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Crystal structure of poly[diaqua-(μ_2 -4,4'-bipyridine- $\kappa^2 N:N'$)manganese(II)] bis(4-chlorobenzenesulfonate) – 4,4'-bipyridine – water (1/1/2) $C_{42}H_{40}Cl_2MnN_6O_{10}S_2$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.27 × 0.21 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.0 cm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{\max}$, completeness:	50°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9887, 3726, 0.048
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2810
$N(\text{param})_{\text{refined}}$:	303
Programs:	Bruker programs [14], SHELX [15]

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Abstract

$C_{42}H_{40}Cl_2MnN_6O_{10}S_2$, monoclinic, $C2/c$ (no. 15), $a = 16.822(14)$ Å, $b = 11.552(9)$ Å, $c = 22.021(17)$ Å, $\beta = 91.920(13)^\circ$, $V = 4277(6)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0641$, $wR_{\text{ref}}(F^2) = 0.1654$, $T = 296$ K.

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A part of 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

A mixture of $Mn(CH_3COO)_2 \cdot 4H_2O$ (122.5 mg, 0.5 mmol) and 4-chlorobenzenesulfonic acid (*Hcbs*) (96.4 mg, 0.5 mmol) and

4,4'-bipyridine (4,4'-bipy) (78.1 mg, 0.5 mmol), was stirred into 20 mL of 50% methanolic solution at room temperature, and refluxed for 20 min. The pH was adjusted to ca. 7 with a 2 mol/L NaOH aqueous solution. The reaction mixture was heated in a 25 mL Teflon-lined reaction vessel for 12 h at 80 °C and then filtered. The yellow block-shaped crystals were separated from the mother liquor by slow evaporation at room temperature after one week.

Experimental details

H atoms bonded to N and O atoms were located in a difference electron density map and refined with distance restraints of O–H = 0.84(2) and N–H = 0.87(2) Å, and with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(N, O)$. Other H atoms were positioned geometrically and refined using a riding model, with C–H = 0.95–0.99 Å and $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$.

Discussion

At the interface between synthetic chemistry and materials science, research on coordination polymers provides an excellent means for studying structure-property relationships in the solid state.

In recent years, metal organic frameworks (MOFs) which are formed by organic ligands and metal ions through self-assembly process, have gained great attention due to the

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Mn1	1.0000	0.36146(6)	0.7500	0.0313(3)
S1	0.21296(10)	0.84187(13)	0.12537(6)	0.0728(5)
O1W	0.87184(18)	0.3339(2)	0.74847(12)	0.0425(7)
O1	0.2602(3)	0.9398(4)	0.1121(2)	0.0987(15)
O2W	0.2534(3)	0.5356(4)	0.24724(19)	0.0832(12)
H2WB	0.229(4)	0.485(5)	0.227(3)	0.100*
H2WA	0.287(3)	0.513(6)	0.273(2)	0.100*
O2	0.2561(3)	0.7347(4)	0.1220(2)	0.0975(14)
O3	0.1730(3)	0.8528(3)	0.18218(17)	0.0823(12)
Cl1	−0.04826(14)	0.8062(3)	−0.07870(11)	0.1330(9)
N1	0.2647(3)	0.4126(5)	0.1359(3)	0.0863(16)
N2	1.0006(2)	0.3926(3)	0.85050(13)	0.0411(8)
N3	1.0000	0.5593(4)	0.7500	0.0513(14)
N4	1.0000	1.1665(3)	0.7500	0.0355(11)
C1	0.1375(4)	0.8354(5)	0.0687(2)	0.0717(16)
C2	0.1520(6)	0.7909(10)	0.0124(4)	0.135(3)
H2A	0.175(6)	0.729(5)	0.026(4)	0.161*
C3	0.0955(5)	0.7800(9)	−0.0317(4)	0.133(4)
H3A	0.1074	0.7457	−0.0685	0.160*
C4	0.0229(4)	0.8184(6)	−0.0225(3)	0.0834(18)
C5	0.0058(5)	0.8659(7)	0.0313(4)	0.112(3)
H5A	−0.0453	0.8933	0.0377	0.135*
C6	0.0629(4)	0.8741(6)	0.0766(3)	0.088(2)
H6A	0.0502	0.9070	0.1136	0.106*
C7	0.2756(4)	0.4593(5)	0.0818(3)	0.0856(19)
H7A	0.2870	0.5380	0.0802	0.103*
C8	0.2712(4)	0.4004(5)	0.0285(3)	0.0767(16)
H8A	0.2803	0.4386	−0.0078	0.092*
C9	0.2534(3)	0.2837(5)	0.0282(3)	0.0647(14)
C10	0.2441(3)	0.2343(5)	0.0842(3)	0.0749(16)
H10A	0.2342	0.1553	0.0872	0.090*
C11	0.2493(4)	0.3006(6)	0.1357(3)	0.0810(17)
H11A	0.2415	0.2645	0.1727	0.097*
C12	1.0652(3)	0.4025(5)	0.88406(18)	0.0601(14)
H12A	1.1127	0.3797	0.8673	0.072*
C13	1.0686(3)	0.4440(5)	0.94241(19)	0.0620(14)
H13A	1.1170	0.4492	0.9638	0.074*
C14	1.0003(3)	0.4775(4)	0.96853(16)	0.0459(11)
C15	0.9342(3)	0.4676(6)	0.9344(2)	0.086(2)
H15A	0.8860	0.4897	0.9504	0.104*
C16	0.9352(3)	0.4254(6)	0.8761(2)	0.0724(17)
H16A	0.8874	0.4199	0.8539	0.087*
C17	0.9368(3)	0.6193(4)	0.7324(2)	0.0593(13)
H17A	0.8916	0.5787	0.7194	0.071*
C18	0.9334(3)	0.7373(4)	0.7320(2)	0.0538(12)
H18A	0.8868	0.7754	0.7199	0.065*
C19	1.0000	0.7988(4)	0.7500	0.0432(14)
C20	1.0000	0.9269(4)	0.7500	0.0369(13)
C21	1.0486(3)	0.9885(3)	0.78934(18)	0.0455(10)
H21A	1.0825	0.9503	0.8169	0.055*
C22	1.0467(3)	1.1067(3)	0.78749(17)	0.0409(10)
H22A	1.0803	1.1472	0.8143	0.049*
H1WB	0.858(3)	0.276(3)	0.7682(18)	0.049*
H1WA	0.836(2)	0.384(3)	0.750(2)	0.049*

wealth of intriguing architectures and topologies [1–8] and their potential applications in magnetism, electric conductivity, molecular adsorption, heterogeneous catalysis, and fluorescent materials [7–13]. Ligands are mainly composed of organic anions containing carboxylate groups, or of neutral N-heterocycles. The metal ions are mainly based on transition metal ions and lanthanide metal ions. Several research efforts are being directed at obtaining predictable frameworks with desired properties by choosing versatile organic ligands and functional metal ions. In this paper, we report the synthesis and the crystal structure of a new manganese (II) complex with 4,4'-bipyridine (4,4'-bipy) and 4-chlorobenzenesulfonate (cbs). The crystallographically unique Mn²⁺ ion of the title complex {[Mn(H₂O)₂](μ-4,4'-bipy)₂] 2(cbs) (4,4'-bipy) 2H₂O}_n is six-coordinated by two symmetry-equivalent water O atoms and four N atoms from 4,4'-bipy group (Mn1–O, 2.178(4) Å, Mn1–N, 2.242(3) Å, 2.286(5) Å), giving rise to an octahedral geometry. Manganese centers are interconnected by neutral 4,4'-bipy ligands giving rise to a uniform two-dimensional cationic distorted square-grid layer. The layers are stacked along the crystallographic *a* axis with lamellar separation of 8.4063 Å. The intralayer space is occupied by uncoordinated cbs anions and 4,4'-bipy. Furthermore, the two-dimensional layers form an extended three-dimensional supramolecular network through intermolecular hydrogen bonds between cbs with coordinated uncoordinated water molecules.

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