

## catena-Poly[[diaquamanganese(II)]- di- $\mu$ -1,1,3,3-tetracyano-2-ethoxy- propenido- $\kappa^4 N^1:N^3$ ]

John A. Schlueter\* and Urs Geiser

Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue,  
Argonne, IL 60439, USA

Correspondence e-mail: jaschlueter@anl.gov

Received 5 February 2003

Accepted 25 February 2003

Online 21 March 2003

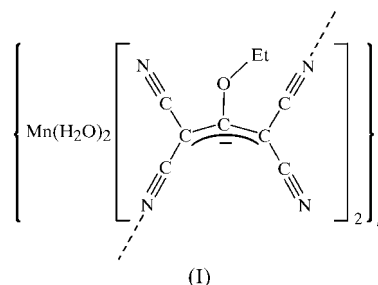
The crystal structure of the title compound,  $[\text{Mn}(\text{C}_6\text{H}_5\text{N}_4\text{O})_2(\text{H}_2\text{O})_2]$ , conventionally denoted  $\text{Mn}(\text{EtO-TCA})_2(\text{H}_2\text{O})_2$ , where EtO-TCA is 2-ethoxy-1,1,3,3-tetracyanopropenide, is described. The EtO-TCA anions bridge  $\text{Mn}^{\text{II}}$  centers through one of the nitrile N atoms of each of their two dicyanomethanide groups, thus forming dibridged chains along *ab*. These chains are linked into two-dimensional sheets through hydrogen bonding. The seven-atom bridge, which results in a long  $\text{Mn} \cdots \text{Mn}$  intrachain interaction [9.0044 (4) Å], as well as the large interchain separations [8.3288 (4) and 8.5220 (4) Å] prohibit long-range magnetic ordering down to temperatures as low as 1.55 K.

### Comment

Coordination polymers formed by linking various transition metal centers with pseudohalides have been intensely studied over the past decade in an attempt to correlate their structural and magnetic properties. The dicyanamide (dca) anion,  $\text{N}(\text{CN})_2^-$ , which has a propensity to act as a bidentate ligand, mediates ferromagnetic coupling in  $\text{Ni}(\text{dca})_2$  at a temperature as high as 21 K (Kurmoo & Kepert, 1998). More recently, various cyanocarbons have been investigated as potential superexchange ligands. We have found that the carbamoyldicyanomethanide (cdm) anion,  $(\text{CN})_2\text{CC}(\text{O})\text{NH}_2^-$ , favors the formation of the mononuclear  $[\text{M}(\text{cdm})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$  complex (*M* is Mn, Co, Ni or Cu; Schlueter *et al.*, 2003). In an attempt to provide additional nitrile binding sites, and thus enhance the probability of forming polymeric structures, we have turned our attention to the crystallization of various polynitrile transition metal complexes.

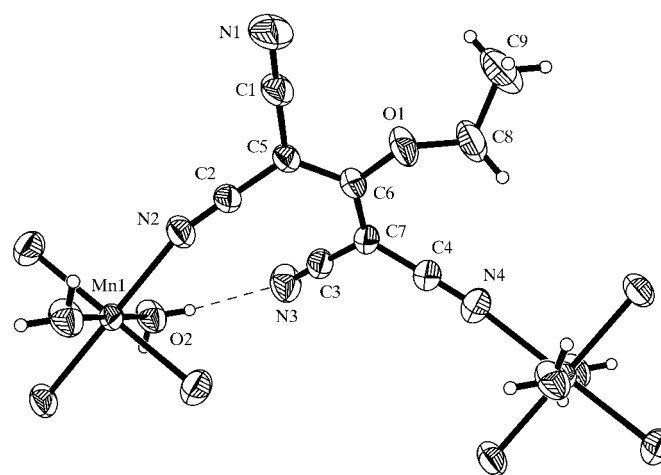
2-Alkoxytetracyanoallyl anions have recently been used as components of charge-transfer salts because of their synthetic versatility, large polarizabilities and potential for intermolecular contacts with the donor molecules. Two 2-ethoxy-1,1,3,3-tetracyanopropenide (EtO-TCA) salts of tetrathio-

tetracene (TTT),  $(\text{TTT})(\text{EtO-TCA})(\text{THF})_{0.25}$  (THF is tetrahydrofuran) and  $(\text{TTT})(\text{EtO-TCA})_2$  exhibit semiconducting behavior (Sekizaki, Tada *et al.*, 2001). The salt with bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF),  $\alpha\text{-(BEDT-TTF)}_2(\text{EtO-TCA})(\text{THF})_{0.5}$ , is also a semiconductor (Sekizaki, Yamochi & Saito, 2001), and the bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) salt,  $(\text{BEDO-TTF})_2(\text{EtO-TCA})$ , exhibits successive metal–semiconductor and semiconductor–metal transitions near 150 and 40 K, respectively (Sekizaki *et al.*, 2002). Until this work, EtO-TCA had not been studied as the bridging component of transition-metal-based coordination polymers. In this paper, we report that EtO-TCA is capable of bridging transition metal ions to form the title  $\text{Mn}(\text{EtO-TCA})_2(\text{H}_2\text{O})_2$  complex, (I).



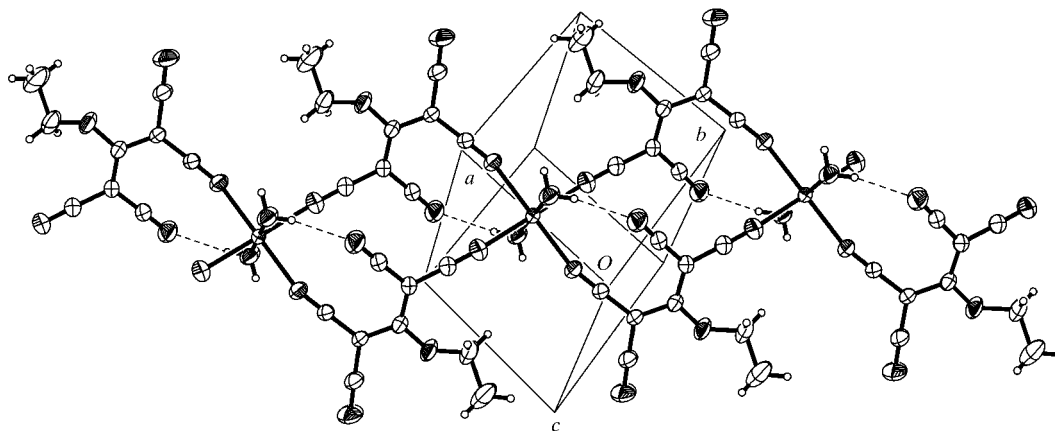
Similar to the data reported for other structures of the EtO-TCA anion (Sekizaki, Tada *et al.*, 2001), the C–C bond lengths of the tetracyanopropenide moiety of (I), 1.4022 (15)–1.4177 (16) Å, are intermediate between typical single and double bonds, indicating a delocalized electronic structure. The  $\text{C}_{\text{methanide}}-\text{C}_{\text{nitrile}}$  bonds are about 0.01 Å longer for the non-coordinated nitrile groups than for the coordinated ones.

The EtO-TCA anions in (I) bridge two Mn atoms through one of the nitrile N atoms of each of their two dicyanomethanide units (Fig. 1). With respect to the ethoxy group, one



**Figure 1**

The atomic numbering scheme of (I), illustrating the EtO-TCA anion and including the coordination sphere of the Mn atoms to which it is bound. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line indicates intrachain hydrogen bonding between atoms H21 and N3.



**Figure 2**

The dibridged chain structure of (I), which runs along the *ab* direction. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

coordinating nitrile is *cis* while the second is *trans*. The seven-atom bridging moiety is markedly distorted from planarity. Intramolecular EtO-TCA planes are as defined by Sekizaki (Sekizaki, Tada *et al.*, 2001). Thus, the propenide C atoms (C5, C6 and C7) define plane 1 (*P1*). The two dicyanomethanide planes, *P2* (N1, C1, C5, C2 and N2) and *P3* (N3, C3, C7, C4 and N4), are canted  $32.08(8)^\circ$  with respect to each other. The r.m.s. deviation of *P2* is  $0.006 \text{ \AA}$ , with the greatest deviation,  $0.010(1) \text{ \AA}$ , occurring for atom C2. Similarly, for *P3*, the r.m.s. deviation is  $0.004 \text{ \AA}$ , with the greatest deviation,  $0.007(1) \text{ \AA}$ , occurring for atom C3. The dihedral angles of *P1* with *P2* and *P3* are  $14.83(15)$  and  $20.64(15)^\circ$ , respectively. The C1—C5...C7—C4 torsion angle is  $55.7(3)^\circ$ . Atoms C6, O1 and C8 define plane 4 (*P4*), which makes a dihedral angle of  $28.7(1)^\circ$  with *P1*.

Crystal-packing forces are responsible for distorting the EtO-TCA<sup>−</sup> anion from the planar structure predicted by molecular orbital calculations. RHF/6-31G\* calculations have been used to predict the *P1*–*P2*, *P2*–*P3*, *P1*–*P3* and *P1*–*P4* dihedral angles as a function of the C1—C5...C7—C4 torsion angle (Sekizaki, Tada *et al.*, 2001). These calculations are in line with the molecular structure of EtO-TCA<sup>−</sup> observed in (I), except for the *P1*–*P4* dihedral angle, which is significantly smaller than predicted. A similar discrepancy was also observed in (TTT)(BuO-TCA) and attributed to crystal-packing forces by Sekizaki, Tada *et al.* (2001).

The centrosymmetric coordination sphere about the Mn atom in (I) consists of the O atoms of two water molecules and the nitrile N atoms (N2 and N4) of four EtO-TCA<sup>−</sup> anions in an essentially octahedral environment. A distortion of  $2.81(5)^\circ$  is seen in the N2—Mn—N4 angle (Table 1). The Mn—N and Mn—O bond lengths (Table 1) are typical for nitrile coordination to Mn (see, for example, Dalai *et al.*, 2002; Schlueter *et al.*, 2003).

The EtO-TCA<sup>−</sup> anions act as bidentate ligands in (I), forming dibridged chains along the *ab* direction (Fig. 2). The coordinating nitrile N atoms are on opposing dicyanomethanide groups of EtO-TCA<sup>−</sup>, resulting in a seven-atom

bridge and an intrachain Mn...Mn separation of  $9.0044(4) \text{ \AA}$ . Slightly shorter interchain Mn...Mn separations of  $8.3288(4)$  and  $8.5220(4) \text{ \AA}$  are also present.

Hydrogen bonding is observed with the H atoms of the coordinated water molecule. An intrachain hydrogen bond occurs between atom H21 and nitrile atom N3 (Fig. 1). Adjacent chains are assembled into sheets [parallel to the (111) plane] by interchain hydrogen bonding between atoms H22 and N1.

The large Mn...Mn separation and the non-planar geometry of EtO-TCA<sup>−</sup> in (I) are not conducive to magnetic ordering, and AC (alternating current) susceptibility measurements down to 1.55 K confirmed that no long-range magnetic order occurs in this structure. It is possible that magnetic ordering could occur in a related structure in which the EtO-TCA<sup>−</sup> anions link transition metals *via* the nitrile N atoms on the same dicyanomethanide group. This would reduce the superexchange pathway from seven to five atoms and shorten the intrachain metal...metal separation by more than an Ångström. Such a structure might be formed through the use of organic solvents, which would open the coordination site occupied by water, or by increasing the metal concentration during the crystallization process, thus increasing the chance of coordination to more than two of the four available nitrile N atoms.

## Experimental

Sodium 2-ethoxy-1,1,3,3-tetracyanopropenide (150 mg, 0.72 mmol), prepared according to the literature procedure of Middleton *et al.* (1957), was dissolved in water (10 ml) and combined with an ethanolic solution (10 ml) of pyrazine (Aldrich, 58 mg, 0.72 mmol). This solution was layered on top of an aqueous solution (10 ml) of manganese(II) nitrate hydrate (Aldrich, 64 mg, 0.36 mmol). After one month, clear colorless block-shaped crystals of (I) were collected from the concentrated solution by filtration. Decomposition began near 453 K as the clear crystals become opaque, possibly as a result of water loss.

## Crystal data

[Mn(C<sub>9</sub>H<sub>5</sub>N<sub>4</sub>O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]  
*M<sub>r</sub>* = 461.31  
 Triclinic, *P* $\bar{1}$   
*a* = 8.3288 (4) Å  
*b* = 8.5220 (4) Å  
*c* = 9.3793 (5) Å  
 $\alpha$  = 81.387 (2)°  
 $\beta$  = 69.135 (2)°  
 $\gamma$  = 64.589 (2)°  
*V* = 561.88 (5) Å<sup>3</sup>  
*Z* = 1

*D<sub>x</sub>* = 1.363 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 1000 reflections  
 $\theta$  = 2.3–32.0°  
 $\mu$  = 0.63 mm<sup>-1</sup>  
*T* = 298 (2) K  
 Block, colorless  
 0.56 × 0.30 × 0.17 mm

## Data collection

Siemens SMART CCD area-detector diffractometer  
 Area-detector  $\omega$  scans  
 Absorption correction: by integration (*SHELXTL*; Sheldrick, 2001)  
*T<sub>min</sub>* = 0.802, *T<sub>max</sub>* = 0.898  
 7918 measured reflections  
 3763 independent reflections  
 3321 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.022  
 $\theta_{\text{max}}$  = 32°  
*h* = -12 → 12  
*k* = -12 → 12  
*l* = -13 → 13  
 109 standard reflections every 1918 frames  
 frequency: 1156 min  
 intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.032  
*wR*(*F*<sup>2</sup>) = 0.091  
*S* = 1.02  
 3763 reflections  
 148 parameters  
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.0745P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.014$   
 $\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$

Ethoxy H atoms were placed geometrically and refined with a riding model, and with *U<sub>iso</sub>* values constrained to be 1.2 or 1.5*U<sub>eq</sub>* of the methylene and methyl C atoms, respectively. Water H-atom positions were refined under distance and angle restraints, with *U<sub>iso</sub>* values constrained to be 1.5*U<sub>eq</sub>* of atom O2.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work, carried out at Argonne National Laboratory, was sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences, under contract W-31-109-ENG-38.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1009). Services for accessing these data are described at the back of the journal.

**Table 1**

Selected geometric parameters (Å, °).

Mn1—O2	2.1743 (10)	N4—C4	1.1432 (16)
Mn1—N2	2.2084 (10)	C1—C5	1.4172 (16)
Mn1—N4 <sup>i</sup>	2.2221 (11)	C2—C5	1.4079 (14)
O1—C6	1.3314 (12)	C3—C7	1.4177 (16)
O1—C8	1.4447 (17)	C4—C7	1.4059 (15)
N1—C1	1.1424 (17)	C5—C6	1.4022 (15)
N2—C2	1.1439 (14)	C6—C7	1.4093 (16)
N3—C3	1.1491 (16)	C8—C9	1.482 (2)
O2 <sup>ii</sup> —Mn1—N2	89.89 (4)	C6—C5—C2	122.20 (10)
O2 <sup>ii</sup> —Mn1—N4 <sup>i</sup>	88.59 (5)	C6—C5—C1	119.45 (10)
N2 <sup>ii</sup> —Mn1—N4 <sup>i</sup>	87.19 (5)	C2—C5—C1	118.29 (10)
C6—O1—C8	122.62 (11)	O1—C6—C5	112.98 (10)
C2—N2—Mn1	164.73 (11)	O1—C6—C7	122.44 (10)
C4—N4—Mn1 <sup>iii</sup>	168.27 (12)	C5—C6—C7	124.55 (10)
N1—C1—C5	178.48 (15)	C4—C7—C6	122.47 (10)
N2—C2—C5	178.50 (14)	C4—C7—C3	115.00 (10)
N3—C3—C7	177.92 (13)	C6—C7—C3	122.46 (10)
N4—C4—C7	178.11 (15)	O1—C8—C9	107.99 (15)
C8—O1—C6—C5	-152.09 (13)	O1—C6—C7—C4	19.80 (18)
C8—O1—C6—C7	29.82 (19)	C5—C6—C7—C4	-158.06 (12)
C2—C5—C6—O1	-162.30 (11)	O1—C6—C7—C3	-163.34 (12)
C1—C5—C6—O1	14.81 (17)	C5—C6—C7—C3	18.80 (19)
C2—C5—C6—C7	15.74 (19)	C6—O1—C8—C9	148.17 (16)
C1—C5—C6—C7	-167.15 (12)		

Symmetry codes: (i) 1 + *x*, *y* - 1, *z*; (ii) 1 - *x*, -*y*, -*z*; (iii) *x* - 1, 1 + *y*, *z*.

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H21...N3	0.819 (18)	2.134 (18)	2.9223 (19)	161.5 (17)
O2—H22...N1 <sup>i</sup>	0.817 (17)	2.021 (17)	2.8365 (18)	175.5 (17)

Symmetry code: (i) 1 + *x*, *y*, *z* - 1.

## References

- Bruker (2001). *SAINT*. Version 6.28a. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dalai, S., Mukherjee, P. S., Zangrando, E. & Chaudhuri, N. R. (2002). *New J. Chem.* **26**, 1185–1189.
- Kurmoo, M. & Kepert, C. J. (1998). *New J. Chem.* **12**, 1515–1524.
- Middleton, W. J., Little, E. L., Coffman, D. D. & Engelhardt, V. A. (1957). *J. Am. Chem. Soc.* **80**, 2795–2806.
- Schlueter, J. A., Geiser, U. & Manson, J. L. (2003). *Acta Cryst.* **C59**, m1–m3.
- Sekizaki, S., Konsha, A., Yamochi, H. & Saito, G. (2002). *Mol. Cryst. Liq. Cryst.* **376**, 207–212.
- Sekizaki, S., Tada, C., Yamochi, H. & Saito, G. (2001). *J. Mater. Chem.* **11**, 2293–2302.
- Sekizaki, S., Yamochi, H. & Saito, G. (2001). *Synth. Met.* **120**, 961–962.
- Sheldrick, G. M. (2001). *SHELXTL*. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1995). *SMART*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.