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A new heterometallic complex: $[Mn(H_2O)_6][Co(dmg)_2(N_3)_2]_2{\cdot}2H_2O$, where dmg is dimethylglyoximate

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Key indicators

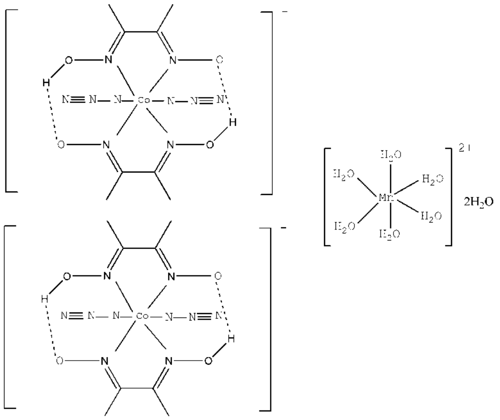
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.031
wR factor = 0.077
Data-to-parameter ratio = 13.2

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

The title heterometallic complex, hexaaquamanganese(II) bis[diazidobis(dimethylglyoximato)cobaltate(III)] dihydrate, $[Mn(H_2O)_6][Co(dmg)_2(N_3)_2]_2{\cdot}2H_2O$ (dmg = dimethylglyoximate, $C_4H_7N_2O_2$), has been synthesized. Each Co atom is surrounded by two dmg ligands and two N_3 groups in an octahedral geometry. The Mn atom is hexacoordinated by six water molecules. Each metal atom lies on a center of symmetry. The Mn-centered cation is linked to four neighboring Co1-centered anions, two Co2-centered anions and two uncoordinated water molecules through extensive intermolecular O—H···N and O—H···O hydrogen bonds, forming a three-dimensional network.

Comment

Recently, the crystal engineering of supramolecular architectures based on metal–organic building blocks has been rapidly expanding due to their new and versatile topologies and potential applications in host–guest chemistry, electrical conductivity, and magnetism (Lehn, 1995; Seo *et al.*, 2000; Oshio *et al.*, 1997). Indeed, it is now realised that weak hydrogen bonds (Steiner & Desiraju, 1998), stacking interactions (Desiraju & Gavezzotti, 1989), and halogen–halogen interactions (Desiraju & Parthasarathy, 1989) can play a significant and predictable structure-determining role. In particular, hydrogen bonds are essential for the rational design and synthesis of new extended supramolecular networks and have yielded a great variety of such frameworks with fascinating structural motifs (Park *et al.*, 2001). In view of the excellent coordination capability of the dimethylglyoximate ligand, several groups including our own have reported the syntheses and X-ray crystal structure analyses of a series of complexes of this ligand with transition metals (Zhan *et al.*, 1999; Birkelbach *et al.*, 1998; Zhang *et al.*, 2003; Liu *et al.*,



(I)

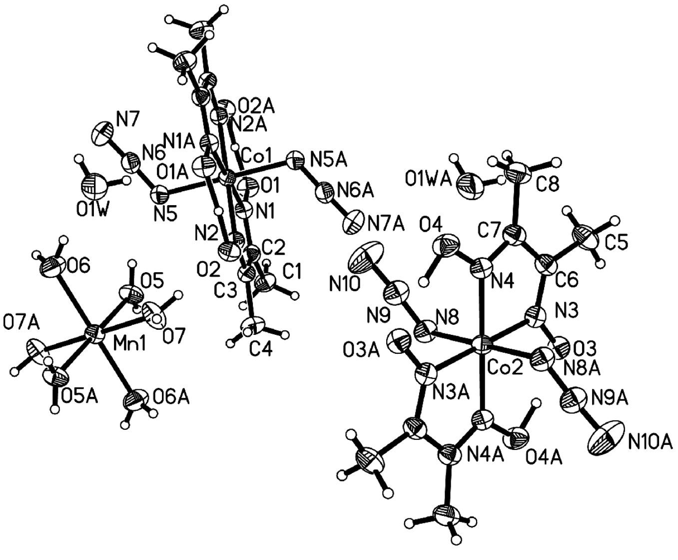


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I) with 35% probability ellipsoids, showing the atom-numbering scheme. Atoms with suffix *A* are generated from the asymmetric unit by inversion symmetry.

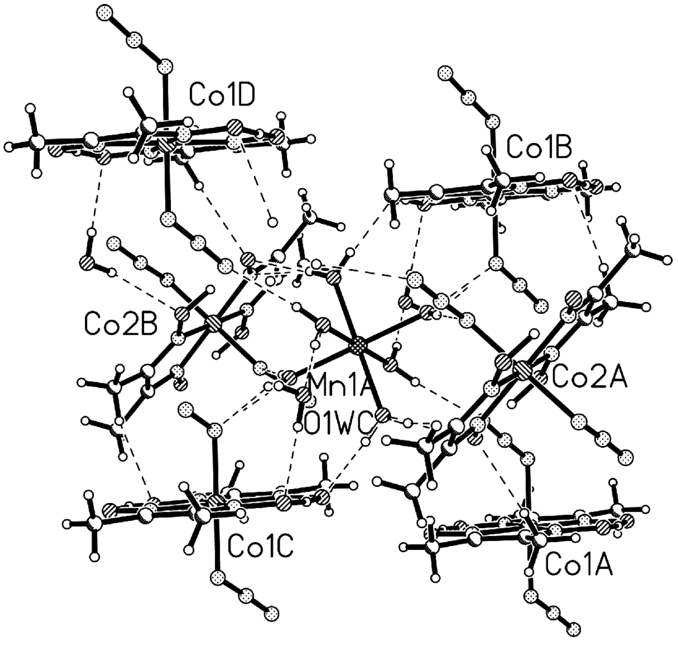


Figure 2
A view of the three-dimensional arrangement of (I), showing hydrogen bonds as dashed lines.

2002). In this present contribution, we have extended our work to design and successfully synthesize a new heretometal complex. We report in this paper the crystal structure of the title compound, (I).

Single-crystal X-ray diffraction results show that the complex (I) consists of five moieties, *viz*. an Mn-centered cation and two Co-centered anions, together with two uncoordinated water molecules. The structure of the complex (I) with the atom-numbering scheme is shown in Fig. 1. The dimethylglyoximate anions act as bidentate ligands, coordinated to Co through their N atoms. A view of the three-dimensional network is shown in Fig. 2.

There are two Co and one Mn atoms in thee unit cell, each located at a center of symmetry. Both of the Co atoms are hexacoordinated with distorted octahedral geometry. Each is surrounded by two dmg and two N_3^- ligands, where the dmg ligands are *trans* to each other, forming four Co—N bonds in the range 1.887 (2)–1.893 (2) Å, and two N_3^- ligands with Co—N bond distances of 1.964 (2) and 1.971 (2) Å. The six-coordinate Mn1 atom is surrounded by six water molecules in a distorted octahedral geometry, with Mn—O distances of 2.136 (2)–2.177 (2) Å. As can be seen from Fig. 2, each Mn-centered cation links to four Co1-centered anions, two Co2-centered anions and two uncoordinated water molecules through extensive intermolecular O—H···N and O—H···O hydrogen bonding to form a three-dimensional network. O—H···N hydrogen bonds exist between the coordinated water molecules and azide ligands, and O—H···O hydrogen bonds link coordinated and uncoordinated water molecules and dmg ligands (Table 2). Fig. 3 shows the packing arrangement of the complex.

Experimental

To a methanol solution (20 ml) containing $CoCl_2·2H_2O$ (0.5 mmol) and H_2dmg (0.5 mmol), $MnCl_2.2H_2O$ (0.5 mmol) was added. The mixture was stirred for 2 h before being left at room temperature for 30 min. The resulting red solution was filtered and allowed to evaporate at room temperature. After 3 d, dark-red crystals of the title complex suitable for X-ray analysis were obtained. They were collected by suction filtration and air-dried. All chemicals were purchased commercially and used without further purification. Because of the oxidization of the air, the Co^{II} was oxidized to Co^{III}.

Crystal data

$[Mn(H_2O)_6][Co(C_4H_7N_2O_2)_2(N_3)_2]_2·2H_2O$
$M_r = 945.51$
Triclinic, $P\overline{1}$
$a = 9.7345$ (14) Å
$b = 9.7893$ (16) Å
$c = 11.4276$ (15) Å
$\alpha = 87.225$ (10)°
$\beta = 67.328$ (9)°
$\gamma = 72.767$ (11)°
$V = 957.0$ (3) $Å^3$
$Z = 1$
$D_x = 1.641$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 34 reflections
$\theta = 5.0$–12.5°
$\mu = 1.27$ mm^{-1}
$T = 293$ (2) K
Prism, dark red
0.4 × 0.2 × 0.2 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.601$, $T_{max} = 0.774$
4022 measured reflections
3369 independent reflections
2918 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.077$
$S = 1.02$
3369 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 1.2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.32$ e $Å^{-3}$
$\Delta\rho_{min} = -0.24$ e $Å^{-3}$

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Table 1
Selected geometric parameters (Å, °).

Co1—N1	1.887 (2)	Co2—N8	1.964 (2)
Co1—N2	1.893 (2)	Mn1—O5	2.173 (2)
Co1—N5	1.971 (2)	Mn1—O6	2.177 (2)
Co2—N3	1.902 (2)	Mn1—O7	2.136 (2)
Co2—N4	1.888 (2)		
N1—Co1—N2	81.11 (9)	N4—Co2—N8	92.38 (10)
N1—Co1—N5	89.82 (10)	O5—Mn1—O6	89.31 (9)
N2—Co1—N5	87.35 (10)	O5—Mn1—O7	90.93 (8)
N3—Co2—N4	81.20 (10)	O6—Mn1—O7	91.93 (9)
N3—Co2—N8	89.07 (10)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*D*···N8$^{\mathrm{i}}$	0.85	1.99	2.836 (3)	174
O5—H5*E*···N5	0.85	2.08	2.892 (3)	159
O6—H6*A*···O1*W*	0.85	1.83	2.678 (4)	172
O6—H6*B*···N7$^{\mathrm{ii}}$	0.85	2.19	3.038 (4)	175
O7—H7*A*···O2	0.85	1.90	2.744 (3)	173
O7—H7*B*···O3$^{\mathrm{iii}}$	0.85	1.90	2.729 (3)	164
O1*W*—H1*D*···O4$^{\mathrm{iv}}$	0.85	2.33	3.138 (4)	160
O1*W*—H1*E*···O1$^{\mathrm{v}}$	0.85	2.09	2.940 (4)	178

Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, -1-y, -z$; (iii) $x, y-1, z$; (iv) $-x, -y, 1-z$; (v) $-x, -y, -z$.

H atoms of the organic ligands were positioned geometrically and the coordinates for H atoms of water were calculated using *HYDROGEN* (Nardelli, 1999). Methyl H atoms were generated theoretically with C—H = 0.96 Å and hydroxyl and water H atoms were found in a difference Fourier map. The water H atoms were moved along their bonds to give O—H distances of 0.85\%A. The H atoms were allowed to ride on their parent atoms in the final refinement, with $U_{\rm iso} = 1.5U_{\rm eq}$ for methyl H atoms and $1.2U_{\rm eq}$ for water H atoms; the displacement parameters of the hydroxyl H atoms were refined.

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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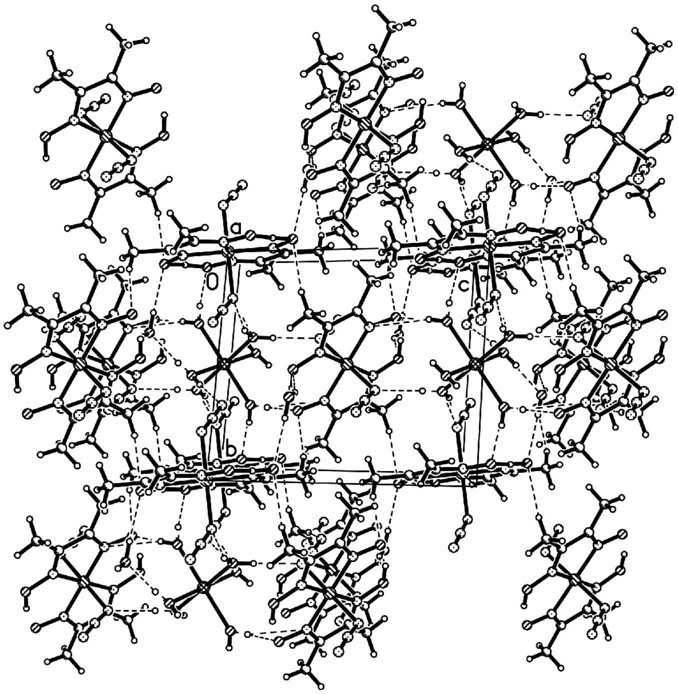

Figure 3
A view of the molecular packing, viewed down the *a* axis.

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