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Poly[[diaquahexa-μ-cyanido-dicyanido-di-μ-pyrimidine-dimanganese(II)molybdate(IV)] trihydrate]

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Key indicators

Single-crystal X-ray study
T = 90 K
Mean σ(C–C) = 0.004 Å
H-atom completeness 67%
Disorder in solvent or counterion
R factor = 0.032
wR factor = 0.088
Data-to-parameter ratio = 14.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $\{[Mn_2Mo(CN)_8(C_4H_4N_2)_2(H_2O)_2]\cdot 3H_2O\}_n$, is built up of Mo^{IV} atoms in a square-antiprismatic coordination, which are linked to distorted octahedrally coordinated Mn^{II} atoms through cyanide bridges to form a three-dimensional structure. The Mn^{II} atoms are also bridged by the pyrimidine ligands.

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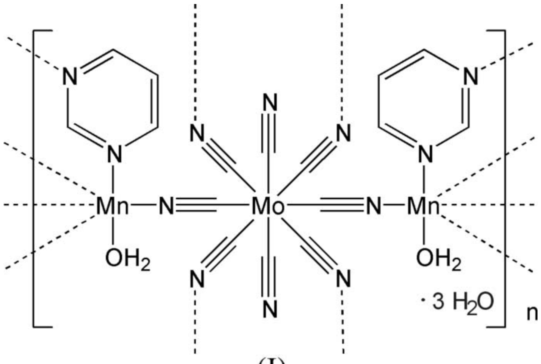
Comment

Cyanide-bridged metal assemblies (Ludi & Güdel, 1973; Babel, 1986) have been intensively studied as functionalized magnetic materials due to their flexible design and simple synthesis. Hexacyanometallate-based magnets are known to exhibit high magnetic ordering temperatures (Ferlay *et al.*, 1995; Hatlevik *et al.*, 1999; Holmes & Girolami, 1999; Ohkoshi *et al.*, 2000) and interesting magnetic properties (Miller, 2000; Verdaguer *et al.*, 2002; Margadonna *et al.*, 2004; Ohkoshi *et al.*, 2004). Recently, octacyanometallate-based magnets have also received much attention, due to their variety of crystal structures and coordination geometries (Przychodzeń *et al.*, 2006). In the case of Mn^{II}–Mo^{IV} octacyanometallate-based assemblies, crystal structures containing organic ligands (Sra *et al.*, 1999; Sieklucka *et al.*, 2000; Rombaut *et al.*, 2000; Herrera *et al.*, 2003; Withers *et al.*, 2005; Shen *et al.*, 2006) and without organic ligands (Willemin *et al.*, 2003) have been reported. In the present work, we report the title Mn^{II}–Mo^{IV} bimetallic complex of composition $\{[Mn_2Mo(CN)_8(C_4H_4N_2)_2(H_2O)_2]\cdot 3H_2O\}_n$, (I).



(I)

The coordination geometry around the Mo and Mn atoms can be described as square-antiprismatic and distorted octahedral, respectively (Fig. 1). Three of the CN groups in the $[Mo(CN)_8]^{4-}$ unit are also connected to Mn1 and three of the CN groups are connected to Mn2. The remaining two CN groups do not act as bridging ligands. Atoms Mn1 and Mn2 are

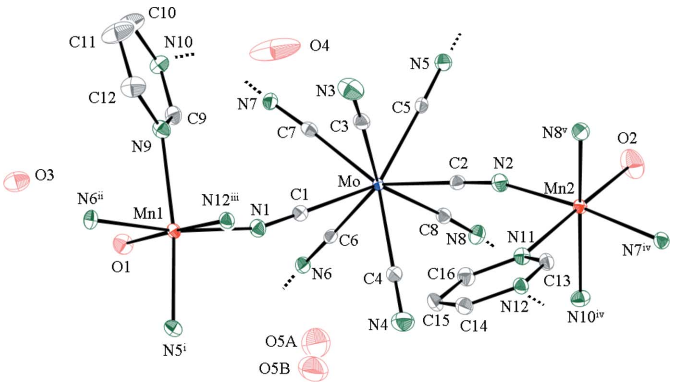


Figure 1

Part of the polymeric structure of compound (I), showing the coordination environment around the Mn and Mo atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

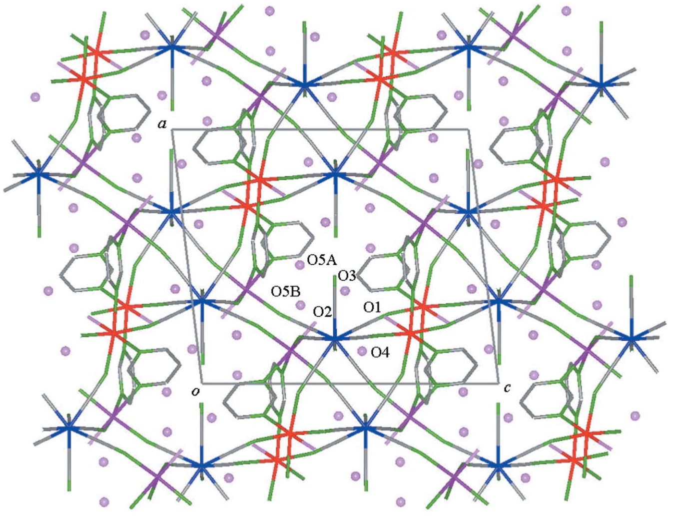


Figure 2

The crystal structure of compound (I), viewed down the *b* axis. Blue, red, dark purple, grey, green and light purple represent Mo, Mn1, Mn2, C, N and O atoms, respectively. H atoms have been omitted.

each coordinated by three cyanide N atoms, two pyrimidine N atoms and one O atom of a water molecule. The Mn atoms are connected by the pyrimidine ligands. From this arrangement, a three-dimensional coordination network is formed (Fig. 2). There are additional water molecules (O3, O4, O5) in the structure, which might be connected *via* hydrogen bonds, but their H atoms were not located in the difference map.

Experimental

Single crystals of compound (I) were prepared by slow diffusion of an aqueous solution (4 ml) containing both $MnSO_4·5H_2O$ (96.4 mg, 0.4 mmol) and pyrimidine (160.1 mg, 2 mmol) into an aqueous solution (20 ml) of $K_4[Mo(CN)_8]·2H_2O$ (99.3 mg, 0.2 mmol). After one week, yellow platelet crystals of (I) were obtained. Elemental analysis, calculated: C 28.93, H 2.73, N 25.30%; found: C 29.01, H 2.71, N 25.33%. The CN stretching vibrations are observed at 2117, 2127, 2132, 2136, 2148, 2151 and 2163 cm^{-1} in the IR spectrum. In the diffuse reflectance spectrum, absorptions at 300, 350 and 430 nm are observed. The absorption at 300 nm was assigned to a charge transfer from Mo^{IV} to the π* orbital of the cyanide group, and the others were attributed to the *d*–*d* transitions of Mo^{IV}.

Crystal data

$[Mn_2Mo(CN)_8(C_4H_4N_2)_2(H_2O)_2]·3H_2O$
M_r = 664.21
Monoclinic, $P2_1/n$
a = 13.0160 (6) Å
b = 12.8648 (4) Å
c = 15.1056 (6) Å
β = 96.7670 (19)°
V = 2511.77 (17) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.53 mm^{-1}
T = 90 (1) K
0.30 × 0.27 × 0.07 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.696, T_{max} = 0.898
24053 measured reflections
5745 independent reflections
4944 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.088
S = 1.00
4944 reflections
346 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Mo—C1	2.150 (2)	Mn1—N5^{i}	2.224 (2)
Mo—C2	2.151 (2)	Mn1—N6^{ii}	2.198 (2)
Mo—C3	2.164 (2)	Mn1—N9	2.344 (2)
Mo—C4	2.160 (2)	Mn1—N12^{iii}	2.296 (2)
Mo—C5	2.164 (2)	Mn2—O2	2.148 (2)
Mo—C6	2.152 (2)	Mn2—N2	2.158 (2)
Mo—C7	2.158 (2)	Mn2—N7^{iv}	2.207 (2)
Mo—C8	2.164 (2)	Mn2—N8^{v}	2.225 (2)
Mn1—O1	2.184 (2)	Mn2—N10^{iv}	2.349 (2)
Mn1—N1	2.176 (2)	Mn2—N11	2.329 (2)
C1—Mo—C2	113.23 (9)	O2—Mn2—N2	89.59 (9)
C1—Mo—C5	142.05 (9)	O2—Mn2—N7^{iv}	90.77 (9)
C1—Mo—C6	77.07 (9)	O2—Mn2—N8^{v}	97.26 (9)
C1—Mo—C7	77.81 (9)	O2—Mn2—N10^{iv}	92.54 (8)
C1—Mo—C8	141.55 (9)	O2—Mn2—N11	177.48 (8)
C2—Mo—C5	79.33 (9)	N2—Mn2—N7^{iv}	173.53 (8)
C2—Mo—C6	143.54 (9)	N2—Mn2—N8^{v}	98.48 (9)
C2—Mo—C7	143.50 (9)	N2—Mn2—N10^{iv}	88.87 (8)
C2—Mo—C8	79.74 (9)	N2—Mn2—N11	89.72 (8)
C5—Mo—C6	114.87 (9)	Mn1—N1—C1	164.7 (2)
C5—Mo—C7	73.09 (10)	Mn2—N2—C2	165.7 (2)
C5—Mo—C8	74.08 (9)	Mn1—N5^{i}—C5^{i}	150.0 (2)
C6—Mo—C7	71.55 (9)	Mn1—N6^{ii}—C6^{ii}	172.2 (2)
C6—Mo—C8	73.13 (9)	Mn2—N7^{iv}—C7^{iv}	170.7 (2)
C7—Mo—C8	114.01 (9)	Mn2—N8^{v}—C8^{v}	151.6 (2)
O1—Mn1—N1	91.72 (8)	Mo—C1—N1	178.6 (2)
O1—Mn1—N5^{i}	91.71 (8)	Mo—C2—N2	178.4 (2)
O1—Mn1—N6^{ii}	90.81 (8)	Mo—C3—N3	177.6 (2)
O1—Mn1—N9	83.82 (7)	Mo—C4—N4	178.5 (2)
O1—Mn1—N12^{iii}	178.04 (7)	Mo—C5—N5	178.3 (2)
N1—Mn1—N5^{i}	97.58 (8)	Mo—C6—N6	176.0 (2)
N1—Mn1—N6^{ii}	171.69 (8)	Mo—C7—N7	176.3 (2)
N1—Mn1—N9	88.14 (8)	Mo—C8—N8	177.0 (2)
N1—Mn1—N12^{iii}	88.68 (8)		

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Acta Cryst. (2007). E**63**, m1220–m1222 Kosaka *et al.* • $[Mn_2Mo(CN)_8(C_4H_4N_2)_2(H_2O)_2]·3H_2O$ **m1221**

The H atoms of the solvent water molecules could not be located. The H atoms of the coordinated water molecules were located in a difference Fourier map and refined as riding, with O—H restraints of 0.95 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(O). The H atoms of the pyrimidine molecules were placed in calculated positions, with C—H = 0.95 Å, and refined using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). Atom O5 is disordered and was refined using a split model using occupancy factors of 0.6 for O5*A* and 0.4 for O5*B*. The highest residual electron-density peak is located 1.25 Å from O5*A*.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *VESTA* (Momma & Izumi, 2006); software used to prepare material for publication: *CrystalStructure*.

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Babel, D. (1986). *Comments Mod. Chem. A, Comments Inorg. Chem.* **5**, 285–320.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Ferlay, S., Mallah, T., Ouahès, R., Veillet, P. & Verdaguer, M. (1995). *Nature (London)*, **378**, 701–703.

Hatlevik, Ø., Buschmann, W. E., Zhang, J., Manson, J. L. & Miller, J. S. (1999). *Adv. Mater.* **11**, 914–918.

Herrera, J. M., Armentano, D., de Munno, G., Lloret, F., Julve, M. & Verdaguer, M. (2003). *New J. Chem.* **27**, 128–133.

Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.

Holmes, S. M. & Girolami, G. S. (1999). *J. Am. Chem. Soc.* **121**, 5593–5594.

Ludi, A. & Güdel, H. U. (1973). *Struct. Bonding (Berlin)*, **14**, 1–21.

Margadonna, S., Prassides, K. & Fitch, A. N. (2004). *J. Am. Chem. Soc.* **126**, 15390–15391.

Miller, J. S. (2000). *Mater. Res. Soc. Bull.* **25**, 60–64.

Momma, K. & Izumi, F. (2006). *IUCr Commission on Crystallographic Computing Newsletter*, pp. 106–119.

Ohkoshi, S., Arai, K., Sato, Y. & Hashimoto, K. (2004). *Nat. Mater.* **3**, 857–861.

Ohkoshi, S., Mizuno, M., Hung, G. J. & Hashimoto, K. (2000). *J. Phys. Chem. B*, **104**, 9365–9367.

Przychodzeń, P., Korzeniak, T., Podgajny, R. & Sieklucka, B. (2006). *Coord. Chem. Rev.* **250**, 2234–2260.

Rigaku (1998). *PROCESS-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.

Rigaku (2006). *CrystalStructure*. Version 3.8. Rigaku Americas Corporation, The Woodlands, Texas, USA.

Rombaut, G., Golhen, S., Ouahab, L., Mathonière, C. & Kahn, O. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3609–3614.

Shen, L., Zhang, Y. & Uiu, J. (2006). *J. Coord. Chem.* **59**, 629–635.

Sieklucka, B., Szklarzewicz, J., Kemp, T. J. & Errington, W. (2000). *Inorg. Chem.* **39**, 5156–5158.

Sra, A. K., Andruh, M., Kahn, O., Golhen, S., Ouahab, L. & Yakhmi, J. V. (1999). *Angew. Chem. Int. Ed.* **38**, 2606–2609.

Verdaguer, M., Galvez, N., Garde, R. & Desplanches, C. (2002). *Electrochem. Soc. Interface*, **11**, 28–32.

Willemin, S., Larionova, J., Clérac, R., Donnadieu, B., Henner, B., Le Goff, X. F. & Guérin, C. (2003). *Eur. J. Inorg. Chem.* pp. 1866–1872.

Withers, J. R., Ruschmann, C., Bojang, P., Parkin, S. & Holmes, S. M. (2005). *Inorg. Chem.* **44**, 352–358.

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