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Coordination Complexes with *cis*-TCNE Radical Anion Ligands. Models of M[TCNE]$_2$ Magnets

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The synthesis and characterization of two manganese(II) complexes formally each featuring two *cis*-tetracyanoethylenide radical anionic ligands (TCNE$^{\bullet/-}$) are reported. In each case, tris(pyrazol-1-ylmethyl)amine serves as a capping ligand, blocking three facial coordination sites. Crystal structures show that the two TCNE anions in each molecule exhibit an intramolecular stacking interaction that forms what can be considered a coordinated (TCNE$_2$)$^{2-}$ moiety. These molecules are presumed to be structural models of some of the local bonding in the family of amorphous, ferrimagnetic, M[TCNE]$_2$$\cdot$*y*(solvent) coordination polymer magnets. Magnetic measurements indicate that the (TCNE$_2$)$^{2-}$ bridge is diamagnetic and not a good mediator of magnetic exchange, a result that might explain the observed lower ordering temperatures in some of the polymer magnets.

In 1991, Manriquez and co-workers reported the synthesis of the first room-temperature molecule-based magnet, V[TCNE]$_2$$\cdot$*y*(solvent).[1] The assumed local structure of this compound consists of *cis*-tetracyanoethylenide (TCNE) radical anions bridging vanadium dications in a three-dimensional network. Related compounds, where the vanadium ion has been replaced by other first-row transition-metal cations, have been described as well, with lower ordering temperatures ranging from 121 to 44 K.[2] However, despite the passage of time, the physics that governs the ordering temperature in these coordination polymers is still not well-understood and the highest ordering temperature has not been increased above that of the original compound. One reason for this lack of progress is the paucity of direct structural information due to the amorphous nature of these materials. Except for recently reported XANES/EXAFS data that suggest a six-coordinate octahedral environment about the vanadium 2+ cation,[3] there is only inference based on IR spectroscopy, compounds with two *trans*-TCNE ligands (vide infra), and chemical intuition.

To address this issue, we have sought to construct discrete molecular species such as squares and cubes featuring multiple tetracyanoethylene radical anions (TCNE$^{\bullet/-}$) as edges and spin-bearing transition cations as corners. These should serve as both structural and magnetic model compounds of the coordination polymer magnets. As an additional reason for this work, nanoscopic single-molecule magnets are of current interest and radical-anion-bridged species, such as those we are targeting, represent an alternative approach to cyanide-bridged and oxo/carboxylato-bridged structures.

We report here the synthesis and structural characterization of two six-coordinate manganese(II) complexes with two *cis*-TCNE radical anions whose structures shed light on the possible bonding modes and the mechanism of magnetic coupling in magnetic coordination polymers. In particular, we note the strong propensity for the radicals to dimerize, intramolecularly, to give diamagnetic species that are apparently incapable of mediating significant magnetic communication. These results suggest that the prevailing picture of the local bonding in the M[TCNE]$_2$ magnets based on isolated TCNE radicals might be incomplete.

Although pseudo-one-dimensional coordination polymers containing two *trans*-TCNE$^{\bullet/-}$ ligands are well-known,[4] the analogous cis complexes are unprecedented. Somewhat related, Ballester and co-workers have reported the pseudooctahedral complex [Ni(trien)(TCNQ)$_2$], where trien = 1,4,7,10-tetraazadecane, which contains nonbridging η^1-*cis*-TCNQ (7,7,8,8-tetracyanoquinodimethane) ligands.[5] Deriving inspiration from preparations of molecular squares found in the literature[6] and other sources,[7] we identified tris(pyrazol-1-ylmethyl)amine, amtp, as a good choice for the ancillary capping ligand because of its simple synthesis, its charge

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neutrality (which should favor coordination of additional ligands), and its ability to perform as a multidentate ligand, leaving cis coordination sites open for TCNE$^{\bullet/-}$ ligation. Manganese was chosen because complexes with amtp were known and because the magnetic properties of octahedral manganese(II) are easily interpreted.

The reaction[8] of Mn(ClO$_4$)$_2$ and amtp in acetonitrile yields an intermediate believed to be Mn(amtp)(S)$_2$(ClO$_4$)$_2$, where S = CH$_3$CN or H$_2$O by analogy to known compounds.[7b] Subsequent reaction with K[TCNE][9] in acetonitrile and crystallization by slow diffusion of diethyl ether into this solution gives Mn(amtp)(CH$_3$CN)(TCNE)$_2$ (**1**) as a mixed solvate.[10]

X-ray diffraction has been used to characterize **1**,[11] which exhibits a tridentate amtp ligand and a coordinated acetonitrile ligand. It also contains the desired two *cis*-TCNE$^{\bullet/-}$ anions (Figure 1). Curiously, the two TCNE$^{\bullet/-}$ ligands are not orthogonal to each other but are instead essentially eclipsed and π-stacked. Such a relationship has previously been reported for uncoordinated (TCNE)$_2^{2-}$ and for (TCNE)$_2^{2-}$ coordinated to non transition metals,[12] where an argument has been made for the existence of a four-center, two-electron bond.[1] The N$_{\text{TCNE}}$−Mn−N$_{\text{TCNE}}$ angles are 77.81(10)° and 77.48(10)° for the two unique molecules in the unit cell. The mean-plane separations between the TCNE ligands are between 3.021(7) and 3.259(8) Å, comparable to C−C distances previously reported for this species when uncoordinated.[13] Additionally, the packing diagram indicates apparently weaker intermolecular π interactions between TCNE radical anions as well, forming a crude infinite stack (Figure S1 in the Supporting Information).

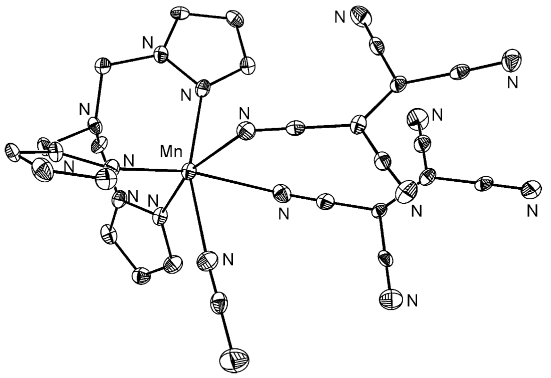

Figure 1. 50% thermal ellipsoid plot of **1** with eclipsed TCNE ligands. Hydrogen atoms and the solvent of crystallization are omitted for clarity.

The IR spectrum for **1** also confirms the existence of a π-(TCNE)$_2^{2-}$ dimer. Absorption peaks at 2195, 2174, and 2154 cm^{-1} are observed in the nitrile C≡N stretching region.[13]

Attempts to prepare a tetranuclear molecular square have so far been unsuccessful. Instead, the corresponding dinuclear species, [Mn(amtp)(CH$_3$CN)]$_2$(μ-TCNE)$_2$(ClO$_4$)$_2$ (**2**), is isolated from the reaction mixture, using essentially the same synthetic method, only varying the solvent.[14]

The crystal structure (Figure 2) indicates that **2** contains (formally) a pair of trans-bridging TCNE$^{\bullet/-}$ radical anions,

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(8) Preparations of air-sensitive compounds were carried out in a nitrogen-filled Vacuum Atmospheres glovebox by utilizing standard Schlenk techniques. All reagents were purchased from Aldrich or Alfa. Reagents were used as received except as noted below. Tetrahydrofuran and diethyl ether were distilled from Na/benzophenone. Acetonitrile was distilled from P$_2$O$_5$. All solvents were degassed with glovebox N$_2$ prior to use. amtp and K[TCNE] were prepared as in refs 7 and 9, respectively. Elemental analyses of C, H, and N were performed by Galbraith Laboratories, Inc.

(9) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Org. Chem.* **1960**, *25*, 1470.

(10) [Mn(amtp)(TCNE)$_2$(CH$_3$CN)] (**1**). Mn(amtp)(CH$_3$CN)(ClO$_4$)$_2$ (180 mg, 0.28 mmol) was dissolved in 8 mL of dichloromethane. To this was added a solution of K[TCNE] (48 mg, 0.28 mol) in 6 mL of acetomitrile, leading to a deep-brown solution, which was stirred for 30 min at room temperature. After this, the solution was filtered, and 15 mL of CH$_2$Cl$_2$ was added slowly to the filtrate to precipitate an air-sensitive blue-back solid. The solid was collected by vacuum filtration, washed with ether, and dried in vacuo. Recrystallization was performed from CH$_3$CN. Yield: 185 mg (53%). A crystal suitable for structural analysis was grown from a solution of CH$_3$CN by slow diffusion of ether. IR: ν(CN) 2195, 2175, 2154, and 2136 cm^{-1}. Anal. Calcd for C$_{26}$H$_{18}$MnN$_{16}$: C, 51.24; H, 2.98; N, 36.77. Found: C, 51.02; H, 3.05; N, 36.56.

(11) Low-temperature (100 K) single-crystal X-ray diffraction data for complexes **1** and **2** were collected on a Oxford Diffraction Xcalibur2 diffractometer equipped with the Enhance X-ray source and a Sapphire 3 CCD detector. The data collection routine, unit cell refinement, and data processing were carried out with the program *CrysAlis*. The structure was solved by direct methods using *SHELXS-97* and refined by full-matrix least squares. The final refinements involved an anisotropic model for all non-hydrogen atoms. All hydrogen atoms in **1** and **2** were either located from the residual e$^-$ density map and refined independently or fixed by a riding model. *CrysAlis*, version 1.171; Oxford Diffraction: Wroclaw, Poland, 2004. Sheldrick, G. M. *SHELXS97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *SHELXL97, Program for Crystal Structural Refinement*; University of Göttingen: Göttingen, Germany, 1997. Crystal data for **1**·C$_4$H$_{10}$O·CH$_3$CN: C$_{52}$H$_{36}$Mn$_2$N$_{32}$·C$_4$H$_{10}$O·CH$_3$CN, fw = 1334.18, triclinic, space group $P1$, a = 11.4726(10) Å, b = 12.1751(9) Å, c = 25.367(2) Å, α = 89.524(6)°, β = 80.612(7)°, χ = 64.543(8)°, V = 3148.8(4) Å^3, Z = 2, D_{calc} = 1.407 Mg/m^3, 21 306 reflections collected, 11 031 unique (R_{int} = 0.0526), R1 = 0.0568, wR2 = 0.0634 [$I > 2\sigma(I)$]. Crystal data for **2**: [C$_{40}$H$_{36}$Mn$_2$N$_{24}$][ClO$_4$]$_2$, fw = 1161.71, monoclinic, space group $C2/c$, a = 16.716(3) Å, b = 21.084(3) Å, c = 16.669(2) Å, α = 90°, β = 117.862(18)°, χ = 90°, V = 5193.9(13) Å^3, Z = 4, D_{calc} = 1.486 Mg/m^3, 16 757 reflections collected, 4539 unique (R_{int} = 0.1220), R1 = 0.1461, wR2 = 0.3172 [$I > 2\sigma(I)$].

(12) Potassium: Bock, H.; Ruppert, K.; Fenske, D.; Goesmann, H. *Z. Anorg. Allg. Chem*. **1991**, *595*, 275−284. Thallium: Johnson, M. T.; Campana, C. F.; Foxman, B. M.; Desmarais, W.; Vela, M. J.; Miller, J. S. *Chem.−Eur. J.* **2000**, *6*, 1805−1810.

(13) (a) Del Sesto, R. E.; Botoshansky, M.; Kaftory, M.; Miller, J. S. *CrystEngComm* **2002**, *4*, 106−108. (b) Del Sesto, R. E.; Miller, J. S.; Lafuente, P.; Novoa, J. J. *Chem.−Eur. J.* **2002**, *8*, 4894−4908.

(14) [Mn(ampt)(CH$_3$CN)]$_2$(μ-TCNE)$_2$)]$_2$(ClO$_4$)$_2$ (**2**). The white solid Mn(ampt)(CH$_3$CN)(ClO$_4$)$_2$ (180 mg, 0.28 mmol) was dissolved in 8 mL of CH$_3$CN and yielded a colorless solution. A yellow solution of K[TCNE] (48 mg, 0.28 mmol) in 6 mL of CH$_3$CN was added to the above-indicated solution, leading to a deep-brown solution. The solution was stirred for 30 min at room temperature and then filtered. An additional 10 mL of CH$_3$CN was added to the filtrate. The filtrate was allowed to stir for 30 min at room temperature. A total of 22 mL of ether was added slowly to precipitate an air-sensitive brown-black solid. The solid was collected by vacuum filtration, washed with ether, and dried in vacuo. Recrystallization was performed from CH$_3$CN. Yield: 177 mg (54%). A crystal suitable for structural analysis was grown from a solution of CH$_3$CN by slow diffusion of ether. IR: ν(CN) 2195, 2175, 2154, and 2137 cm^{-1}. Anal. Calcd for C$_{40}$H$_{36}$Mn$_2$N$_{24}$Cl$_2$O$_8$: C, 37.63; H, 2.83; N, 26.34. Found: C, 37.96; H, 2.50; N, 27.12.

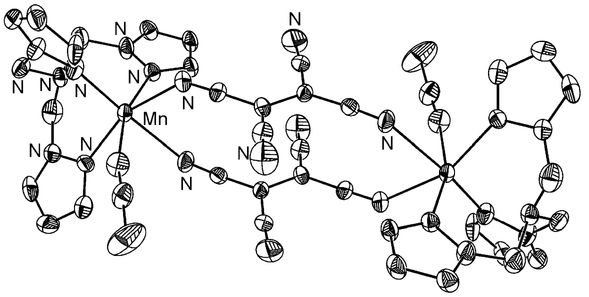

Figure 2. 30% thermal ellipsoid plot of **2** showing eclipsed bridging TCNE ligands. Hydrogen atoms and perchlorate ions are omitted for clarity.

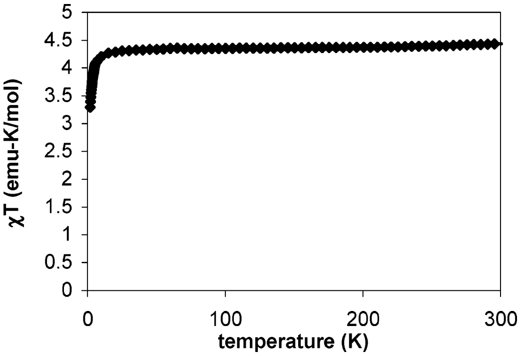

Figure 3. χT vs T plot for **1**.

connecting two manganese(II) centers.[11] As with the mononuclear species, the N−Mn−N bond angles to the bridging ligands similarly deviate significantly from 90° [77.3(3)°] because of the intramolecular π stacking of the TCNEs. The intramolecular mean-plane distance between TCNE radicals is 3.08(2) Å, again indicating dimerization to form a $(TCNE)_2{}^{2-}$ species.

Given these two structures, we next investigated their magnetic properties. Uncoordinated $(TCNE)_2{}^{2-}$ has previously been reported to be diamagnetic, but its ability to mediate superexchange between two spin centers is of critical importance if it exists in the coordination polymer magnets to any great extent. Using a Quantum Design MPMS SQUID magnetometer in an applied field of 5000 G, the magnetic properties of **1** and **2** were determined. The magnetic properties[15] of **1** (Figure 3) are characteristic of high-spin, spin-only manganese(II) with $g = 2.0$ ($\chi T_{\mathrm{calc}} = 4.38$ emu·K/mol; $\chi T_{300\,\mathrm{K}} = 4.43$ emu·K/mol) with no contribution from the $TCNE^{\bullet/-}$ radical and no significant intermolecular interactions. This result supports the idea of a diamagnetic $(TCNE)_2{}^{2-}$ moiety.

The corresponding dinuclear species, **2** (Figure 4), also exhibits essentially temperature-independent χT vs T; the data are consistent with two independent manganese(II) centers ($\chi T_{\mathrm{calc}} = 8.75$ emu·K/mol, assuming $g = 2.0$; $\chi T_{300\,\mathrm{K}} = 8.81$ emu·K/mol). On the basis of a diamagnetic $(TCNE)_2{}^{2-}$ bridge, it is not surprising that there is evidence for only very weak intramolecular magnetic coupling between the two manganese(II) centers.

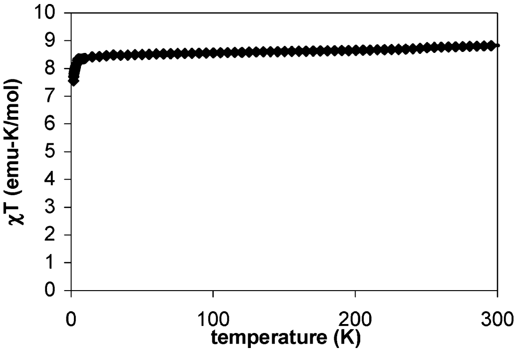

Figure 4. χT vs T plot for **2**.

The flexibility of the tridentate amtp ligand is probably important from a geometric perspective for allowing the formation of the $(TCNE)_2{}^{2-}$ dimer in these complexes. The three N−Mn−N bond angles from the ancillary ligand range from 99.65° to 110.65° and average 105.4°, rather than the ideal 90°. In some sense, this "allows" the N−Mn−N angle involving the two $TCNE^{\bullet/-}$ ligands to be small enough to achieve π stacking. It is possible that a more rigid ancillary ligand that more nearly enforced 90° angles would not allow the dimer to form intramolecularly. However, in the $M[TCNE]_2$ magnets, there are no ancillary ligands, so it seems likely that the $(TCNE)_2{}^{2-}$ dimer should exist in the three-dimensional polymers. In the corresponding known magnetic polymers with *trans*-TCNE radical anions, the presence of the tetraazamacrocycle prevents the formation of an intermolecular dimer.[4]

Clearly, these results show that the $(TCNE)_2{}^{2-}$ dimer represents a potential "weak link" to long-range magnetic order. Perhaps the coordination environment around manganese(II) is somehow very different from that of vanadium(II), such that the latter avoids the formation of $(TCNE)_2{}^{2-}$ dimers, thus explaining why T_c is higher for the vanadium coordination polymer than for the corresponding manganese compound. In any case, the model of the polymer magnets that consists of an idealized network of bridging (isolated) radical anions between transition-metal cations should be reevaluated.

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Supporting Information Available: X-ray crystallographic files in CIF format and a packing diagram of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) All magnetic measurements were performed on a 7-T Quantum Design MPMS SQUID magnetometer. Measurements of magnetization as a function of temperature were performed from 1.8 to 300 K in a 5000-G applied field as indicated. Powder samples were cooled in zero applied field and measured upon warming. Diamagnetic corrections were estimated based on Pascal's constants. Samples are presumed to be fully desolvated, as indicated by elemental analysis.