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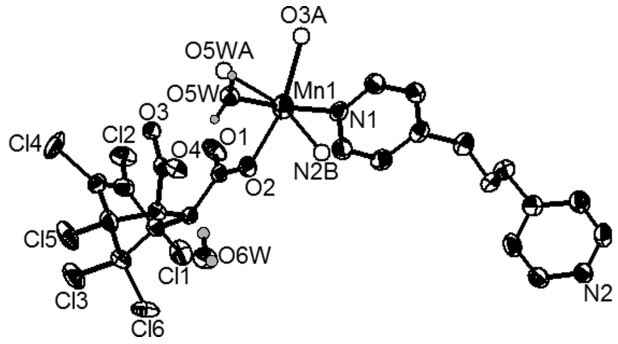
Hydrothermal synthesis and crystal structure of poly[aqua-(μ_2-1,3-bis(4-pyridyl)propane-$\kappa^2N:N'$)-(μ_2-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylato-$\kappa^2O:O'$)manganese(II) hydrate, $C_{22}H_{20}Cl_6N_2O_6Mn$



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Abstract

$C_{22}H_{20}Cl_6N_2O_6Mn$, monoclinic, $P2_1/c$ (no. 14), $a = 12.0080(7)$ Å, $b = 14.9289(8)$ Å, $c = 15.2997(8)$ Å, $\beta = 103.590(2)°$, $V = 2665.9(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0428$, $wR_{ref}(F^2) = 0.1147$, $T = 296$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixtures of chlorendic acid (H_2clda, 38.9 mg, 0.1 mmol), 1,3-bis(4-pyridyl)propane (bpp, 39.8 mg, 0.2 mmol) Mn $(OAc)_2{\cdot}4H_2O$ (49.1 mg, 0.2 mmol), and H_2O (7 mL) was placed in a 23 mL teflon-lined autoclave at 393 K for 4 days, then cooled to room temperature. Colourless block crystals were obtained in ca. 62% yield. Elemental analysis calcd. (%) for $C_{22}H_{20}Cl_6N_2O_6Mn$: C, 39.12; H, 3.02; N, 4.16. Found: C, 39.09; H, 2.98; N, 4.14.

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Table 1: Data collection and handling.

Crystal:	Block, colorless
Size:	0.43 × 0.36 × 0.29 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.14 mm^{-1}
Diffractometer, scan mode:	Bruker SMART, φ and ω-scans
$2\theta_{max}$, completeness:	25.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	17205, 4870, 0.047
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3725
$N(param)_{refined}$:	334
Programs:	Bruker programs [1], SHELX [2]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Mn1	−0.03103(4)	0.51665(3)	0.10778(3)	0.02432(15)
N1	−0.1423(3)	0.60346(19)	0.17483(18)	0.0302(7)
N2	−0.0562(3)	0.54301(19)	0.75843(19)	0.0317(7)
O1	0.0520(2)	0.72189(16)	0.03397(18)	0.0377(6)
O2	0.1088(2)	0.60709(15)	0.12725(15)	0.0322(6)
O3	0.1775(2)	0.56227(15)	−0.04814(15)	0.0288(5)
O4	0.2823(2)	0.47397(15)	0.05850(18)	0.0378(6)
C1	−0.0998(3)	0.6783(2)	0.2183(2)	0.0360(9)
H1	−0.0334	0.7027	0.2068	0.043*
C2	−0.1498(3)	0.7207(2)	0.2793(2)	0.0372(9)
H2	−0.1170	0.7727	0.3076	0.045*
C3	−0.2481(3)	0.6868(2)	0.2988(2)	0.0297(8)
C4	−0.2931(3)	0.6107(2)	0.2517(2)	0.0357(9)
H4	−0.3603	0.5856	0.2611	0.043*
C5	−0.2392(3)	0.5718(3)	0.1911(2)	0.0369(9)
H5	−0.2719	0.5210	0.1602	0.044*
C6	−0.3016(3)	0.7294(2)	0.3685(2)	0.0355(9)
H6A	−0.3797	0.7080	0.3599	0.043*
H6B	−0.3047	0.7937	0.3593	0.043*
C7	−0.2370(3)	0.7099(2)	0.4653(2)	0.0327(8)
H7A	−0.1599	0.7337	0.4752	0.039*
H7B	−0.2751	0.7400	0.5063	0.039*
C8	−0.2309(3)	0.6102(2)	0.4857(2)	0.0349(9)
H8A	−0.1905	0.5807	0.4458	0.042*
H8B	−0.3080	0.5862	0.4733	0.042*
C9	−0.1710(3)	0.5889(2)	0.5824(2)	0.0321(8)
C10	−0.0536(3)	0.5933(3)	0.6106(3)	0.0415(10)
H10	−0.0102	0.6120	0.5710	0.050*
C11	−0.0001(3)	0.5700(3)	0.6978(2)	0.0395(9)
H11	0.0794	0.5734	0.7150	0.047*

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C12	−0.1706(3)	0.5416(2)	0.7314(2)	0.0373(9)
H12	−0.2124	0.5242	0.7726	0.045*
C13	−0.2296(3)	0.5644(3)	0.6464(2)	0.0387(9)
H13	−0.3092	0.5635	0.6317	0.046*
C14	0.2528(3)	0.7016(2)	0.0997(2)	0.0239(7)
H14	0.2839	0.7084	0.1646	0.029*
C15	0.3263(3)	0.6295(2)	0.0643(2)	0.0264(7)
H15	0.3868	0.6087	0.1150	0.032*
C16	0.3823(3)	0.6849(2)	0.0006(3)	0.0343(8)
C17	0.2908(4)	0.7196(3)	−0.0776(2)	0.0390(10)
C18	0.2303(3)	0.7812(2)	−0.0477(2)	0.0347(9)
C19	0.2790(3)	0.7887(2)	0.0529(2)	0.0266(7)
C20	0.4071(3)	0.7755(2)	0.0538(2)	0.0322(8)
C21	0.2571(3)	0.5480(2)	0.0210(2)	0.0259(7)
C22	0.1265(3)	0.6766(2)	0.0843(2)	0.0264(7)
Cl1	0.25004(9)	0.88878(6)	0.10369(7)	0.0421(3)
Cl2	0.12265(11)	0.84501(8)	−0.10694(9)	0.0696(4)
Cl3	0.46410(10)	0.86032(7)	−0.00383(8)	0.0524(3)
Cl4	0.27637(15)	0.68444(9)	−0.18500(7)	0.0768(5)
Cl5	0.50094(11)	0.63207(8)	−0.02473(10)	0.0670(4)
Cl6	0.49859(9)	0.76513(7)	0.16193(8)	0.0544(3)
O5W	0.0688(2)	0.42052(15)	0.03827(15)	0.0295(5)
H1W	0.0455	0.3682	0.0211	0.044*
H2W	0.1414	0.4236	0.0490	0.044*
O6W	0.4549(5)	0.4764(4)	0.2287(4)	0.164(3)
H4W	0.4795	0.4260	0.2511	0.246*
H3W	0.3943	0.4836	0.1876	0.246*

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

The coordination polymers assembled by metal ions, multicarboxylate ligands and *N*-donor coligands are rapidly increasing not only owing to their versatile intriguing architectures but also for their potential applications in many areas [3–9]. In multi-carboxylate ligands, rigid benzene multicarboxylate ligands have been widely applied for the synthesis and assembly of various coordination polymers. Recently, the steric, non-coplanar backbone carboxylate ligands for the formation of coordination polymers has been some investigated [10–12]. Among them, chlorendic acid (H_2clda), which can display biological activity with the steric and non-coplanar features is rarely reported as an educt of a dicarboxylate ligand. Furthermore, the six Cl atoms in the chlorendic acid may alter its spatial conformation and steric hindrance and further influence coordination modes. Therefore, we select chlorendic acid (H_2clda), as a precusor of the main ligand and the bpp (1,3-di(4-pyridyl)propane) as a *N*-donor auxiliary linker [13, 14] to construct the target compound.

The crystal structure determination reveals that the compound features a one-dimensional chain structure. The asymmetric unit contains one Mn(II) ion, one clda dianion, one bpp molecule, one coordinated water and one free water molecule (A: $-x$, $1-y$, $-z$; B: $-x$, $1-y$, $1-z$) (*cf*. the figure). The Mn(II) ion shows a six-coordinated environment with distorted octahedral manner [MnN_2O_4] by two N atoms from two symmetry-related bpp ligands (N1, N2B), four oxygen atoms (O2, O3A, O5W, O5WA) from two symmetry-related clda dianions and two coordinating water molecules. The Mn-O bond lengths are in the range of 2.120(2) to 2.367(2) Å, and the Mn-N bond lengths are 2.252(3) and 2.272(3) Å, respectively. Two Mn(II) neighbours are connected by two clda dianions adopting monodentate coordination mode (*cf*. the figure). The μ_2-bridging mode of the dianionic dicarboxylato ligand is a well known feature for such ligands [15]. Two coordinated water molecules adopt a bridging-coordination mode to form one dinuclear unit with the Mn···Mn distance of 3.5825(7) Å. The adjacent dinuclear moieties are extended along the *c* direction by paired bpp co-ligands to produce a 1D coordination polymer with the Mn···Mn separation of 11.8592(9) Å. In the complex, as the result of the presence of one coordinated water molecule, there exist intra-chain hydrogen bonding interactions between the coordinated water and the carboxylate oxygen atoms of the clda dianions (O(5W)-H(1W)···O(1): d = 2.663(3) Å and O(5W)-H(2W)···O(4): d = 2.663 Å). The adjacent chains are interlinked by inter-chain hydrogen bonds *via* the participation of the O atoms from free water molecules and carboxylate O atom and Cl atom from clda anion (O(6W)-H(3W)···O(4): d = 2.923(6) Å and O(6W)-H(4W)···Cl(6): d = 3.552(6) Å) to form a three-dimensional supramolecular structure.

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