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catena-Poly[[bis(ethanol-κO)manganese(II)]-μ-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olato)-$\kappa^4O^1,O^6:O^3,O^4$]

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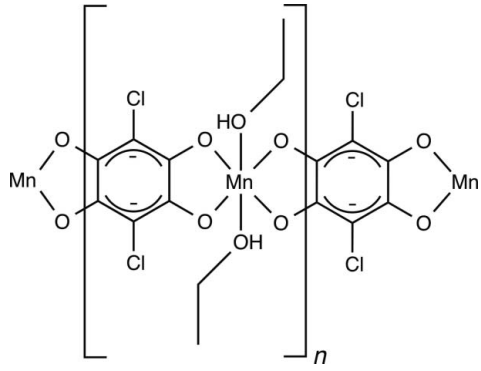
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.003 Å; R factor = 0.032; wR factor = 0.095; data-to-parameter ratio = 16.5.

In the title coordination polymer, $[Mn(C_6Cl_2O_4)(C_2H_5OH)_2]_n$, the Mn^{II} atom and the chloranilate [systematic name: 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate)] ion lie on crystallographic inversion centers. The geometry around the Mn^{II} atom is a distorted octahedron involving four O atoms of two chloranilate ions and two O atoms from two ethanol molecules. The chloranilate ion serves as a bridging ligand between the Mn^{II} ions, leading to an infinite linear chain along the b-axis direction. The chains are linked by O—H···O hydrogen bonds between the apically coordinating ethanol molecule and the chloranilate ion, affording a two-dimensional layer expanding parallel to the ab plane.

Related literature

For metal complexes of chloranilic acid, see: Kawata *et al.* (1995, 1998); Kitagawa *et al.* (1996); Kitagawa & Kawata (2002); Abrahams *et al.* (2011).



Experimental

Crystal data

$[Mn(C_6Cl_2O_4)(C_2H_6O)_2]$
M_r = 354.05
Triclinic, $P\overline{1}$
a = 5.0784 (5) Å
b = 8.1255 (8) Å
c = 8.9003 (9) Å
α = 102.718 (4)°
β = 105.175 (5)°
γ = 101.092 (3)°
V = 333.35 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.41 mm^{-1}
T = 200 K
0.50 × 0.25 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min} = 0.406, T_{max} = 0.869
3298 measured reflections
1534 independent reflections
1434 reflections with $I > 2\sigma(I)$
R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.095
S = 1.17
1534 reflections
93 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—O1	2.1884 (13)	Mn1—O3	2.2042 (16)
Mn1—O2	2.1491 (11)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O1^{i}	0.76 (4)	2.07 (3)	2.8200 (17)	167 (4)

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

Data collection: *RAPID-AUTO* (Rigaku, 2002); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalStructure*; software used to prepare material for publication: *CrystalStructure* (Rigaku, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: IS5335).

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supporting information

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catena-Poly[[bis(ethanol-κO)manganese(II)]-μ-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olato)-$\kappa^4O^1,O^6:O^3,O^4$]

Seiya Tanaka, Akiko Himegi, Tomomi Ohishi, Akira Fuyuhiro and Satoshi Kawata

S1. Comment

Benzoquinones and their derivatives have been used and known as bis-bidentate ligands and are good candidates to provide transition metal coordination polymers (Kawata *et al.*, 1995, 1998; Kitagawa *et al.*, 1996; Kitagawa & Kawata, 2002; Abrahams *et al.*, 2011). The background of this chemistry prompts us to utilize chloranilate (CA) chains of Mn as a building block for high dimensional structures. We have succeeded in the synthesis and characterization of a one-dimensional coordination polymer having a hydrogen-bonding link, $[Mn(CA)(EtOH)_2]_n$ (Fig. 1). The four O atoms of the CA^{2-} anion and the Mn^{II} atom form a basal plane, because the Mn—O distances [2.1884 (13) and 2.1491 (11) Å] are shorter than the two apical Mn—O(EtOH) distances [2.2042 (16) Å]. The hydrogen-bond donor EtOH serves as a woof in the synthesis of a woven polymer: the straight one-dimensional $[Mn(CA)(EtOH)_2]_n$ chains are linked by two hydrogen bonds [O3—H1···O1 distance: 2.8200 (17) Å] between the apically coordinated EtOH molecule and the O atom of CA^{2-} anion in the nearest neighbor chain to afford a two-dimensional layer (Fig. 2). A similar hydrogen bond is also found between O atoms of water molecules and CA^{2-} anion in $[Mn(CA)(H_2O)_2(phz)]_n$ (Kawata *et al.*, 1998), where the straight chains are linked by hydrogen bonds [2.751 (2) Å] shorter than those in the title compound. The inter-chain hydrogen bonds lead to short nearest neighbor Mn···Mn distances [5.6784 (5) Å], and the geometry of the two-dimensional sheet can be regarded as a rectangular array of manganese atoms. The title complex is a good example of lattice structures formed by hydrogen bonds. The fabrication of two-dimensional polymers from warp and woof components has been shown to be quite useful in the construction of tetragonal Mn lattices. This concept can also be applied to a wide variety of compounds having square lattices.

S2. Experimental

Aqueous solution of $MnCl_2{\cdot}4H_2O$ (5 ml, 30 mmolL^{-1}) was transferred to a glass tube, and ethanolic solution of H_2CA (5 ml, 90 mmolL^{-1}) was poured into the glass tube without mixing the solutions. Green crystals began to form at ambient temperature within one week.

S3. Refinement

The C-bound H atoms in the ethanol molecule were placed at calculated positions with C—H = 0.98 or 0.99 Å, and were treated as riding on their parent atoms with U_{iso}(H) set to 1.2U_{eq}(C). The O-bound H atom in the ethanol molecule was located in a difference Fourier map and refined freely.

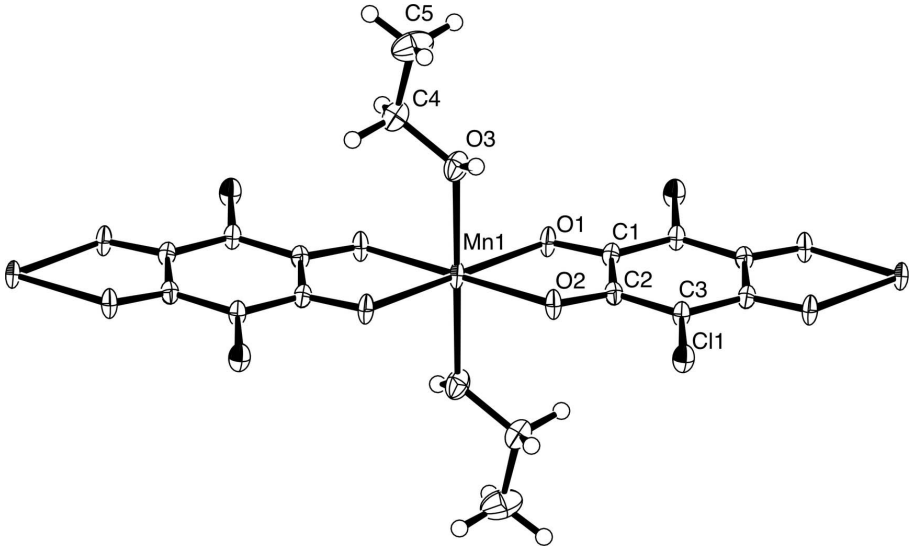

Figure 1

An *ORTEP* drawing of the title complex, showing 50% probability displacement ellipsoids.

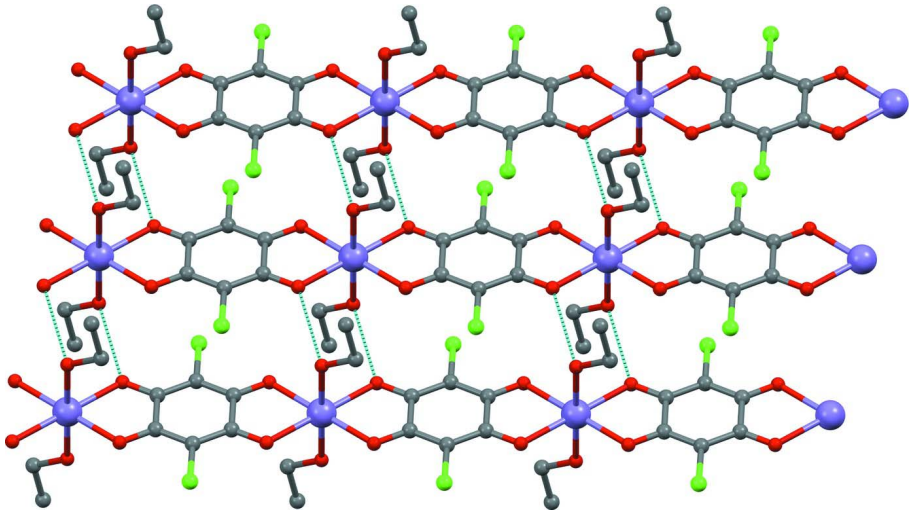

Figure 2

A packing view of the title compound, showing a two-dimensional structure. Blue lines indicate O—H···O hydrogen bonds. H atoms have been omitted for clarity.

catena-Poly[[bis(ethanol-_κO_)manganese(II)]-_μ_-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olato)-_κ_^{4}_O_^{1},_O_^{6}:_O_^{3},_O_^{4}]

Crystal data

$[Mn(C_6Cl_2O_4)(C_2H_6O)_2]$
M_r = 354.05
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 5.0784 (5) Å
b = 8.1255 (8) Å
c = 8.9003 (9) Å
α = 102.718 (4)°
β = 105.175 (5)°
γ = 101.092 (3)°
V = 333.35 (6) Å^3
Z = 1
$F(000)$ = 179.00
D_x = 1.764 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 3040 reflections

θ = 3.1–27.5°
μ = 1.41 mm^{-1}
T = 200 K

Block, green
0.50 × 0.25 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID II diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)
T_{min} = 0.406, T_{max} = 0.869
3298 measured reflections

1534 independent reflections
1434 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.029
θ_{max} = 27.5°
h = −6→6
k = −10→9
l = −11→11

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.095
S = 1.17
1534 reflections
93 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.0437P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}

Special details

Refinement. Refinement was performed using all reflections. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	1.0000	1.0000	0.0000	0.01772 (15)
Cl1	0.38362 (8)	0.36866 (5)	−0.26023 (5)	0.02047 (16)
O1	1.2640 (3)	0.84608 (14)	0.10826 (15)	0.0196 (3)
O2	0.7400 (3)	0.73489 (15)	−0.09699 (15)	0.0197 (3)
O3	0.8359 (3)	1.03778 (16)	0.20763 (16)	0.0256 (3)
C1	1.1523 (3)	0.68293 (19)	0.06530 (18)	0.0154 (3)
C2	0.8514 (3)	0.6189 (2)	−0.05794 (18)	0.0152 (3)
C3	0.7193 (4)	0.43901 (19)	−0.11994 (19)	0.0162 (3)
C4	0.8660 (5)	1.2048 (3)	0.3176 (3)	0.0278 (4)
C5	0.7319 (5)	1.1860 (4)	0.4470 (3)	0.0426 (6)
H1	0.691 (7)	0.975 (4)	0.187 (4)	0.049 (8)*
H4A	0.7772	1.2778	0.2552	0.0334*
H4B	1.0697	1.2656	0.3696	0.0334*
H5A	0.5295	1.1279	0.3960	0.0511*
H5B	0.7570	1.3021	0.5189	0.0511*
H5C	0.8219	1.1158	0.5104	0.0511*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0186 (3)	0.0085 (2)	0.0267 (3)	0.00490 (15)	0.00650 (16)	0.00590 (15)
Cl1	0.0161 (3)	0.0159 (3)	0.0247 (3)	0.00325 (16)	0.00050 (17)	0.00448 (17)
O1	0.0177 (6)	0.0086 (5)	0.0296 (7)	0.0025 (5)	0.0034 (5)	0.0055 (5)
O2	0.0183 (6)	0.0107 (6)	0.0296 (7)	0.0049 (5)	0.0041 (5)	0.0078 (5)
O3	0.0236 (7)	0.0177 (6)	0.0340 (7)	0.0020 (6)	0.0125 (6)	0.0037 (5)
C1	0.0157 (8)	0.0110 (7)	0.0204 (8)	0.0039 (6)	0.0071 (6)	0.0043 (6)
C2	0.0149 (7)	0.0128 (7)	0.0204 (8)	0.0051 (6)	0.0069 (6)	0.0065 (6)
C3	0.0148 (7)	0.0109 (7)	0.0215 (8)	0.0035 (6)	0.0033 (6)	0.0049 (6)
C4	0.0275 (10)	0.0221 (9)	0.0308 (10)	0.0060 (7)	0.0092 (8)	0.0022 (7)
C5	0.0331 (11)	0.0515 (14)	0.0345 (12)	0.0023 (10)	0.0145 (9)	−0.0018 (10)

Geometric parameters (Å, º)

Mn1—O1	2.1884 (13)	C1—C2	1.5410 (19)
Mn1—O1^{i}	2.1884 (13)	C1—C3^{ii}	1.392 (3)
Mn1—O2	2.1491 (11)	C2—C3	1.402 (2)
Mn1—O2^{i}	2.1491 (11)	C4—C5	1.504 (4)
Mn1—O3	2.2042 (16)	O3—H1	0.76 (3)
Mn1—O3^{i}	2.2042 (16)	C4—H4A	0.990
Cl1—C3	1.7285 (15)	C4—H4B	0.990
O1—C1	1.2646 (18)	C5—H5A	0.980
O2—C2	1.255 (3)	C5—H5B	0.980
O3—C4	1.442 (3)	C5—H5C	0.980
O1—Mn1—O1^{i}	180.00 (7)	O2—C2—C1	116.48 (13)
O1—Mn1—O2	75.40 (5)	O2—C2—C3	124.00 (13)
O1—Mn1—O2^{i}	104.60 (5)	C1—C2—C3	119.52 (15)
O1—Mn1—O3	89.94 (6)	Cl1—C3—C1^{ii}	119.54 (10)
O1—Mn1—O3^{i}	90.06 (6)	Cl1—C3—C2	119.10 (13)
O1^{i}—Mn1—O2	104.60 (5)	C1^{ii}—C3—C2	121.29 (13)
O1^{i}—Mn1—O2^{i}	75.40 (5)	O3—C4—C5	112.07 (17)
O1^{i}—Mn1—O3	90.06 (6)	Mn1—O3—H1	112 (3)
O1^{i}—Mn1—O3^{i}	89.94 (6)	C4—O3—H1	112 (3)
O2—Mn1—O2^{i}	180.00 (8)	O3—C4—H4A	109.195
O2—Mn1—O3	90.47 (5)	O3—C4—H4B	109.194
O2—Mn1—O3^{i}	89.53 (5)	C5—C4—H4A	109.198
O2^{i}—Mn1—O3	89.53 (5)	C5—C4—H4B	109.199
O2^{i}—Mn1—O3^{i}	90.47 (5)	H4A—C4—H4B	107.893
O3—Mn1—O3^{i}	180.00 (7)	C4—C5—H5A	109.468
Mn1—O1—C1	115.42 (10)	C4—C5—H5B	109.470
Mn1—O2—C2	116.70 (9)	C4—C5—H5C	109.467
Mn1—O3—C4	125.08 (13)	H5A—C5—H5B	109.476
O1—C1—C2	115.83 (15)	H5A—C5—H5C	109.471
O1—C1—C3^{ii}	125.09 (13)	H5B—C5—H5C	109.475
C2—C1—C3^{ii}	119.07 (13)		

O1—Mn1—O2—C2	−3.21 (9)	O3—Mn1—O2^{i}—C2^{i}	−86.98 (10)
O2—Mn1—O1—C1	0.99 (9)	O2^{i}—Mn1—O3^{i}—C4^{i}	165.27 (10)
O1—Mn1—O2^{i}—C2^{i}	−176.79 (9)	O3^{i}—Mn1—O2^{i}—C2^{i}	93.02 (10)
O2^{i}—Mn1—O1—C1	−179.01 (9)	Mn1—O1—C1—C2	0.92 (19)
O1—Mn1—O3—C4	119.34 (10)	Mn1—O1—C1—C3^{ii}	−179.43 (11)
O3—Mn1—O1—C1	91.49 (10)	Mn1—O2—C2—C1	4.67 (19)
O1—Mn1—O3^{i}—C4^{i}	60.66 (10)	Mn1—O2—C2—C3	−175.03 (11)
O3^{i}—Mn1—O1—C1	−88.51 (10)	Mn1—O3—C4—C5	−179.70 (9)
O1^{i}—Mn1—O2—C2	176.79 (9)	O1—C1—C2—O2	−3.8 (3)
O2—Mn1—O1^{i}—C1^{i}	179.01 (9)	O1—C1—C2—C3	175.92 (15)
O1^{i}—Mn1—O2^{i}—C2^{i}	3.21 (9)	O1—C1—C3^{ii}—Cl1^{ii}	1.2 (3)
O2^{i}—Mn1—O1^{i}—C1^{i}	−0.99 (9)	O1—C1—C3^{ii}—C2^{ii}	−175.82 (16)
O1^{i}—Mn1—O3—C4	−60.66 (10)	C2—C1—C3^{ii}—Cl1^{ii}	−179.14 (13)
O3—Mn1—O1^{i}—C1^{i}	88.51 (10)	C2—C1—C3^{ii}—C2^{ii}	3.8 (3)
O1^{i}—Mn1—O3^{i}—C4^{i}	−119.34 (10)	C3^{ii}—C1—C2—O2	176.54 (15)
O3^{i}—Mn1—O1^{i}—C1^{i}	−91.49 (10)	C3^{ii}—C1—C2—C3	−3.7 (3)
O2—Mn1—O3—C4	−165.27 (10)	O2—C2—C3—Cl1	0.6 (3)
O3—Mn1—O2—C2	−93.02 (10)	O2—C2—C3—C1^{ii}	−176.48 (16)
O2—Mn1—O3^{i}—C4^{i}	−14.73 (10)	C1—C2—C3—Cl1	−179.11 (13)
O3^{i}—Mn1—O2—C2	86.98 (10)	C1—C2—C3—C1^{ii}	3.8 (3)
O2^{i}—Mn1—O3—C4	14.73 (10)		

Symmetry codes: (i) −*x*+2, −*y*+2, −*z*; (ii) −*x*+2, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O1^{iii}	0.76 (4)	2.07 (3)	2.8200 (17)	167 (4)

Symmetry code: (iii) *x*−1, *y*, *z*.