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Manganese(II) and cobalt(II) complexes of 1,4-bis(diphenylphosphinoyl)butane

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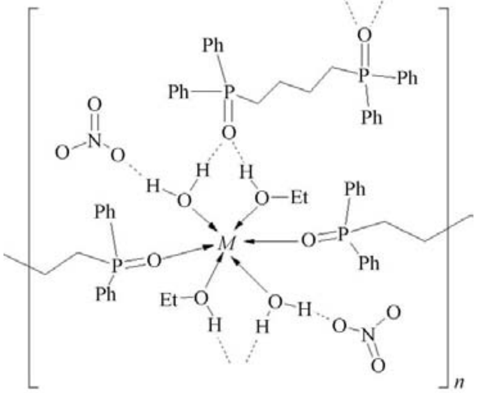
The title complexes, *catena*-poly[[[diaquadiethanolmanganese(II)]-μ-1,4-bis(diphenylphosphinoyl)butane-κ^2O:O'] dinitrate 1,4-bis(diphenylphosphinoyl)butane solvate], $\{[Mn(C_2H_6O)_2(C_{28}H_{28}O_2P_2)(H_2O)_2](NO_3)_2{\cdot}C_{28}H_{28}O_2P_2\}_n$, (I), and *catena*-poly[[[diaquadiethanolcobalt(II)]-μ-1,4-bis(diphenylphosphinoyl)butane-κ^2O:O'] dinitrate 1,4-bis(diphenylphosphinoyl)butane solvate], $\{[Co(C_2H_6O)_2(C_{28}H_{28}O_2P_2)(H_2O)_2](NO_3)_2{\cdot}C_{28}H_{28}O_2P_2\}_n$, (II), are isostructural and centrosymmetric, with the M^{II} ions at centres of inversion. The coordination geometry is octahedral, with each metal ion coordinated by two *trans* ethanol molecules, two *trans* water molecules and two bridging 1,4-bis(diphenylphosphinoyl)butane ligands which link the coordination centres to form one-dimensional polymeric chains. Parallel chains are linked by hydrogen bonds to uncoordinated 1,4-bis(diphenylphosphinoyl)butane molecules, which are bisected by a centre of inversion. Further hydrogen bonds, weak C—H$\cdots$O interactions to nitrate anions, and weak C—H$\cdots\pi$ interactions serve to stabilize the structure. This study reports a development of the coordination chemistry of bis(diphenylphosphinoyl)alkanes, with the first reported structures of complexes of the first-row transition metals with 1,4-bis(diphenylphosphinoyl)butane.

Comment

In combination with various transition metals, 1,4-bis(diphenylphosphino)butane (dppb) has proved to be an effective catalyst for many organic reactions (see, for example, Bogado *et al.*, 2003; Farnetti & Marsich, 2004; Sundermeier *et al.*, 2003). Because of these catalytic effects, the coordination chemistry of dppb has received much attention. Although there are many structurally characterized examples of dppb complexes of the transition metals [for example: Ni^{II} (Câmpian *et al.*, 2007), Ag^{I} (Aslanidis *et al.*, 2004) and Ru^{II} (Brito *et al.*, 2007)], the oxidized form of the ligand, 1,4-bis(diphenylphosphinoyl)butane (dppbO$_2$) has received little attention. There are examples of dppbO$_2$ coordination to the lanthanides (Spichal *et al.*, 2006) and to tin (Teo *et al.*, 2008), and there are examples of 1,3-bis(diphenylphosphinoyl)propane (dpppO$_2$) coordination to Co^{II} (Harding *et al.*, 2007) and Cu^{II} (Platt & Lees, 2007), but to date there are no characterized examples of dppbO$_2$ coordination to the *d*-block elements. We report here the first examples of the coordination of dppbO$_2$ to the first-row transition metals.



(I) M = Mn
(II) M = Co

The structures of (I) and (II), *viz.* $\{trans\text{-}[M(EtOH)_2(\mu\text{-dppbO}_2)(H_2O)_2](NO_3)_2{\cdot}\text{dppbO}_2\}_n$, are essentially isomorphous. The structures are centrosymmetric and the coordination geometry is octahedral, MO_6, with the M^{II} ions located on centres of inversion. Each metal ion is coordinated by two ethanol molecules, two water molecules and two bridging dppbO$_2$ ligands in an all-*trans* configuration to form one-dimensional polymeric chains. Parallel chains are linked by hydrogen bonds to uncoordinated dppbO$_2$ molecules. M—O bond lengths [2.111 (1)–2.242 (2) Å for Mn and 2.045 (2)–2.147 (2) Å for Co] are typical of those of other octahedrally coordinated O-donor Mn^{II} and Co^{II} complexes, for example, $[Mn(C_{14}H_8N_2O_6)(H_2O)_4]_n$ [2.141 (2)–2.226 (2) Å; Tang *et al.*, 2007], $[Mn(C_{10}H_8O_5S)(H_2O)_4]_n$ [2.153 (2)–2.244 (2) Å; Su *et al.*, 2006], $\{[Co(C_8H_7NO_2)_2(H_2O)_2](NO_3)_2\}_n$ [2.063 (1)–2.108 (1) Å; Domasevitch, 2008] and $[Co(dbm)_2(\mu\text{-dppeO}_2)]_n$ [dbm is 1,3-diphenylpropane-1,3-dionate and dppeO$_2$ is 1,2-bis(diphenylphosphinoyl)ethane] [2.153 (2)–2.244 (2) Å; Harding *et al.*, 2007].

The coordination geometries of the M^{II} ions each show elongation along one axis. Both complexes show similar elongation along the axis of the *trans*-coordinated water molecules, *viz.* O3—Co—O3($1-x, 1-y, 1-z$). Lengthening of these bonds is consistent with the water molecules being hydrogen bonded to adjacent phosphine oxide groups (O3—H3$A\cdots$O7) and nitrate anions (O3—H3$A\cdots$O6). Such elongation is also consistent with Jahn–Teller distortion, and this may be expected to be observed in complexes of the Co^{II} d^7 ion. For the Mn^{II} d^5 ion, however, Jahn–Teller effects are not expected to be significant. The greater distortion observed in the Mn^{II} complex is attributed to the role of hydrogen bonding having a greater influence over the generally weaker M—O bonds in the Mn complex. All M—O bonds are longer in the Mn complex than the Co complex, in keeping with the

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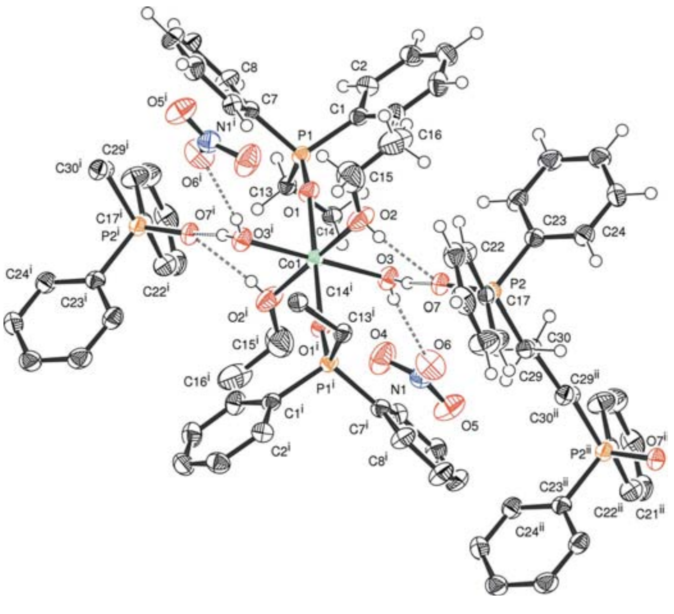

Figure 1
A view of (II), showing the atom-labelling scheme. Compound (I) is isostructural. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii and have been omitted from symmetry-generated atoms for clarity. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, 1 - y, 1 - z$.]

Irving–Williams series, which indicates stability in the order Mn < Fe < Co.

The metal centres are linked by bridging dppbO$_2$ ligands, which are bisected by an inversion centre. The aliphatic chains of the dppbO$_2$ ligands adopt an all-*anti* conformation, aligning the P=O groups in a strict antiparallel arrangement which affords the linear propagation of the coordination polymer along the crystallographic *b* axis. Adjacent chains are linked *via* hydrogen bonds to form a two-dimensional network running parallel to the (001) plane.

The hydrogen-bonding network consists of classical O—H$\cdots$O hydrogen bonds and C—H$\cdots$O interactions. One hydrogen bond, O3—H3*B*$\cdots$O6, binds the nitrate ion to a coordinated water molecule. Two other hydrogen bonds, O3—H3*A*$\cdots$O7 and O2—H2*E*$\cdots$O7, are the primary means of attachment of the uncoordinated dppbO$_2$ molecules which form the link between the parallel polymeric chains. Weaker C—H$\cdots$O interactions serve to stabilize further both the position of the nitrate ion within the structure and the orientation of the dppbO$_2$ molecules. The hydrogen-bonding parameters for (I) are given in Table 2, and those for (II) are given in Table 4.

Weak methylene–phenyl and phenyl–phenyl (edge-to-face) C—H$\cdots\pi$ interactions, with H$\cdots\pi$ (centroid) distances of 2.83 and 2.79 Å, respectively, in (I), and 2.80 and 2.76 Å, respectively, in (II), stabilize the arrangements between polymer chains and dppbO$_2$ molecules within the (001) sheets. In the first of these interactions, methylene atom C29 acts as donor, *via* atom H29*B*, to the C7–C12 ring at $(1 - x, 1 - y, 1 - z)$. In the second interaction, phenyl atom C21 acts as donor, *via* atom H21, to the C1–C6 ring at $(x, -1 + y, z)$. The stacking of the (001) sheets is stabilized by two further C—H$\cdots\pi$ interactions: a phenyl–phenyl (edge-to-face) interaction between neighbouring dppbO$_2$ molecules, with H$\cdots\pi$ (centroid) distances of 2.90 [in (I)] and 2.89 Å [in (II)], and a methyl–phenyl interaction between adjacent polymeric chains, with H$\cdots\pi$ (centroid) distances of 2.91 [in (I)] and 2.96 Å [in (II)]. In the phenyl–phenyl interaction, atom C26 acts as donor, *via* atom H26, to the C17–C22 ring at $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$, and in the methyl–phenyl interaction, atom C16 acts as donor, *via* atom H16*B*, to the C1–C6 ring at $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$. The observed H$\cdots\pi$ (centroid) distances for the four interactions in both structures (2.76–2.96 Å) are markedly shorter than those reported for similar interactions in the solid-state alkyl bis-diphenylphosphine oxides (3.00–3.65 Å; Calcagno *et al.*, 2000). We attribute this to the effects of both coordinate bonding to the metal atoms and intramolecular hydrogen bonding stabilizing the dppbO$_2$ molecules in closer proximity.

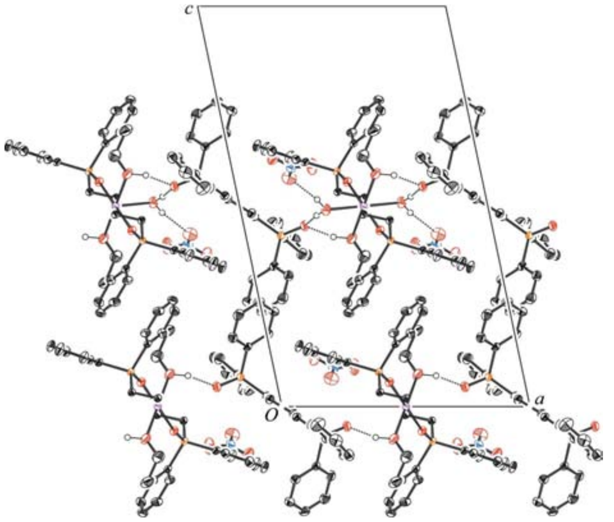

Figure 2
The molecular packing in (I), viewed normal to the (010) plane, showing intermolecular hydrogen bonds parallel to the (001) plane and the edge-to-face alignment of phenyl rings between chains along the *c* axis. Only selected H atoms are shown for clarity. The packing in (II) is similar.

Experimental

The hydrated metal nitrate, Mn(NO$_3$)$_2$·4H$_2$O (250 mg, 1.0 mmol) or Co(NO$_3$)$_2$·4H$_2$O (290 mg, 1.0 mmol), was dissolved in ethanol (10 ml). The solution was heated and mixed with a hot solution of dppbO$_2$ (920 mg, 2.0 mmol) in ethanol (20 ml). Slow evaporation of the resulting solutions led to the formation of crystals suitable for X-ray diffraction studies.

Compound (I)

Crystal data

[Mn(C$_2$H$_6$O)$_2$(C$_{28}$H$_{28}$O$_2$P$_2$)-(H$_2$O)$_2$](NO$_3$)$_2$·C$_{28}$H$_{28}$O$_2$P$_2$
M_r = 1224.02
Monoclinic, $P2_1/c$
a = 13.4134 (3) Å
b = 10.3270 (3) Å
c = 22.1028 (6) Å
β = 101.9000 (10)°
V = 2995.88 (14) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 120 (2) K
0.24 × 0.22 × 0.03 mm

Table 1
Selected geometric parameters (Å, °) for (I).

Mn1—O1	2.1109 (14)	P1—O1	1.4964 (15)
Mn1—O2	2.1998 (17)	P2—O7	1.5036 (16)
Mn1—O3	2.2415 (16)		
O1—Mn1—O1^{i}	180.0	O2—Mn1—O2^{i}	180.0
O1—Mn1—O2	88.84 (6)	O2—Mn1—O3	83.16 (7)
O1—Mn1—O2^{i}	91.16 (6)	O2—Mn1—O3^{i}	96.84 (7)
O1—Mn1—O3	93.28 (6)	O3^{i}—Mn1—O3	180.00 (10)
O1^{i}—Mn1—O3	86.72 (6)		

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

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*E*···O7	1.06 (4)	1.67 (4)	2.652 (2)	152 (3)
O3—H3*A*···O7	0.88 (4)	1.93 (4)	2.784 (2)	163 (4)
O3—H3*B*···O6	0.88 (4)	1.99 (4)	2.828 (3)	159 (4)
C8—H8···O4^{ii}	0.95	2.52	3.465 (3)	177
C12—H12···O6^{i}	0.95	2.64	3.271 (3)	124
C13—H13*B*···O4^{ii}	0.99	2.33	3.310 (3)	171
C24—H24···O5^{iii}	0.95	2.49	3.387 (3)	158
C30—H30*A*···O6	0.99	2.58	3.500 (3)	155

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y+1, -z+1$.

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.912$, $T_{\max} = 0.988$
40734 measured reflections
6856 independent reflections
5673 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.111$
$S = 1.05$
6856 reflections
382 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{\max} = 0.71$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}

Compound (II)

Crystal data

$[Co(C_2H_6O)_2(C_{28}H_{28}O_2P_2)(H_2O)_2](NO_3)_2 \cdot C_{28}H_{28}O_2P_2$
$M_r = 1228.01$
Monoclinic, $P2_1/c$
$a = 13.3646$ (5) Å
$b = 10.2517$ (5) Å
$c = 22.0744$ (11) Å
$\beta = 101.920$ (3)°
$V = 2959.2$ (2) Å^3
$Z = 2$
Mo *K*α radiation
$\mu = 0.47$ mm^{-1}
$T = 120$ (2) K
0.16 × 0.14 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.929$, $T_{\max} = 0.986$
36332 measured reflections
6806 independent reflections
4594 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.093$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.135$
$S = 1.03$
6806 reflections
382 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

Co1—O1	2.045 (2)	P1—O1	1.492 (2)
Co1—O2	2.097 (3)	P2—O7	1.500 (2)
Co1—O3	2.147 (2)		
O1—Co1—O1^{i}	180.0	O2—Co1—O2^{i}	180.0
O1—Co1—O2	88.46 (10)	O2—Co1—O3	84.30 (11)
O1—Co1—O2^{i}	91.54 (10)	O2—Co1—O3^{i}	95.70 (11)
O1—Co1—O3	92.75 (9)	O3—Co1—O3^{i}	180.00 (15)
O1^{i}—Co1—O3	87.25 (9)		

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

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*E*···O7	0.68 (5)	2.01 (5)	2.660 (4)	163 (6)
O3—H3*A*···O7	0.82 (5)	1.97 (5)	2.774 (3)	166 (5)
O3—H3*B*···O6	0.74 (5)	2.13 (5)	2.832 (4)	157 (5)
C8—H8···O4^{ii}	0.95	2.47	3.418 (4)	178
C12—H12···O6^{i}	0.95	2.58	3.224 (4)	126
C13—H13*B*···O4^{ii}	0.99	2.32	3.292 (4)	169
C24—H24···O5^{iii}	0.95	2.48	3.383 (4)	158
C30—H30*A*···O6	0.99	2.61	3.541 (4)	157

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y+1, -z+1$.

All C-bound H atoms were refined isotropically in idealized positions, with aromatic C—H = 0.95 Å, methylene C—H = 0.99 Å and methyl C—H = 0.98 Å, and were constrained to ride on their parent atoms. The H atoms of each functional group were assigned a common refined isotropic displacement parameter. O-bound H atoms were located in a difference map and refined isotropically with a common isotropic displacement parameter.

For both compounds, data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3094). Services for accessing these data are described at the back of the journal.

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