Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Tetraaquabis(carbamoyldicyanomethanido-*κN*)manganese(II) dihydrate

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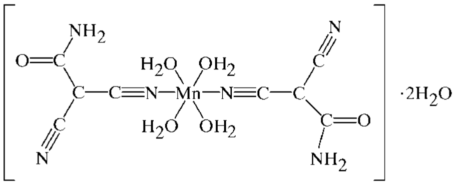
Received 30 October 2002
Accepted 7 November 2002
Online 10 December 2002

The crystal structure of $[Mn(C_4H_2N_3O)_2(H_2O)_4]\cdot 2H_2O$, conventionally abbreviated $[Mn(cdm)_2(H_2O)_4]\cdot 2H_2O$, where cdm is carbamoyldicyanomethanide, is described. The bond lengths and distances are comparable to those previously reported for the isomorphous Ni and Co analogs. Molecular units are formed by coordination of the nitrile N atoms of two cdm anions and four water molecules to the manganese(II) cation. Although these mononuclear molecular species are connected *via* hydrogen bonding, no magnetic ordering was observed down to 1.55 K.

Comment

Pseudohalide–transition metal complexes have been increasingly studied over the past decade because of their interesting structural and magnetic properties. The dicyanamide anion, $N(CN)_2^-$, has been shown to be a versatile ligand because it can coordinate to a metal ion in several ways (Manson, 2002). Bidentate bonding through the nitrile N atoms is a common mode for the formation of coordination polymers. Several of these materials exhibit co-operative magnetic behavior, including ferromagnetism at temperatures as high as 21 K for $Ni[N(CN)_2]_2$ (Kurmoo & Kepert, 1998). More recently, attention has turned to other polynitrile ligands as prospective building blocks for the construction of polymeric transition metal complexes. The tricyanomethanide (tcm) anion, $C(CN)_3^-$, is one of the simplest that is capable of forming infinite chains or sheets (Hoshino *et al.*, 1999). Another promising candidate is the carbamoyldicyanomethanide (cdm) anion, $CN_2CC(O)NH_2^-$ (Trofimenko *et al.*, 1962), which is a derivative of tcm in which one nitrile group is replaced by $C(O)NH_2$. It is possible that co-operative magnetic behavior would occur in a polymeric structure in which cdm acts as a bidentate ligand coordinating to adjacent metal centers through its nitrile N atoms. While attempting to synthesize the anionic polymeric network $[Mn(cdm)_3]^-$, we obtained the previously unreported title salt, $[Mn\{(CN)_2CC(O)NH_2\}_2(H_2O)_4]\cdot 2H_2O$, (I), and its structure is presented here.



(I)

The synthesis of $[M(cdm)_2]\cdot 6H_2O$, with M = Co, Ni and Cu, has been reported previously (Skopenko & Lampeka, 1981). It was erroneously inferred from the IR spectroscopic data of the Co and Ni salts that the inner coordination sphere contained only the cdm anion. Subsequently, the crystal structures of the Co (Shi *et al.*, 2002) and Ni (Shi *et al.*, 2001) salts, determined by single-crystal X-ray diffraction, revealed that these salts are mononuclear complexes, in which the metal atom is coordinated in a slightly distorted octahedron by the nitrile N atoms of two cdm anions and the O atoms of four water molecules. The crystal structure contains cavities in which non-coordinated water molecules reside.

Compound (I), the Mn derivative of $[M\{(CN)_2CC(O)NH_2\}_2(H_2O)_4]\cdot 2H_2O$, is isomorphous with the Co and Ni analogs. The structure is characterized by mononuclear $[Mn\{(CN)_2CC(O)NH_2\}_2(H_2O)_4]$ units (Fig. 1). The Mn atom is located on an inversion center. The coordination sphere consists of the O atoms of four water molecules and the nitrile N atoms of two cdm anions. The M—N and M—O bonds (Table 1) are about 0.10 to 0.15 Å longer, respectively, in the Mn structure than in the Co and Ni derivatives. The cdm anion is essentially planar (r.m.s. deviation 0.0129 Å), with the greatest deviation from planarity being 0.0233 (10) Å for methanide atom C3. The C—C—C angles about the methanide C atom are 118.04 (10), 119.76 (9), and 122.15 (9)°, and sum to 359.95°, indicating essentially sp^2 hybridization.

It was clear from the examination of difference-map plots that water atoms O3 and O4 had, in each case, one of the two H atoms disordered over two adjacent sites. Initial refinement of tied occupancy values for these disordered H atoms led to values which were not markedly different from a 50/50 disorder and, in the final refinement cycles, the disordered H-atom occupancies were set at 0.5 (see *Experimental*).

The plane of the cdm ligand lies at an angle of 71.87 (3)° with respect to the N1—Mn1—O2 plane and at an angle of 19.76 (5)° with respect to the N1—Mn1—O3 plane. The cdm ligands of neighboring molecules interdigitate along the **a**+**c** diagonal, forming cdm layers which are separated by a water-rich layer containing both the coordinated and non-coordinated water molecules (Fig. 2).

Extensive hydrogen bonding gives the structure of (I) three-dimensional character. Carbonyl atom O1 projects toward the water-rich layer, forming hydrogen-bonding interactions with all three (both the coordinated and non-coordinated) water molecules. The amine H atoms have interactions with both atom O4 of the non-coordinated water molecule and non-

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DOI: 10.1107/S0108270102020334

coordinated nitrile atom N2. Atom N2 is also bound to one of the H atoms of O2. Hydrogen-bonding contacts are present between the coordinated water molecule associated with atom O3 and the non-coordinated water molecule associated with atom O4. This latter contact was found to be disordered where, half of the time, the hydrogen bonding was through atom H32, with atom O3 acting as the hydrogen-bond donor and atom O4 the acceptor, and the other half of the time, the hydrogen bonding was through atom H43, with atom O4 the donor and atom O3 the acceptor (see Table 2).

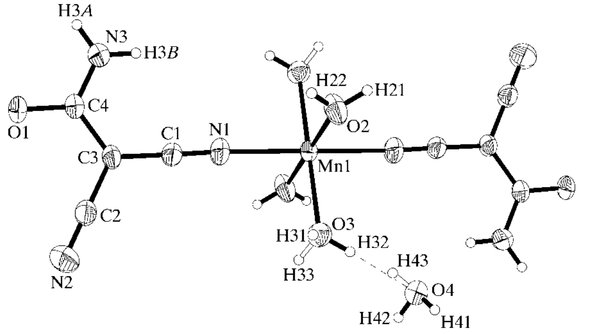

Figure 1
A view of the title mononuclear complex, (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabeled atoms are related by an inversion center to the labeled atoms. H-atom positions H32, H33, H42 and H43 are all half-occupied. Thus, half of the time, hydrogen bonding occurs between atoms H32 and O4 (pictured), while the other half of the time, hydrogen bonding occurs between atoms H43 and O3 (not pictured).

The closest Mn atoms in the structure of (I) are separated by 7.4144 (3) Å [Mn1 at ($\frac{1}{2}$,0,0) to Mn1 at (1,$\frac{1}{2}$,$\frac{1}{2}$)]. An efficient superexchange pathway, preferably one containing covalent bonds between magnetic centers, is required for long-range magnetic order to occur. The molecular nature of the structure of (I) is not conducive to magnetic ordering. An AC (alternating current) susceptibility measurement down to 1.55 K confirmed that no magnetic ordering occurs in this structure. It is possible that magnetic ordering could occur in a related structure in which the coordinated water molecules were replaced by bridging ligands. Such a structure might be formed through the use of organic solvents or by introducing a neutral bidentate coordinating ligand such as pyrazine.

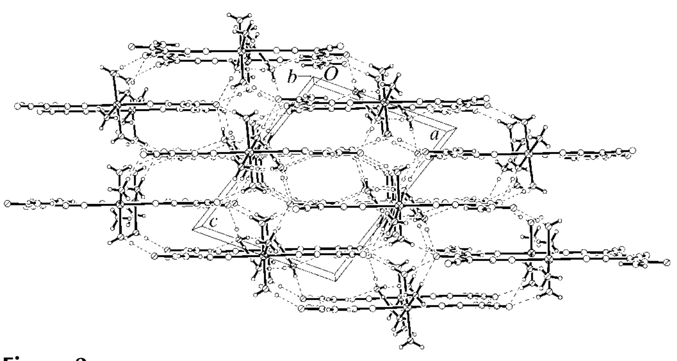

Figure 2
A packing diagram for (I), projected approximately along the *b* axis. Equivalent isotropic spheres are drawn at the 50% probability level.

Experimental

Tetrabutylammonium bromide (322 mg, 1 mmol) and potassium carbamoyldicyanomethanide (441 mg, 3 mmol) (Trofimenko *et al.*, 1962) were combined in water (20 ml). The resulting solution was layered on top of an aqueous solution (10 ml) of manganese(II) bromide (215 mg, 1 mmol) and this crystallization mixture was allowed to evaporate slowly. After three months, clear colorless blocks of (I) were collected from the concentrated solution by filtration. Upon heating to 373 K, the crystals turned opaque white, presumably as a result of the loss of the non-coordinated water. Further heating to 498 K resulted in decomposition.

Crystal data

$[Mn(C_4H_2N_3O)_2(H_2O)_4]\cdot 2H_2O$
$M_r = 379.21$
Monoclinic, $P2_1/n$
$a = 9.5234\ (4)$ Å
$b = 7.4343\ (4)$ Å
$c = 12.1939\ (6)$ Å
$\beta = 108.777\ (2)^\circ$
$V = 817.38\ (7)$ Å^3
$Z = 2$

$D_x = 1.541$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 834 reflections
$\theta = 3.3$–28.1°
$\mu = 0.86$ mm^{-1}
$T = 298\ (2)$ K
Block, colorless
$0.44 \times 0.35 \times 0.30$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
Area-detector ω scans
Absorption correction: by integration (*SHELXTL*; Sheldrick, 2001)
$T_{\min} = 0.728$, $T_{\max} = 0.807$
5354 measured reflections
1927 independent reflections

1789 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\max} = 28.3^\circ$
$h = -12 \rightarrow 12$
$k = -9 \rightarrow 7$
$l = -16 \rightarrow 16$
133 standard reflections
frequency: 781 min
intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Mn1—O2	2.1580 (9)	N2—C2	1.1436 (17)
Mn1—O3	2.2059 (8)	N3—C4	1.3322 (14)
Mn1—N1	2.2081 (9)	C1—C3	1.4016 (14)
O1—C4	1.2686 (12)	C2—C3	1.4111 (16)
N1—C1	1.1445 (14)	C3—C4	1.4285 (14)
O2—Mn1—O3	88.51 (4)	C1—C3—C4	122.15 (9)
O3—Mn1—N1	87.39 (4)	C2—C3—C4	119.76 (9)
C1—N1—Mn1	177.06 (11)	O1—C4—N3	119.30 (10)
N1—C1—C3	178.81 (13)	O1—C4—C3	120.90 (9)
N2—C2—C3	179.50 (14)	N3—C4—C3	119.79 (9)
C1—C3—C2	118.04 (10)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···N2$^{\rm i}$	0.86	2.52	3.3688 (16)	168
N3—H3*B*···O4$^{\rm ii}$	0.86	2.26	3.0078 (14)	145
O2—H21···O1$^{\rm iii}$	0.841 (15)	1.937 (15)	2.7721 (12)	171.8 (15)
O2—H22···N2$^{\rm iv}$	0.815 (15)	2.048 (16)	2.8587 (14)	173.8 (16)
O3—H31···O1$^{\rm v}$	0.790 (14)	1.942 (14)	2.7317 (12)	177.6 (16)
O3—H32···O4	0.83 (2)	1.96 (2)	2.7877 (12)	173 (3)
O3—H33···O4$^{\rm vi}$	0.86 (2)	1.93 (2)	2.7797 (13)	174 (3)
O4—H41···O1$^{\rm vii}$	0.788 (15)	2.086 (16)	2.8664 (13)	170.9 (16)
O4—H42···O3$^{\rm vi}$	0.80 (3)	1.99 (3)	2.7797 (13)	173 (3)
O4—H43···O3	0.80 (2)	2.01 (3)	2.7877 (12)	165 (3)

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, -y, -z$; (iii) $1+x, y, z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vi) $1-x, -1-y, -z$; (vii) $1+x, y-1, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.059$
$S = 1.07$
1927 reflections
131 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0305P)^2 + 0.1424P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

The H atoms bonded to N3 were placed geometrically and refined with a riding model. Coordinates for the disordered and non-disordered water H atoms were obtained from difference maps and were refined subject to an O—H *DFIX* restraint (Sheldrick, 2001) of 0.82 (3) Å (eight restraints). All the H-atom $U_{\rm iso}$ values were constrained to be 1.2 times the $U_{\rm eq}$ value of the carrier atom.

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

This work was sponsored by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences (Contract W-31-109-ENG-38).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1671). Services for accessing these data are described at the back of the journal.

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