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catena-Poly[manganese(II)-(μ_2-3,5-di-2-pyridyl-1,2,4-triazolato)-μ_2-formato]

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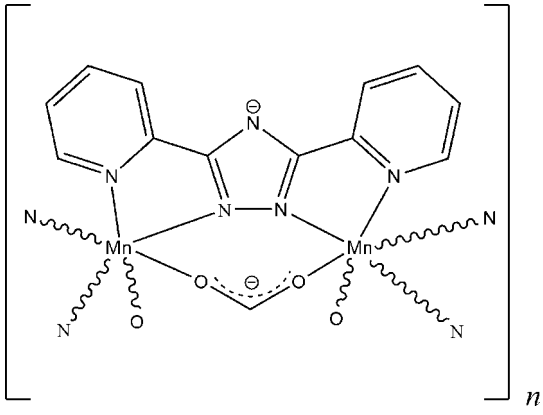
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.056; wR factor = 0.122; data-to-parameter ratio = 13.9.

Owing to the presence of crystallographic twofold rotation axes (site symmetry 2, Wyckoff letters *e* and *f*), the asymmetric unit of the title compound, $[Mn(C_{12}H_8N_5)(CHO_2)]_n$, contains one-half of an Mn^{II} cation, one-half of a bpt anion (Hbpt is 3,5-di-2-pyridyl-4*H*-1,2,4-triazole) and one-half of a formate anion. The bpt and formate ligands occupy the same C_2 symmetry, while the Mn^{II} ion resides on another crystallographic twofold rotation axis. Each bpt ligand acts as a *cis*-bis-chelate to ligate two Mn^{II} ions into a one-dimensional chain running along the crystallographic 4_1 screw axis. Adjacent Mn^{II} ions are further bridged by a μ_2-formate ligand, completing the distorted octahedral coordination geometry of the cation.

Related literature

For related literature, see: Zhang (2005); Chen & Tong (2007). For related structures, see: Cheng *et al.* (2007*a*,*b*).



Experimental

Crystal data

$[Mn(C_{12}H_8N_5)(CHO_2)]$
M_r = 322.20
Tetragonal, $I4_1/acd$
a = 19.124 (5) Å
c = 14.9120 (4) Å
V = 5454 (2) Å^3
Z = 16
Mo $K\alpha$ radiation
μ = 0.98 mm^{-1}
T = 293 (2) K
0.15 × 0.09 × 0.06 mm

Data collection

Bruker APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.867, T_{max} = 0.944
14412 measured reflections
1346 independent reflections
1225 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.121
S = 1.09
1346 reflections
97 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: SI2099).

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supporting information

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S1. Comment

Recently, solvothermal *in situ* ligand reactions have been a rapidly growing field concerning with the formation of *in situ* generated mixed-ligand coordination polymers that can not be easily obtained: a. one-pot synthesis of some unusual organic ligands that are inaccessible or not easily obtainable *via* conventional methods, and b. which are very promising as a bridge between coordination and synthetic organic chemistry (Zhang, 2005; Chen & Tong, 2007). During our research of the reaction mechanisms of different organonitriles with hydrazine hydrate (Cheng *et al.*, 2007*a*,*b*), a new one-dimensional mixed-ligand polymeric manganese(II) complex, [Mn(bpt)0.5(HCOO)0.5]*n* (Hbpt = 3,5-bis(2-pyridyl)-4*H*-1,2,4-triazole) has been synthesized and characterized by single-crystal X-ray diffraction.

The asymmetric unit of the title compound contains half a Mn^{II} cation, half a bpt and half a formato anion. In the compound, the Mn^{II} ion lies on a twofold rotation axis, at position (x, 1/4 + x, 1/8), Wyckoff letter f. Neighboring twofold rotation axes in the high symmetric space group I 4_1/a 2/c 2/d, running through atoms C7, H7A in the formato anion and through atom N3 of the triazole group, at positions (3/4, 3/4 + x, 0) and (x, 0, 1/4), respectively, both with Wyckoff letter e. The Mn^{II} ion displays a slightly distorted octahedral geometry, being surrounded by two chelating bpt ligands and two oxygen atoms from two μ_2-formato ligands, linking the half molecules in the complex to a one-dimensional chain extending along the crystallographic 4_1-screw axis. The shortest Mn···Mn distance in the chain is 4.366 (5) Å.

S2. Experimental

A mixture of 4-cyanopyridine (0.416 g, 4.0 mmol), 80% hydrazine hydrate (2 ml), $Mn(HCOO)_2.2H_2O$ (0.181 g, 1 mmol) and DMF (6 ml) was heated in a 15-ml Teflon-lined autoclave at 180° for 3 days, followed by slow cooling (5° h-1) to room temperature. The resulting mixture was washed with water, and pale-yellow block crystals were collected and dried in air [yield 1.0% (3.2 mg) based on Mn^{II}].

S3. Refinement

H atoms were positioned geometrically and refined using a riding model with constraint distances C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C).

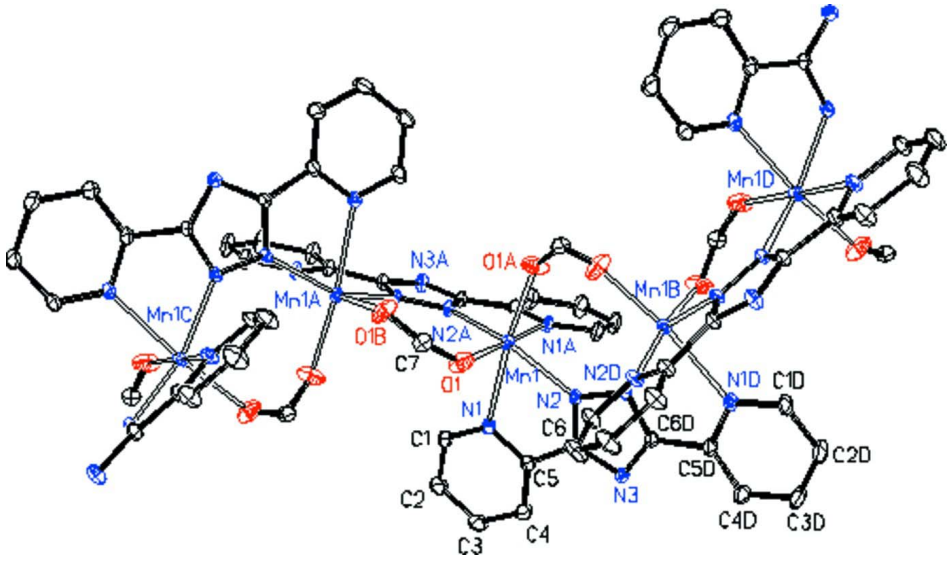

Figure 1

The one-dimensional chain of the title compound with 30% thermal ellipsoids. All the hydrogen atoms are omitted for clarity. Symmetry codes: a: 5/4 - *x*, -1/4 - *y*, 1/4 - *z*; b: 3/2 - *x*, *y*, 1/2 - *z*; c: 1/4 + *x*, -1/4 - *y*, -1/4 + *z*; d: *x*, -*y*, 1/2 - *z*.

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c = 14.9120 (4) Å
V = 5454 (2) Å^3
Z = 16
$F(000)$ = 2608
D_x = 1.570 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 810 reflections
θ = 2.5–28.0°
μ = 0.98 mm^{-1}
T = 293 K
Needle-like, yellow
0.15 × 0.09 × 0.06 mm

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Bruker APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.867, T_{max} = 0.944
14412 measured reflections
1346 independent reflections
1225 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 26.0°, θ_{min} = 2.1°
h = −23→18
k = −23→23
l = −18→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.121
S = 1.09
1346 reflections
97 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-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 25.4234P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mn1	0.69057 (3)	−0.05943 (3)	0.1250	0.0215 (2)
C1	0.56957 (19)	−0.11100 (19)	−0.0239 (2)	0.0318 (8)
H1A	0.6082	−0.1244	−0.0576	0.038*
C2	0.5042 (2)	−0.1237 (2)	−0.0580 (2)	0.0402 (10)
H2A	0.4989	−0.1454	−0.1134	0.048*
C3	0.4464 (2)	−0.1038 (2)	−0.0088 (3)	0.0431 (10)
H3A	0.4015	−0.1118	−0.0305	0.052*
C4	0.45662 (19)	−0.0717 (2)	0.0735 (2)	0.0358 (9)
H4A	0.4187	−0.0579	0.1082	0.043*
C5	0.52424 (17)	−0.06066 (18)	0.1029 (2)	0.0259 (7)
C6	0.54152 (16)	−0.02572 (17)	0.1886 (2)	0.0214 (7)
C7	0.7500	0.0594 (3)	0.0000	0.0300 (11)
H7A	0.7500	0.1080	0.0000	0.036*
N1	0.58042 (15)	−0.08037 (14)	0.05536 (18)	0.0250 (6)
N2	0.60816 (13)	−0.01663 (13)	0.20974 (16)	0.0196 (6)
N3	0.4964 (2)	0.0000	0.2500	0.0272 (9)
O1	0.70537 (14)	0.03180 (15)	0.0481 (2)	0.0501 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0221 (3)	0.0221 (3)	0.0203 (4)	0.0017 (3)	0.00432 (19)	−0.00432 (19)
C1	0.0325 (19)	0.041 (2)	0.0219 (17)	0.0094 (16)	−0.0010 (15)	−0.0133 (15)
C2	0.041 (2)	0.051 (2)	0.0280 (18)	0.0110 (19)	−0.0106 (17)	−0.0199 (18)
C3	0.033 (2)	0.060 (3)	0.037 (2)	0.0061 (18)	−0.0149 (17)	−0.019 (2)
C4	0.0266 (19)	0.048 (2)	0.0325 (19)	0.0032 (16)	−0.0025 (16)	−0.0150 (17)
C5	0.0272 (18)	0.0303 (18)	0.0202 (16)	0.0008 (14)	−0.0028 (13)	−0.0057 (14)
C6	0.0210 (16)	0.0264 (17)	0.0167 (14)	0.0000 (13)	−0.0021 (12)	−0.0049 (13)
C7	0.032 (3)	0.023 (2)	0.035 (3)	0.000	0.001 (2)	0.000
N1	0.0279 (15)	0.0275 (15)	0.0197 (14)	0.0018 (12)	−0.0009 (11)	−0.0086 (11)
N2	0.0225 (14)	0.0210 (14)	0.0154 (12)	−0.0015 (10)	−0.0012 (11)	−0.0058 (10)
N3	0.0205 (19)	0.039 (2)	0.0217 (18)	0.000	0.000	−0.0090 (17)

O1	0.0370 (16)	0.0438 (16)	0.069 (2)	0.0047 (13)	0.0165 (15)	0.0253 (15)

Geometric parameters (Å, º)

Mn1—O1	2.107 (3)	C3—H3A	0.9300
Mn1—O1^{i}	2.107 (3)	C4—C5	1.382 (5)
Mn1—N2^{i}	2.180 (3)	C4—H4A	0.9300
Mn1—N2	2.180 (3)	C5—N1	1.341 (4)
Mn1—N1	2.382 (3)	C5—C6	1.480 (4)
Mn1—N1^{i}	2.382 (3)	C6—N2	1.324 (4)
C1—N1	1.335 (4)	C6—N3	1.350 (4)
C1—C2	1.372 (5)	C7—O1	1.234 (3)
C1—H1A	0.9300	C7—O1^{ii}	1.234 (3)
C2—C3	1.379 (5)	C7—H7A	0.9300
C2—H2A	0.9300	N2—N2^{iii}	1.359 (5)
C3—C4	1.386 (5)	N3—C6^{iii}	1.350 (4)
O1—Mn1—O1^{i}	94.23 (17)	C2—C3—H3A	120.6
O1—Mn1—N2^{i}	103.46 (11)	C4—C3—H3A	120.6
O1^{i}—Mn1—N2^{i}	95.84 (10)	C5—C4—C3	118.7 (3)
O1—Mn1—N2	95.84 (10)	C5—C4—H4A	120.6
O1^{i}—Mn1—N2	103.46 (11)	C3—C4—H4A	120.6
N2^{i}—Mn1—N2	151.55 (13)	N1—C5—C4	122.6 (3)
O1—Mn1—N1	91.19 (11)	N1—C5—C6	113.9 (3)
O1^{i}—Mn1—N1	172.74 (12)	C4—C5—C6	123.5 (3)
N2^{i}—Mn1—N1	87.58 (9)	N2—C6—N3	114.0 (3)
N2—Mn1—N1	71.13 (9)	N2—C6—C5	118.6 (3)
O1—Mn1—N1^{i}	172.74 (12)	N3—C6—C5	127.4 (3)
O1^{i}—Mn1—N1^{i}	91.19 (11)	O1—C7—O1^{ii}	129.3 (5)
N2^{i}—Mn1—N1^{i}	71.13 (9)	O1—C7—H7A	115.3
N2—Mn1—N1^{i}	87.58 (9)	O1^{ii}—C7—H7A	115.3
N1—Mn1—N1^{i}	83.84 (14)	C1—N1—C5	117.8 (3)
N1—C1—C2	123.2 (3)	C1—N1—Mn1	126.6 (2)
N1—C1—H1A	118.4	C5—N1—Mn1	115.5 (2)
C2—C1—H1A	118.4	C6—N2—N2^{iii}	105.75 (17)
C1—C2—C3	119.0 (3)	C6—N2—Mn1	120.59 (19)
C1—C2—H2A	120.5	N2^{iii}—N2—Mn1	133.48 (7)
C3—C2—H2A	120.5	C6—N3—C6^{iii}	100.6 (4)
C2—C3—C4	118.7 (4)	C7—O1—Mn1	139.8 (3)

Symmetry codes: (i) $y+3/4, x-3/4, -z+1/4$; (ii) $-x+3/2, y, -z$; (iii) $x, -y, -z+1/2$.