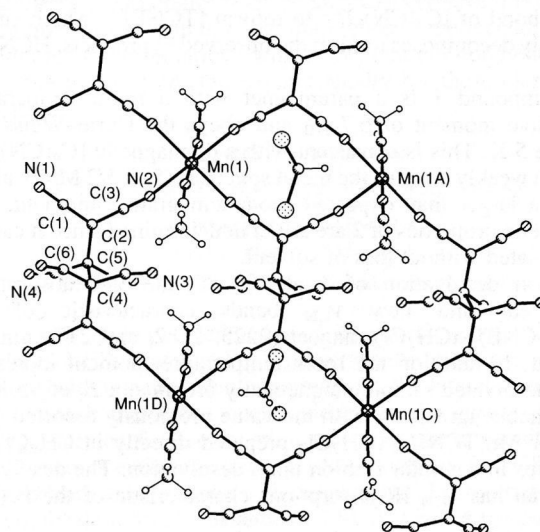
octahedral  $M^{II}$  centres ( $M = Mn, Fe$ ) in a plane with the  $MeCN$  molecules filling the axial coordination sites, and the non-coordinated  $CH_2Cl_2$  (**1**) and  $MeCN$  (**2**) lying in diamond-shaped holes in the structure, Figs. 1 and 2. Adjacent planes are eclipsed. The interlayer  $M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

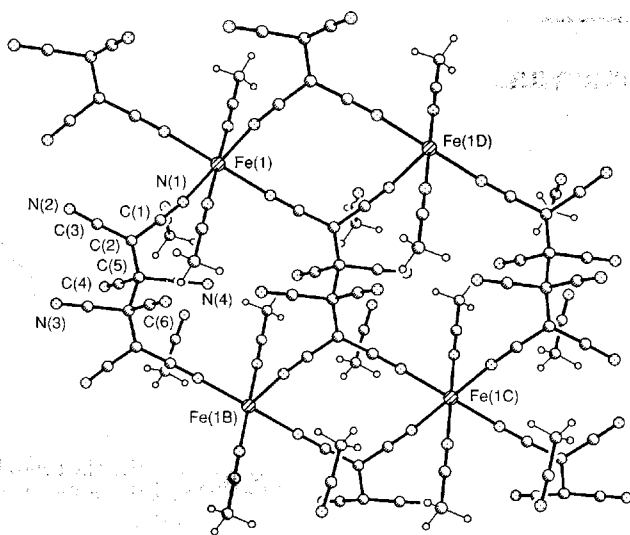
1.398(11) and 1.508(9) Å, respectively, for  $M = Fe$ . The central  $C-C$  bond is 1.59(2) ( $M = Mn$ ) and 1.627(14) Å ( $M = Fe$ ). The terminal  $C_4$ -backbone carbon atoms are  $sp^2$  hybridized as indicated by the average angle of 119.0° ( $M = Mn$ ) and 119.8° ( $M = Fe$ ) while the central 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  $\sigma$ -dimer of  $[TCNE]^-$ , however, several examples of a structurally related  $\sigma$ -dimer of  $[TCNQ]^-$  ( $TCNQ = 7,7,8,8$ -tetracyano-*p*-quinodimethane) have been reported.<sup>7</sup> The backbone  $C-C$  bonds are significantly longer<sup>8</sup> 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  $\sigma$ -dimers of  $[TCNQ]^-$  (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),  $N(2)-C(3)$  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  $\text{Fe}[\text{C}_4(\text{CN})_8](\text{NCMe})_2 \cdot \text{MeCN}$ . Selected bond lengths (Å) and angles ( $^\circ$ ): 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(1 $^c$ ) 2.224(6), C(2)–C(5) 1.508(9), C(2 $^b$ )–C(5 $^b$ ) 1.508(9), C(5 $^b$ )–C(5 $^a$ )–C(5 $^a$ ) 1.627(14); N(1)–Fe(1)–N(2 $^d$ ) 86.4(2), C(1 $^d$ )–N(1 $^d$ )–Fe(1 $^c$ ) 163.0(6), Fe(1 $^c$ )–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(2 $^d$ )–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(2 $^b$ )–C(5 $^b$ )–C(5 $^a$ ) 113.2(7), C(5 $^a$ )–C(2 $^a$ )–C(3 $^a$ ) 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  $\text{CH}_2\text{Cl}_2$ , **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  $^\circ\text{C}$  and formation of  $\text{C}_2\text{N}_2$  begins at *ca.* 150  $^\circ\text{C}$  and peaks at 320  $^\circ\text{C}$ . We have observed similar thermal decomposition processes in other compounds containing  $[\text{TCNE}]^-$  such as  $[\text{NBu}_4][\text{TCNE}]$  and  $\text{K}[\text{TCNE}]$ . Thus, we believed that desolvation leads to cleavage of the long central C–C bond of  $[\text{C}_4(\text{CN})_8]^{2-}$  to reform  $[\text{TCNE}]^-$  which subsequently decomposes to form the observed byproducts, HCN and  $\text{C}_2\text{N}_2$ .

Compound **1** is a paramagnet with a room temperature effective moment of 6.7  $\mu_B$  and obeys the Curie–Weiss law above 5 K. This is consistent with a diamagnetic  $[\text{C}_4(\text{CN})_8]^{2-}$  which weakly couples the metal spin sites ( $S = 5/2 \text{ Mn}^{\text{II}}$ ), 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  $^\circ\text{C}$  the  $\nu_{\text{CN}}$  absorptions disappear and new  $\nu_{\text{CN}}$  bands characteristic of the  $\text{Mn}(\text{TCNE})_2 \cdot x\text{CH}_2\text{Cl}_2$  magnet (2225, 2182, and 2170  $\text{cm}^{-1}$ )<sup>6</sup> 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  $\text{Mn}(\text{TCNE})_2 \cdot x\text{CH}_2\text{Cl}_2$  prepared directly in  $\text{CH}_2\text{Cl}_2$ .<sup>6</sup> **2** behaves in a similar fashion upon desolvation. The desolvated material has  $\nu_{\text{CN}}$  IR absorptions characteristic of the  $\text{Fe}(\text{TCNE})_2 \cdot x\text{MeCN}$  ( $x = 1.7$ ) magnet (2280, 2220, 2164 and 2117  $\text{cm}^{-1}$ ) and orders magnetically at *ca.* 6 K [ $\text{Fe}(\text{TCNE})_2 \cdot x\text{MeCN}$  orders at *ca.* 8 K].<sup>6</sup> These observations are consistent with the TGA–MS data and indicate that desolvation leads to formation of  $S = 1/2 [\text{TCNE}]^-$  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  $\sigma$ -dimers of  $[\text{TCNQ}]^-$ .<sup>7a</sup>

The authors gratefully acknowledge discussions with D. K. Rittenberg and the support of the Department of Energy (Grant Nos. DE-FG03-93ER45504 and DEFG-0296ER12198).

## Notes and References

† E-mail: jsmiller@chemistry.utah.edu

‡ Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday.

§ *Crystal data*:  $\text{Mn}[\text{C}_4(\text{CN})_8](\text{NCMe})_2 \cdot \text{CH}_2\text{Cl}_2$ , **1**:  $\text{C}_{17}\text{H}_8\text{C}_{12}\text{MnN}_{10}$ , triclinic, space group  $P\bar{1}$ ,  $a = 7.5805(6)$ ,  $b = 7.6259(6)$ ,  $c = 9.3443(7)$  Å,  $\alpha = 89.1436(12)$ ,  $\beta = 88.8320(20)$ ,  $\gamma = 87.2979(14)^\circ$ ,  $V = 538.85(7)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 223(2)$  K,  $D_c = 1.472$  g  $\text{cm}^{-3}$ ,  $R(F) = 0.0501$ ,  $R(wF^2) = 0.1512$  for 1103 independent observed reflections ( $3 \leq 2\theta \leq 58^\circ$ ).

$\text{Fe}[\text{C}_4(\text{CN})_8](\text{NCMe})_2 \cdot \text{MeCN}$ , **2**:  $\text{C}_{20}\text{H}_{12}\text{FeN}_{12}$ , monoclinic, space group  $P2_1/c$ ,  $a = 7.5623(5)$ ,  $b = 16.1971(11)$ ,  $c = 9.3682(6)$  Å,  $\beta = 90.8167(9)^\circ$ ,  $V = 1147.37(13)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 233(2)$  K,  $D_c = 1.379$  g  $\text{cm}^{-3}$ ,  $R(F) = 0.0796$ ,  $R(wF^2) = 0.2149$  for 1324 independent observed reflections ( $3 \leq 2\theta \leq 58^\circ$ ). Further details of either crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting depositary number CSD-407730 and 407731, respectively. CCDC 182/887.

- Recent reviews: P. Cassoux and J. S. Miller, *Chemistry of Advanced Materials: A New Discipline*, ed. L. V. Interrante and M. Hampton-Smith, VCH Publishers, New York, 1998, 19; M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.
- Recent reviews: J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385, *Angew. Chem.*, 1994, **106**, 399; *Adv. Chem. Ser.*, 1995, **245**, 161. D. Gatteschi, *Adv. Mater.*, 1994, **6**, 635; O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, 1993.
- O. W. Webster, *Kirk-Othmer Encyclo. Chem. Tech.*, 1993, **7**, 809; R. P. Suprayan and P. G. Rasmussen, *Trend. Polym. Sci.*, 1995, **3**, 165.
- W. E. Buschmann, A. M. Arif and J. S. Miller, *J. Chem. Soc., Chem. Commun.*, 1995, 2343.
- J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein and J. S. Miller, *Science*, 1991, **252**, 1415; J. S. Miller, G. T. Yee, J. M., Manriquez and A. J. Epstein, in *Proceedings of Nobel Symposium #NS-81, Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*, Oxford University Press, 1993, 461; *La Chim.*, 1992, **74**, 845; A. J. Epstein and J. S. Miller, in *Proceedings of Nobel Symposium #NS-81, Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure*, Oxford University Press, 1992, 475; *La Chim.*, 1993, **75**, 185.
- J. Zhang, J. Ensling, V. Ksenofontov, P. Gütllich, A. J. Epstein and J. S. Miller, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 656.
- (a) R. H. Harms, H. J. Keller, D. Nöthe, M. Werner, D. Grundel, H. Sixl, Z. G. Soos and R. M. Metzger, *Mol. Cryst., Liq. Cryst.*, 1981, **65**, 179; S. K. Hoffman, P. J. Corvan, P. Singh, C. N. Sethukleshmi, R. M. Metzger and W. E. Hatfield, *J. Am. Chem. Soc.*, 1983, **105**, 4608; (b) V. Dong, H. Endres, H. J. Keller, W. Moroni and D. Nöthe, *Acta Crystallogr., Sect. B*, 1977, **33**, 2428; H. Zhao, R. A. Heintz, K. R. Dunbar and R. D. Rogers, *J. Am. Chem. Soc.*, 1996, **118**, 12844; B. Morosin, H. J. Plastas, L. B. Coleman and J. M. Stewart, *Acta Crystallogr., Sect. B*, 1978, **34**, 540.
- G. Kaupp and J. Boy, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 48.

Received in Bloomington, IN, USA, 23rd March 1998; 8/022731