Crystal structure of *catena*-{[μ_3-5-methylisophthalato][μ_2-1,6-bis(imidazol-1-yl)-hexane]manganese(II)}, $Mn(C_9H_6O_4)(C_{12}H_{18}N_4)$

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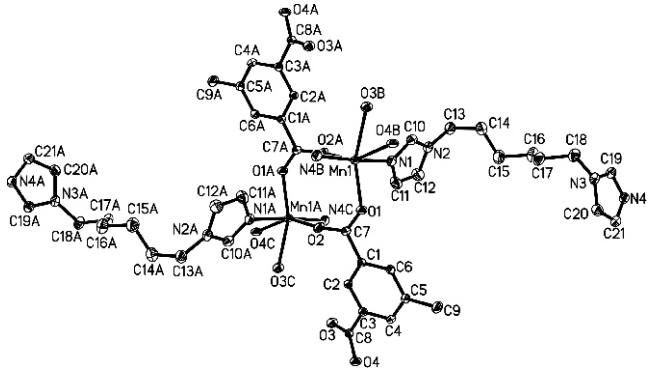

Abstract

$C_{21}H_{24}MnN_4O_4$, triclinic, $P\bar{1}$ (no. 2), a = 8.3393(9) Å, b = 10.296(1) Å, c = 12.026(1) Å, α = 80.738(1)°, β = 84.484(1)°, γ = 83.436(1)°, V = 1009.2 Å^3, Z = 2, $R_{gt}(F)$ = 0.033, $wR_{ref}(F^2)$ = 0.087, T = 296 K.

Source of material

1,6-bis(imidazol-1-yl)-hexane (22 mg, 0.1 mmol), 5-methylisophthalic acid (17.9 mg, 0.1 mmol), $Mn(OAc)_2 \cdot 4H_2O$ (24.4 mg, 0.1 mmol) and KOH (11.2 mg, 0.2 mmol) were added to water (12 ml) in a Teflon-lined stainless steel vessel. The mixture was heated at 433 K for 3 d, and then slowly cooled down to room temperature. Yellow block-like crystals of the title complex were obtained.

Discussion

In the last decade, metal-organic hybrid materials with paramagnetic metal ions have been of particular interest as these crystalline solids may give rise to various framework structures with potential applications in the fields of molecular magnetism and material chemistry. The high-spin Mn(II) contains five unpaired electrons and is quite oxophilic. Thus, the assembly of Mn(II) with aromatic multicarboxylates is inclined to the formation of large clusters with extended structures [1-6].

The crystal structure of the title complex comprises one mip molecule, one Mn(II) ion, and one bih molecule in the asymmetric unit. Both carboxylate groups of the mip are deprotonated. Mip acts as a μ_3-bridge linking three Mn atoms, in which one carboxylate group adopts a μ_2-η^1:η^1 bridging coordination mode connecting to two Mn atoms, while another adopts a μ_1-η^1:η^1 chelating coordination mode coordinating to one Mn atom. The Mn(II) ion is six-coordinated by two *cis* nitrogen atoms of two bih and four carboxylic oxygen atoms from three mip ligands. The Mn—N distances are 2.240(2) Å and 2.249(2) Å, the Mn—O distances are in the range of 2.125(1) - 2.320(1) Å. The Mn ions are bridged by the mip ligands to form a chain. The infinite chain comprises 8- and 16-membered rings built up by Mn(II) ion and mip anion. The 8-membered ring is formed by two symmetry related bridging carboxylate groups with d(Mn—Mn) = 4.45 Å. The 16-membered ring is formed by $[Mn(C_5O_2)]_2$. Such ribbon chains are further interlinked by the rigid bih ligands to form a 2D net with two kinds of windows (4.45 × 13.96 Å^2 and 10.30 × 13.96 Å^2).

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.19 × 0.27 × 0.31 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.91 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7755, 3734
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3272
$N(param)_{refined}$:	271
Programs:	SHELXS-97, SHELXL-97, SHELXTL [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(2)	2*i*		1.0564	0.8404	0.1008	0.028
H(4)	2*i*		1.0633	0.9282	0.4136	0.034
H(6)	2*i*		1.1114	0.5496	0.3645	0.033
H(9A)	2*i*	0.50	1.1052	0.7642	0.5718	0.069
H(9B)	2*i*	0.50	1.2182	0.6396	0.5432	0.069
H(9C)	2*i*	0.50	1.0311	0.6322	0.5670	0.069
H(9D)	2*i*	0.50	1.1311	0.5931	0.5495	0.069
H(9E)	2*i*	0.50	1.0181	0.7178	0.5782	0.069
H(9F)	2*i*	0.50	1.2052	0.7251	0.5543	0.069
H(10)	2*i*		0.6786	0.1657	0.2478	0.043
H(11)	2*i*		0.7210	0.5431	0.1968	0.058
H(12)	2*i*		0.4536	0.5126	0.2925	0.060
H(13A)	2*i*		0.3599	0.1795	0.2922	0.053
H(13B)	2*i*		0.2787	0.3104	0.3327	0.053
H(14A)	2*i*		0.2999	0.1221	0.4794	0.066
H(14B)	2*i*		0.4874	0.1283	0.4667	0.066
H(15A)	2*i*		0.2696	0.3338	0.5346	0.070
H(15B)	2*i*		0.4586	0.3269	0.5324	0.070
H(16A)	2*i*		0.3089	0.2636	0.7177	0.071
H(16B)	2*i*		0.2920	0.1306	0.6749	0.071
H(17A)	2*i*		0.5870	0.2168	0.7106	0.062
H(17B)	2*i*		0.5740	0.0861	0.6626	0.062
H(18A)	2*i*		0.4434	–0.0037	0.8359	0.054
H(18B)	2*i*		0.6158	0.0326	0.8535	0.054
H(19)	2*i*		0.2069	0.1033	0.9454	0.042
H(20)	2*i*		0.6133	0.2676	0.9430	0.051
H(21)	2*i*		0.4033	0.3752	1.0630	0.049

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	2*i*	1.00500(4)	0.30300(3)	0.11546(2)	0.0361(2)	0.0191(2)	0.0228(2)	–0.0014(1)	–0.0015(1)	–0.0050(1)
O(1)	2*i*	1.0871(2)	0.4574(1)	0.1881(1)	0.0561(9)	0.0193(7)	0.0321(8)	–0.0058(6)	–0.0059(7)	–0.0046(6)
O(2)	2*i*	1.0985(2)	0.6150(1)	0.0384(1)	0.063(1)	0.0308(8)	0.0244(8)	–0.0001(7)	–0.0094(7)	–0.0061(6)
O(3)	2*i*	0.9544(2)	1.0861(1)	0.1153(1)	0.0496(9)	0.0242(7)	0.0336(8)	0.0010(6)	–0.0097(7)	–0.0028(6)
O(4)	2*i*	1.0709(2)	1.1338(1)	0.2587(1)	0.0544(9)	0.0211(7)	0.0391(8)	–0.0064(6)	–0.0074(7)	–0.0076(6)
N(1)	2*i*	0.7592(2)	0.3425(2)	0.2034(1)	0.038(1)	0.035(1)	0.0283(9)	–0.0004(8)	–0.0007(8)	–0.0055(7)
N(2)	2*i*	0.5168(2)	0.3138(2)	0.2900(1)	0.036(1)	0.041(1)	0.0279(9)	–0.0017(8)	–0.0032(8)	–0.0049(8)
N(3)	2*i*	0.4361(2)	0.1533(2)	0.9166(2)	0.033(1)	0.041(1)	0.0300(9)	–0.0005(8)	–0.0001(8)	–0.0062(8)
N(4)	2*i*	0.2473(2)	0.2506(2)	1.0258(2)	0.038(1)	0.037(1)	0.0301(9)	–0.0026(8)	0.0014(8)	–0.0075(8)
C(1)	2*i*	1.0855(2)	0.6785(2)	0.2207(2)	0.0250(9)	0.0208(9)	0.025(1)	–0.0021(7)	–0.0002(8)	–0.0053(7)
C(2)	2*i*	1.0635(2)	0.8131(2)	0.1779(2)	0.026(1)	0.0218(9)	0.0231(9)	–0.0023(7)	–0.0035(8)	–0.0029(7)
C(3)	2*i*	1.0523(2)	0.9063(2)	0.2509(2)	0.0247(9)	0.0217(9)	0.029(1)	–0.0024(7)	–0.0010(8)	–0.0050(8)
C(4)	2*i*	1.0683(2)	0.8652(2)	0.3656(2)	0.035(1)	0.026(1)	0.027(1)	–0.0051(8)	–0.0007(8)	–0.0113(8)
C(5)	2*i*	1.0919(2)	0.7313(2)	0.4102(2)	0.035(1)	0.029(1)	0.023(1)	–0.0050(8)	–0.0015(8)	–0.0035(8)
C(6)	2*i*	1.0982(2)	0.6394(2)	0.3361(2)	0.036(1)	0.0200(9)	0.026(1)	–0.0027(8)	–0.0017(8)	–0.0004(8)
C(7)	2*i*	1.0905(2)	0.5762(2)	0.1427(2)	0.026(1)	0.024(1)	0.027(1)	–0.0007(7)	–0.0044(8)	–0.0071(8)
C(8)	2*i*	1.0240(2)	1.0515(2)	0.2053(2)	0.030(1)	0.0206(9)	0.030(1)	–0.0021(8)	0.0042(8)	–0.0064(8)
C(9)	2*i*	1.1136(3)	0.6879(2)	0.5344(2)	0.073(2)	0.039(1)	0.026(1)	–0.007(1)	–0.007(1)	–0.0037(9)
C(10)	2*i*	0.6567(3)	0.2565(2)	0.2470(2)	0.040(1)	0.034(1)	0.035(1)	0.0002(9)	–0.005(1)	–0.0092(9)
C(11)	2*i*	0.6793(3)	0.4622(2)	0.2192(2)	0.049(1)	0.031(1)	0.058(2)	0.002(1)	0.008(1)	0.001(1)
C(12)	2*i*	0.5309(3)	0.4463(2)	0.2722(2)	0.048(1)	0.036(1)	0.062(2)	0.009(1)	0.007(1)	–0.007(1)
C(13)	2*i*	0.3737(3)	0.2466(3)	0.3376(2)	0.037(1)	0.058(2)	0.039(1)	–0.010(1)	–0.002(1)	–0.007(1)
C(14)	2*i*	0.3841(3)	0.1816(3)	0.4604(2)	0.059(2)	0.056(2)	0.048(2)	–0.011(1)	0.005(1)	–0.004(1)
C(15)	2*i*	0.3675(4)	0.2741(3)	0.5453(2)	0.067(2)	0.057(2)	0.048(2)	–0.002(1)	0.001(1)	–0.006(1)
C(16)	2*i*	0.3605(3)	0.2018(3)	0.6690(2)	0.062(2)	0.074(2)	0.041(1)	–0.005(2)	0.001(1)	–0.008(1)
C(17)	2*i*	0.5200(3)	0.1452(3)	0.7128(2)	0.051(2)	0.062(2)	0.042(1)	–0.007(1)	0.011(1)	–0.019(1)
C(18)	2*i*	0.5082(3)	0.0693(2)	0.8334(2)	0.047(1)	0.046(1)	0.041(1)	0.008(1)	0.004(1)	–0.012(1)
C(19)	2*i*	0.2812(3)	0.1581(2)	0.9599(2)	0.033(1)	0.040(1)	0.032(1)	–0.0010(9)	–0.0039(9)	–0.0077(9)
C(20)	2*i*	0.5065(3)	0.2479(2)	0.9578(2)	0.038(1)	0.049(1)	0.041(1)	–0.013(1)	–0.000(1)	–0.005(1)
C(21)	2*i*	0.3896(3)	0.3067(2)	1.0241(2)	0.050(1)	0.042(1)	0.033(1)	–0.011(1)	–0.002(1)	–0.009(1)

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