Crystal structure of di-μ_2-benzoato-di-[tris(pyrazolyl)methane-aqua-manganese(II)] benzoate, $C_{24}H_{22}N_6MnO_5$

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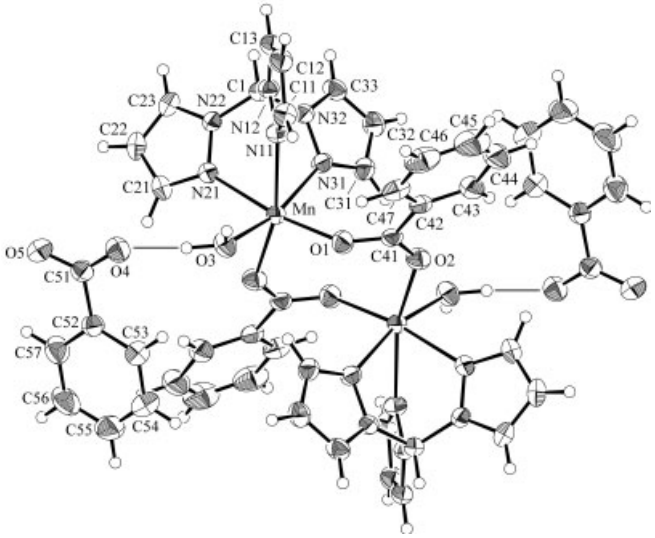

Abstract

$C_{24}H_{22}MnO_5N_6$, triclinic, $P\bar{1}$ (No. 2), a = 11.126(1) Å, b = 12.953(1) Å, c = 9.0895(9) Å, α = 109.241(8)°, β = 102.835(8)°, γ = 71.273(8)°, V = 1161.3 Å^3, Z = 2, $R_{gt}(F)$ = 0.042, $wR_{ref}(F^2)$ = 0.136, T = 293 K.

Source of material

The complex was made by reacting $MnCl_2 \cdot 4H_2O$ in water with sodium benzoate and the ligand pz_3CH and was characterized by IR spectroscopy which showed pz_3CH and benzoate bands (1598 cm^{-1}).

Experimental details

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation. The water-bound H atoms were located from a difference map but were not refined.

Discussion

The structure comprises centrosymmetric dinuclear dications and benzoates that provide the charge balance. The two manganese atoms are bridged symmetrically by two bidentate carboxylates, d(Mn–O1, O2^i) = 2.065(2) Å and 2.086(2) Å, respectively, leading to the formation of an eight-membered ring that adopts an extended chair conformation. The Mn···Mn separation is 4.2710(8) Å, as expected for *anti*, *syn* bridging of the benzoate groups. The coordination geometry is distorted octahedral and is defined by a N_3O_3 donor set. The d(Mn—N11, N21, N31) = 2.300(2) Å, 2.281(2) Å and 2.315(2) Å, respectively, and d(Mn—O3), from a coordinated water molecule, = 2.152(2) Å. The dinuclear units are linked into a chain via hydrogen bonding interactions involving both water-bound hydrogens and the O4 atom of the non-coordinated benzoates. These associations occur about a centre of inversion so that an eight-membered $[O\cdots H–O–H]_2$ ring is formed. The parameters associated with these interactions are d(O3–H···O4) = 1.73 Å, d(O3···O4) = 2.699(3) Å with angle at H = 166°, and d(O3–H···O4^{ii}) = 1.87 Å, d(O3···O4^{ii}) = 2.711(3) Å and angle at H of 162°; symmetry operation *ii*: –x, 1–y, 1–z. Magnetic studies showed weak antiferromagnetic coupling of the S = 5/2 Mn(II) ions with J of –0.7 cm^{-1}. Studies of Mn complexes of pz_3CH were aimed at comparing them to related triazacyclonane (tacn) complexes used by Wieghardt [1] as models for Mn catalase enzymes and for Mn sites in photosystem II. Other Mn carboxylate enzymes are of much interest [2] and some, such as Concavalin A, contain bridging carboxylate groups similar to those found here.

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.13 × 0.16 × 0.26 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	6.18 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	55.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5829, 5544
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 3764
$N(param)_{refined}$:	326
Programs:	teXsan [3], SHELXS-86 [4], SHELXL-97 [5], DIFABS [6], PLATON [7], ORTEPII [8]

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

Atom	Site	x	y	z	U_{iso}
H(2)	2*i*	0.1170	0.5536	0.5370	0.073
H(3)	2*i*	0.1288	0.4418	0.4252	0.073
H(1)	2*i*	0.1720	0.6728	–0.0114	0.091
H(11)	2*i*	0.0747	0.7908	0.5367	0.073
H(12)	2*i*	–0.0550	0.9253	0.3864	0.073
H(13)	2*i*	0.0135	0.8464	0.1216	0.073
H(21)	2*i*	0.2018	0.3106	0.0887	0.073
H(22)	2*i*	0.1115	0.3172	–0.1824	0.073
H(23)	2*i*	0.1017	0.5060	–0.1959	0.073
H(31)	2*i*	0.5910	0.5839	0.3204	0.073
H(32)	2*i*	0.5979	0.6601	0.1075	0.073
H(33)	2*i*	0.3805	0.6936	–0.0372	0.073
H(43)	2*i*	0.5719	0.8417	0.7263	0.073
H(44)	2*i*	0.4867	1.0333	0.8343	0.073

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(45)	2*i*	0.2854	1.1000	0.9055	0.073
H(46)	2*i*	0.1661	0.9782	0.8668	0.073
H(47)	2*i*	0.2438	0.7890	0.7526	0.073
H(53)	2*i*	0.2020	0.2807	0.5153	0.073
H(54)	2*i*	0.3600	0.1445	0.6067	0.073
H(55)	2*i*	0.3915	–0.0408	0.4670	0.073
H(56)	2*i*	0.2665	–0.0928	0.2340	0.073
H(57)	2*i*	0.1028	0.0428	0.1442	0.073

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	2*i*	0.30837(4)	0.53347(3)	0.38354(5)	0.0353(2)	0.0359(2)	0.0389(2)	–0.0089(2)	0.0034(2)	0.0131(2)
O(1)	2*i*	0.3868(2)	0.6146(2)	0.6024(2)	0.065(1)	0.053(1)	0.043(1)	–0.025(1)	–0.0003(9)	0.0127(9)
O(2)	2*i*	0.5821(2)	0.6347(2)	0.6477(2)	0.050(1)	0.040(1)	0.061(1)	–0.0033(9)	0.0087(9)	0.0151(9)
O(3)	2*i*	0.1757(2)	0.4982(2)	0.4881(2)	0.050(1)	0.048(1)	0.060(1)	–0.0147(9)	0.0178(9)	0.011(1)
O(4)	2*i*	0.0169(2)	0.3647(2)	0.3421(3)	0.052(1)	0.050(1)	0.070(1)	–0.011(1)	0.014(1)	0.015(1)
O(5)	2*i*	–0.0481(2)	0.2316(2)	0.1523(3)	0.075(2)	0.074(2)	0.066(2)	–0.025(1)	–0.018(1)	0.032(1)
N(11)	2*i*	0.1582(2)	0.6958(2)	0.3462(3)	0.042(1)	0.044(1)	0.042(1)	–0.0061(9)	0.0075(9)	0.014(1)
N(12)	2*i*	0.1346(2)	0.7171(2)	0.2060(3)	0.037(1)	0.036(1)	0.042(1)	–0.0063(9)	0.0048(9)	0.0134(9)
N(21)	2*i*	0.2166(2)	0.4676(2)	0.1330(3)	0.045(1)	0.039(1)	0.042(1)	–0.015(1)	0.002(1)	0.012(1)
N(22)	2*i*	0.1815(2)	0.5319(2)	0.0333(2)	0.038(1)	0.039(1)	0.036(1)	–0.0115(9)	0.0003(9)	0.0102(9)
N(31)	2*i*	0.4062(2)	0.5957(2)	0.2420(3)	0.037(1)	0.050(1)	0.040(1)	–0.0126(9)	0.0014(9)	0.019(1)
N(32)	2*i*	0.3374(2)	0.6337(2)	0.1195(2)	0.037(1)	0.041(1)	0.038(1)	–0.0127(9)	0.0040(9)	0.015(1)
C(1)	2*i*	0.2033(2)	0.6415(2)	0.0788(3)	0.038(1)	0.037(1)	0.041(1)	–0.010(1)	0.002(1)	0.014(1)
C(11)	2*i*	0.0800(3)	0.7821(3)	0.4324(3)	0.046(1)	0.048(2)	0.048(2)	–0.009(1)	0.011(1)	0.007(1)
C(12)	2*i*	0.0069(3)	0.8582(2)	0.3501(4)	0.048(2)	0.036(2)	0.061(2)	–0.006(1)	0.007(1)	0.006(1)
C(13)	2*i*	0.0444(3)	0.8147(2)	0.2053(4)	0.043(1)	0.035(1)	0.058(2)	–0.008(1)	0.000(1)	0.015(1)
C(21)	2*i*	0.1887(3)	0.3721(3)	0.0501(4)	0.051(2)	0.044(2)	0.054(2)	–0.021(1)	0.011(1)	0.008(1)
C(22)	2*i*	0.1375(3)	0.3750(3)	–0.1016(4)	0.047(2)	0.055(2)	0.053(2)	–0.025(1)	0.007(1)	–0.001(1)
C(23)	2*i*	0.1328(2)	0.4778(3)	–0.1091(3)	0.039(1)	0.058(2)	0.042(2)	–0.015(1)	0.000(1)	0.009(1)
C(31)	2*i*	0.5218(3)	0.6041(3)	0.2469(3)	0.039(1)	0.054(2)	0.052(2)	–0.015(1)	0.003(1)	0.017(1)
C(32)	2*i*	0.5270(3)	0.6467(3)	0.1283(4)	0.047(2)	0.065(2)	0.069(2)	–0.023(1)	0.011(1)	0.025(2)
C(33)	2*i*	0.4081(3)	0.6649(3)	0.0495(4)	0.052(2)	0.053(2)	0.055(2)	–0.016(1)	0.012(1)	0.024(1)
C(41)	2*i*	0.4652(3)	0.6730(2)	0.6530(3)	0.048(1)	0.041(2)	0.032(1)	–0.010(1)	–0.001(1)	0.016(1)
C(42)	2*i*	0.4154(3)	0.7960(2)	0.7270(3)	0.047(1)	0.039(2)	0.036(1)	–0.003(1)	0.000(1)	0.014(1)
C(43)	2*i*	0.4891(3)	0.8690(3)	0.7528(4)	0.066(2)	0.047(2)	0.062(2)	–0.014(2)	0.001(2)	0.017(2)
C(44)	2*i*	0.4384(5)	0.9828(3)	0.8184(5)	0.114(3)	0.043(2)	0.089(3)	–0.022(2)	–0.012(3)	0.016(2)
C(45)	2*i*	0.3185(5)	1.0227(4)	0.8604(5)	0.121(4)	0.046(2)	0.079(3)	0.020(2)	0.002(3)	0.001(2)
C(46)	2*i*	0.2477(4)	0.9506(4)	0.8368(5)	0.076(2)	0.073(3)	0.068(2)	0.022(2)	0.014(2)	0.017(2)
C(47)	2*i*	0.2942(3)	0.8380(3)	0.7698(4)	0.052(2)	0.060(2)	0.048(2)	0.002(1)	0.003(1)	0.021(2)
C(51)	2*i*	0.0271(3)	0.2634(3)	0.2655(3)	0.047(1)	0.056(2)	0.043(2)	–0.017(1)	0.008(1)	0.020(1)
C(52)	2*i*	0.1358(3)	0.1755(3)	0.3195(3)	0.042(1)	0.052(2)	0.052(2)	–0.013(1)	0.008(1)	0.021(1)
C(53)	2*i*	0.2140(3)	0.2048(3)	0.4582(4)	0.057(2)	0.063(2)	0.061(2)	–0.019(2)	–0.000(2)	0.021(2)
C(54)	2*i*	0.3083(4)	0.1239(4)	0.5124(5)	0.070(2)	0.087(3)	0.091(3)	–0.021(2)	–0.021(2)	0.043(3)
C(55)	2*i*	0.3268(4)	0.0144(4)	0.4296(7)	0.057(2)	0.088(3)	0.144(4)	–0.013(2)	–0.010(2)	0.068(3)
C(56)	2*i*	0.2520(4)	–0.0168(3)	0.2916(6)	0.079(3)	0.044(2)	0.144(4)	–0.010(2)	0.014(3)	0.027(2)
C(57)	2*i*	0.1552(3)	0.0642(3)	0.2374(5)	0.062(2)	0.053(2)	0.080(2)	–0.016(2)	0.011(2)	0.010(2)

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