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trans-Diaquadichloridobis(*N*,*N*-dimethylformamide-κ*O*)manganese(II)

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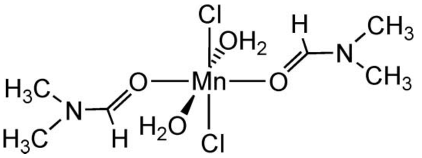
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(N–C) = 0.001 Å; R factor = 0.017; wR factor = 0.051; data-to-parameter ratio = 30.8.

The title complex, $[MnCl_2(C_3H_7NO)_2(H_2O)_2]$, was obtained upon dissolution of a dimethoxyethane adduct of $MnCl_2$ in *N*,*N*-dimethylformamide. In the crystal structure, each Mn^{II} ion is located on a crystallographic inversion center, coordinated by two Cl [Mn—Cl = 2.53423 (17) Å] and four O [Mn—O = 2.1847 (5) and 2.2199 (6) Å] atoms in a distorted octahedral geometry. The complexes are linked into chains by complementary pairs of O—H⋯Cl hydrogen bonds. Adjacent chains pack *via* weaker O—H⋯Cl interactions or by interdigitation of —NMe_2 groups. The H atoms of two symmetry-related methyl groups are disordered between two orientations in a 0.51:0.49 ratio.

Related literature

For the initial synthesis and characterization of the title compound and its precursor, see: Kim *et al.* (1981, 1985); Fowles *et al.* (1969). For recent examples of related coordination polymers, see: Chan *et al.* (2007); Deng *et al.* (2007).



Experimental

Crystal data

$[MnCl_2(C_3H_7NO)_2(H_2O)_2]$
M_r = 308.06
Triclinic, $P\overline{1}$
a = 6.1224 (1) Å
b = 6.8021 (1) Å
c = 8.7056 (1) Å
α = 110.539 (1)°
β = 105.431 (1)°
γ = 94.732 (1)°
V = 320.99 (1) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 1.44 mm^{-1}
T = 298 (2) K
0.48 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.534, T_{max} = 0.746
10584 measured reflections
2435 independent reflections
2300 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017
$wR(F^2)$ = 0.051
S = 1.06
2435 reflections
79 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H11⋯Cl1^{i}	0.830 (8)	2.314 (9)	3.1424 (6)	177.2 (13)
O1—H12⋯Cl1^{ii}	0.846 (8)	2.543 (9)	3.3505 (6)	159.9 (13)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2357).

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supplementary materials

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trans-Diaquadichloridobis(*N*,*N*-dimethylformamide-*κO*)manganese(II)

I. M. Sluch and **L. M. Slaughter**

Comment

Kim *et al.* (1981) reported that [$MnCl_2(H_2O)_2(C_3H_7NO)_2$] crystallized from solutions of $MnCl_2$ in water—*N*,*N*-dimethylformamide (DMF) mixtures containing greater than 10.4% DMF by mass, with [$MnCl_2(H_2O)_4$] becoming predominant at lower DMF concentrations. These authors characterized the complex by elemental analysis, thermal analysis, and infrared spectroscopy (Kim *et al.*, 1985), but no structural data or other subsequent studies have been reported.

The title compound, (I), is centrosymmetric with all-*trans* stereochemistry about the metal center (Fig. 1), reflecting the absence of any high-field ligand that would disfavor such an arrangement. The DMF ligands are *O*-bound as previously proposed on the basis of infrared spectral data (Kim *et al.*, 1981). The Mn—O distances of 2.2199 (6) Å (H_2O) and 2.1847 (5) Å (DMF) and the Mn—Cl distance of 2.53423 (17) Å are normal for Mn^{II} complexes, and the angles between coordinated atoms are in the range 90.080 (17)—92.903 (17)°. Molecules of (I) form hydrogen-bonded chains along the crystallographic *a* axis *via* complementary pairs of O—H···Cl interactions with O···Cl separations of 3.1424 (6) Å (Fig. 2). Weaker complementary O—H···Cl hydrogen bonds with O···Cl distances of 3.3505 (6) Å connect neighboring chains in the *b* direction. The —NMe_2 groups are interdigitated with those of adjacent complexes lying along the [101] and [111] directions.

Although DMF complexes of first row transition metals are not as well known as complexes of other common donor solvents, some interesting examples of Mn^{II} coordination polymers containing *O*-bound DMF have recently appeared (Chan *et al.*, 2007; Deng *et al.*, 2007), suggesting that DMF is a useful ligand for stabilizing Mn^{II}.

Experimental

A sample of 10 mg of the dimethoxyethane adduct of $MnCl_2$, [$MnCl_2(C_4H_{10}O_2)$] (Fowles *et al.*, 1969) was dissolved in wet *N*,*N*-dimethylformamide, and the solution was allowed to slowly evaporate. Over the course of 3 weeks, clusters of pale pink, rodlike crystals formed. The specimen used in this study was excized from a longer rod and mounted on a glass fiber for *x*-ray diffraction analysis. The crystals were washed with hexanes and dried prior to melting point determination and analysis by IR spectroscopy. These characterization data matched those previously reported reported for (I) (Kim *et al.*, 1981; Kim *et al.*, 1985).

Refinement

The amide C—H distance was fixed at 0.93 Å and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were located in the difference Fourier map. The O—H distances were restrained to 0.85 (1) Å with $U_{iso}(H) = 1.5U_{eq}(O)$, and the other positional parameters were allowed to refine freely. Use of a longer O—H distance of 0.95 (1) Å resulted in a better match of standard uncertainties of anisotropic displacement parameters along the Mn—O1 bond (Hirshfeld test), but this also gave higher values of $R[F^2>2\sigma(F^2)]$ and $wR(F^2)$, so the shorter O—H distance restraint was chosen. Methyl H atoms were placed with idealized threefold symmetry and fixed C—H distances of 0.96 Å, and they were refined in a riding model with U_{iso}(H) = 1.5U_{eq}(C). For C2, the locations of difference Fourier peaks suggested a disorder model in which two orientations of the methyl group were rotated by 60° relative to each other. Application of this disorder model resulted in improvements of 0.21% in $R[F^2>2\sigma(F^2)]$ and 0.84% in $wR(F^2)$, with the occupancy ratio of the two orientations refining to 0.51:0.49.

Figures

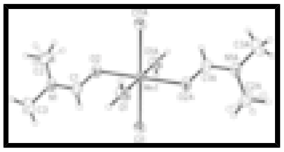

Fig. 1. The molecular structure of the title compound with displacement ellipsoids at the 50% probability level and the atomic numbering [symmetry code: (A) $1 - x$, $1 - y$, $1 - z$]. Dashed lines indicate the second orientation of a rotationally disordered methyl group.

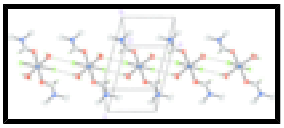

Fig. 2. Packing diagram of (I) showing part of an infinite chain of complexes linked by complementary O—H···Cl hydrogen bonding (dashed lines) along the *a* axis. Methyl H-atoms omitted for clarity.

trans-Diaquadichloridobis(*N*,*N*-dimethylformamide-\ κ*O*)manganese(II)

Crystal data

$[MnCl_2(C_3H_7NO)_2(H_2O)_2]$

$M_r = 308.06$

Triclinic, $P\overline{1}$

Hall symbol: -P 1

$a = 6.1224 (1)$ Å

$b = 6.8021 (1)$ Å

$c = 8.7056 (1)$ Å

$\alpha = 110.539 (1)°$

$\beta = 105.431 (1)°$

$\gamma = 94.732 (1)°$

$V = 320.992 (8)$ Å^3

$Z = 1$

$F_{000} = 159$

$D_x = 1.594$ Mg m^{-3}

Melting point = 362–364 K

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 5092 reflections

$\theta = 2.6–40.4°$

$\mu = 1.44$ mm^{-1}

$T = 298 (2)$ K

Block, light pink

0.48 × 0.25 × 0.20 mm

Data collection

Bruker SMART APEX II CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 0.75 pixels mm^{-1}

$T = 298(2)$ K

phi and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2000)

$T_{min} = 0.534$, $T_{max} = 0.746$

10584 measured reflections

2435 independent reflections

2300 reflections with $I > 2\sigma(I)$

$R_{int} = 0.016$

$\theta_{max} = 33.1°$

$\theta_{min} = 2.6°$

$h = -9\rightarrow9$

$k = -10\rightarrow10$

$l = -13\rightarrow13$

Refinement

Refinement on F^2	2 restraints
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.0323P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.051$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
2435 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}
79 parameters	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Restraints used: the O1—H11 and O1—H12 distances were restrained to 0.85 (1) Å.

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

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Mn1	0.5000	0.5000	0.5000	0.02292 (5)	
Cl1	0.73368 (3)	0.20741 (3)	0.43902 (2)	0.03151 (5)	
O1	0.72383 (10)	0.71285 (10)	0.43607 (9)	0.03632 (13)	
H11	0.8667 (15)	0.729 (2)	0.4685 (17)	0.054*	
H12	0.691 (2)	0.8319 (16)	0.4380 (17)	0.054*	
O2	0.71479 (10)	0.63553 (10)	0.77117 (7)	0.03374 (12)	
C1	0.92887 (12)	0.66040 (12)	0.82274 (9)	0.02796 (13)	
H1	1.0043	0.6194	0.7402	0.034*	
N1	1.05599 (11)	0.74139 (10)	0.98734 (8)	0.02987 (12)	
C2	0.94941 (19)	0.80913 (15)	1.12328 (10)	0.04124 (18)	
H21	0.8188	0.8697	1.0868	0.062*	0.494 (15)
H22	1.0597	0.9145	1.2264	0.062*	0.494 (15)
H23	0.8994	0.6879	1.1463	0.062*	0.494 (15)
H24	1.0332	0.7783	1.2196	0.062*	0.506 (15)
H25	0.7922	0.7336	1.0800	0.062*	0.506 (15)
H26	0.9525	0.9602	1.1600	0.062*	0.506 (15)
C3	1.30653 (16)	0.76926 (19)	1.03786 (14)	0.0492 (2)	
H31	1.3537	0.7207	0.9362	0.074*	

H32	1.3573	0.6875	1.1062	0.074*
H33	1.3739	0.9179	1.1045	0.074*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01952 (7)	0.02749 (8)	0.01909 (7)	0.00350 (5)	0.00352 (4)	0.00810 (5)
Cl1	0.02622 (8)	0.03127 (9)	0.03567 (9)	0.00895 (6)	0.00892 (6)	0.01130 (7)
O1	0.0272 (3)	0.0381 (3)	0.0503 (3)	0.0061 (2)	0.0137 (2)	0.0240 (3)
O2	0.0293 (2)	0.0414 (3)	0.0225 (2)	0.0053 (2)	0.00112 (18)	0.0085 (2)
C1	0.0300 (3)	0.0289 (3)	0.0214 (3)	0.0024 (2)	0.0043 (2)	0.0091 (2)
N1	0.0294 (3)	0.0306 (3)	0.0227 (2)	0.0009 (2)	0.0000 (2)	0.0096 (2)
C2	0.0568 (5)	0.0390 (4)	0.0228 (3)	0.0113 (4)	0.0092 (3)	0.0082 (3)
C3	0.0294 (4)	0.0592 (6)	0.0472 (5)	−0.0032 (4)	−0.0046 (3)	0.0217 (4)

Geometric parameters (Å, °)

Mn1—O2^{i}	2.1847 (5)	N1—C2	1.4549 (12)
Mn1—O2	2.1847 (5)	N1—C3	1.4549 (11)
Mn1—O1	2.2199 (6)	C2—H21	0.9600
Mn1—O1^{i}	2.2199 (6)	C2—H22	0.9600
Mn1—Cl1^{i}	2.53419 (17)	C2—H23	0.9600
Mn1—Cl1	2.53423 (17)	C2—H24	0.9600
O1—H11	0.830 (8)	C2—H25	0.9600
O1—H12	0.846 (8)	C2—H26	0.9600
O2—C1	1.2430 (9)	C3—H31	0.9600
C1—N1	1.3208 (9)	C3—H32	0.9600
C1—H1	0.9300	C3—H33	0.9600
O2^{i}—Mn1—O2	180.0	N1—C2—H22	109.5
O2^{i}—Mn1—O1	88.54 (2)	H21—C2—H22	109.5
O2—Mn1—O1	91.46 (2)	N1—C2—H23	109.5
O2^{i}—Mn1—O1^{i}	91.46 (2)	H21—C2—H23	109.5
O2—Mn1—O1^{i}	88.54 (2)	H22—C2—H23	109.5
O1—Mn1—O1^{i}	180.0	N1—C2—H24	109.5
O2^{i}—Mn1—Cl1^{i}	89.920 (17)	H21—C2—H24	141.1
O2—Mn1—Cl1^{i}	90.081 (17)	H22—C2—H24	56.3
O1—Mn1—Cl1^{i}	87.097 (17)	H23—C2—H24	56.3
O1^{i}—Mn1—Cl1^{i}	92.903 (17)	N1—C2—H25	109.5
O2^{i}—Mn1—Cl1	90.080 (17)	H21—C2—H25	56.3
O2—Mn1—Cl1	89.920 (17)	H22—C2—H25	141.1
O1—Mn1—Cl1	92.903 (17)	H23—C2—H25	56.3
O1^{i}—Mn1—Cl1	87.096 (17)	H24—C2—H25	109.5
Cl1^{i}—Mn1—Cl1	180.000 (6)	N1—C2—H26	109.5
Mn1—O1—H11	122.5 (10)	H21—C2—H26	56.3
Mn1—O1—H12	119.7 (10)	H22—C2—H26	56.3
H11—O1—H12	107.3 (13)	H23—C2—H26	141.1

C1—O2—Mn1	124.95 (5)	H24—C2—H26	109.5
O2—C1—N1	124.15 (7)	H25—C2—H26	109.5
O2—C1—H1	117.9	N1—C3—H31	109.5
N1—C1—H1	117.9	N1—C3—H32	109.5
C1—N1—C2	120.85 (7)	H31—C3—H32	109.5
C1—N1—C3	121.02 (8)	N1—C3—H33	109.5
C2—N1—C3	118.12 (7)	H31—C3—H33	109.5
N1—C2—H21	109.5	H32—C3—H33	109.5
O1—Mn1—O2—C1	−48.73 (7)	Mn1—O2—C1—N1	−179.54 (5)
O1^{i}—Mn1—O2—C1	131.27 (7)	O2—C1—N1—C2	−0.08 (12)
Cl1^{i}—Mn1—O2—C1	−135.83 (6)	O2—C1—N1—C3	−178.88 (8)
Cl1—Mn1—O2—C1	44.17 (6)		

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H11···Cl1^{ii}	0.830 (8)	2.314 (9)	3.1424 (6)	177.2 (13)
O1—H12···Cl1^{iii}	0.846 (8)	2.543 (9)	3.3505 (6)	159.9 (13)

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

Fig. 1

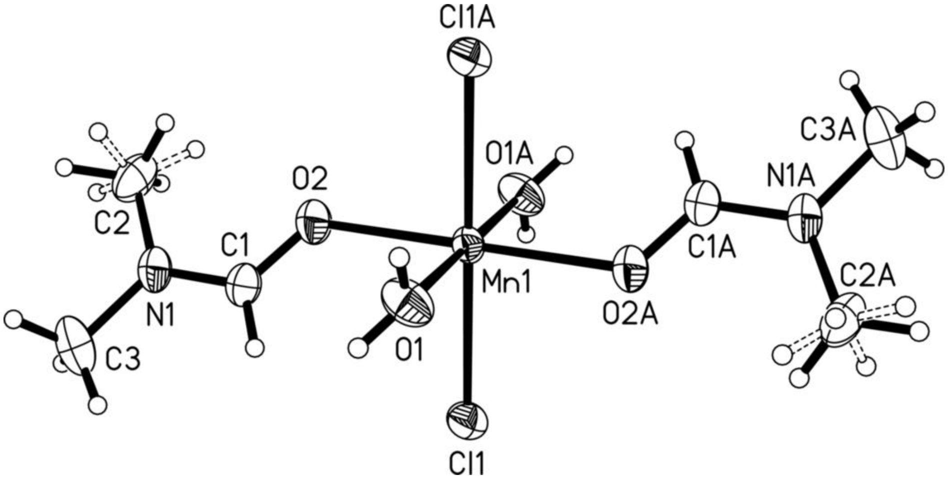

Fig. 2