

NOVEL 3D METAL-ORGANIC FRAMEWORK

WITH PRUSSIAN BLUE TOPOLOGY:

[Mn(HCOO)₃]_n·xH₂O

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A novel complex, [Mn(HCOO)₃]_n·xH₂O, has been synthesized and studied by X-ray crystallography. The structure is trigonal, space group *R*-3c, *a* = 8.327(1) Å, *c* = 22.890(6) Å, *V* = 1374.4(5) Å³, *Z* = 6; final *R* = 0.045. The crystal structure reveals both O-atoms of the formic acid ligand coordinated to Mn(III) to form a three-dimensional porous framework with the topology of Prussian Blue.

Keywords: coordination polymer, three-dimensional framework, porous structure, manganese(III).

Metal complexes with triethylenetetramine can be utilized in various applications [1, 2], such as to cleave DNA via hydrolysis mechanism, whereas N-methyl pyrrole derivatives can recognize AT and TA base pairs in the minor groove of DNA [3]. As an extension of this research, the compound N,N-bis(1-methyl-4-nitropyrrole-2-formyl)triethylenetetramine (I) was synthesized. A solution of compound (I) in dimethylformamide (DMF) was mixed with aqueous MnCl₂·4H₂O at room temperature. It was expected that compound (I) and Mn(II) will form a complex species that can specifically cleave DNA at predetermined site. However, the final crystalline product obtained in this experiment was not a target complex but rather a complex of formate and Mn(III). Presumably, formic acid was formed as a result of the hydrolysis of DMF under the conditions used, and the acid reacted with MnCl₂ which was simultaneously oxidized by air oxygen. The elucidation of the mechanism of the processes requires additional work. Meanwhile, this preliminary communication reports on the crystal structure of the title complex, an unexpected product of the above experiment.

Compound (I) (0.0692 g, 0.15 mmol) was dissolved in DMF (20 ml) and MnCl₂·4H₂O (0.0304 g, 0.15 mmol) was dissolved in H₂O (3 ml). The two solutions were mixed and stirred at room temperature overnight. The solution was allowed to stand at room temperature for several days until colorless crystals of the title complex were obtained.

A single crystal (block) with dimensions of 0.4×0.3×0.2 mm was selected and studied. Unit cell parameters and diffraction intensity data were measured using a Smart 1 K CCD area detector system with graphite-monochromated MoK_α radiation (*λ* = 0.71073 Å) at 293 K in the range of 6.68 < 2θ < 49.94°. The structure of the title complex was solved by direct methods and refined using anisotropic approximation for non-hydrogen atoms. All calculations were performed with SHELXS-97 software. Crystal data for the complex are listed in Table 1. Atomic coordinates and isotropic thermal parameters are given in Table 2. Selected interatomic distances and bond angles for the complex are given in Table 3. Structural information on the reported structure was deposited with CCDC database (deposition no. 603562) and is freely available via www.ccdc.cam.ac.uk.

The crystal structure of the title compound consists of [Mn(OCHO)₃]_n polymeric complex (host) and water

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TABLE 1. Crystal Data for the Title Compound and the Parameters of XRD Experiment

Parameter	[Mn(HCOO) ₃] _n ·xH ₂ O
Formula	C ₃ H ₃ MnO ₆ , x(H ₂ O)
<i>M</i> (host only)	190.0
Crystal system	Trigonal
Space group	<i>R</i> -3c
Temperature, K	293(2)
<i>a</i> , <i>c</i> , Å	8.327(1), 22.890(6)
<i>V</i> , Å ³	1374.4(5)
<i>Z</i>	6
<i>d</i> _{calc} , g/cm ³	1.667
Reflections collected	1250
Unique reflections	275
<i>R</i> _{int}	0.051
Parameters refined	26
<i>GOOF</i>	1.326
<i>R</i> factors (<i>I</i> > 2σ ₁)	<i>R</i> ₁ = 0.045, <i>wR</i> ₂ = 0.046
<i>R</i> factors (all data)	<i>R</i> ₁ = 0.120, <i>wR</i> ₂ = 0.123
Residual extrema, e/Å ³	−0.54, 0.65
CCDC deposition No.	603562

TABLE 2. Atomic Coordinates (×10⁴) and Equivalent Thermal Parameters (Å²×10³)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mn(1)	10000	10000	0	25(1)
O(1)	9898(2)	7789(3)	545(1)	41(1)
C(1)	11185(5)	7851(5)	833	34(1)
OW1	6667	3333	309(4)	45(2)
OW2	7512(11)	3333	833	91(3)

TABLE 3. Selected Interatomic Distances and Bond Angles for the Title Compound

Bond	<i>d</i> , Å	Angle	ω, deg
Mn(1)–O(1)	2.190(2)	O(1)–Mn(1)–O(1C)	89.22(7)
O(1)–C(1)	1.237(2)	O(1)–Mn(1)–O(1B)	90.78(7)
		O(1)–Mn(1)–O(1A)	180.00(9)

molecules (guest) included in the voids of the structure. The complex forms an electrically neutral 3D framework with the topology of Prussian Blue [4]. The structure of the complex with an atomic numbering scheme is shown in Fig. 1. The coordination geometry around Mn(III) is an octahedron, with the central Mn(III) atom bound to six O-atoms of the formate ligand. The Mn–O distance is 2.190(2) Å, which is similar to the distance of 2.12–2.23 Å in Mn(HCOO)₂·1/3(C₄H₈O₂) [5]. Each formate ion is coordinated to two manganese ions acting as a bridge. The distance between Mn(1) and Mn(1A) is 6.137(8) Å.

A fragment of the host framework is shown in Fig. 2. The element of this structure is a distorted cube with six Mn(III) cations in the vertices connected at the distance of 6.14 Å by six bridging formate-anions. In the center of this cube, there is a cavity approximately of 4 Å in diameter. The cavity is suitable for small guest molecules. The DMF molecule used in the experiment is too big and the molecules of solvent water (two alternative symmetrically distinct positions) were located in the cavity instead.

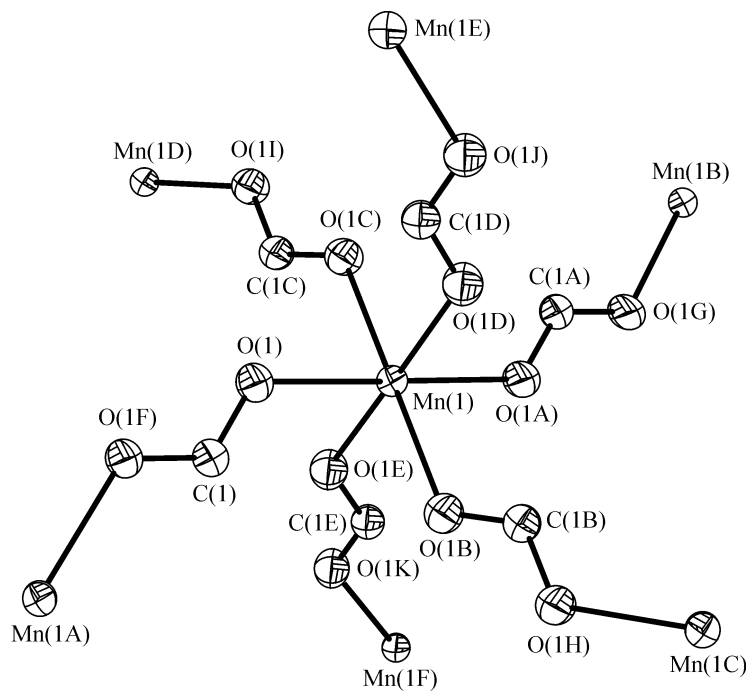


Fig. 1. Coordination environment of Mn(III) in the structure.

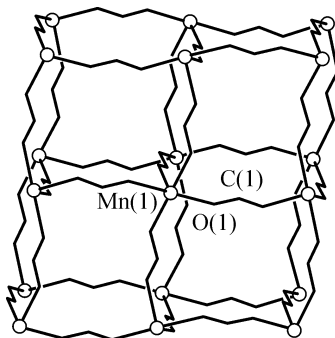


Fig. 2. A fragment of host framework in the title compound.

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