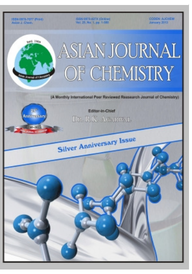
Asian Journal of Chemistry; Vol. 25, No. 4 (2013), 2349-2350

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13746B



NOTE

Synthesis and Structure of a Three-Dimensional Mn(COO)$_3$ Anionic Framework

ZHIQIANG JIANG

Biology and Chemistry Engineering College of Panzhihua University, Sichuan 617000, P.R. China

Corresponding author: E-mail: myjiangzq@163.com

(*Received*: 17 March 2012; *Accepted*: 31 October 2012) AJC-12355

Manganese-crystallization of formic acid from the decomposition of *N,N*-dimethylformamide solvent was synthesized and characterized by single-crystal X-ray diffraction. This compound crystallized in a hexagonal space group of R-3c with a = b = 8.3319(5) Å, c = 22.851(2) Å, $\alpha = \beta = 90.00°$, $\lambda = 120.00°$, V = 1373.81(17) Å^3 and Z = 2. This compound possessed 6-connected three-dimensional Mn(COO)$_3$ anionic framework.

Key Words: Synthesis, Three-dimensional, Formic acid, Mn(COO)$_3$.

Coordination polymers represent a new class of functional materials[1-5]. They consist generally of monomers of metal cations or of metal clusters and rigid or flexible organic ligands, leading to polymeric structures of different dimensionality. Coordination polymers with manganese ions or manganese clusters are of high concern owing to giving rise to novel framework structures with potential applications in the fields of molecular magnetism. Such frameworks may be considered as hybrids between classical 3D magnetic solids and molecular magnets[6-8]. Herein, we report the synthesis and structure of a three-dimensional Mn(COO)$_3$ anionic framework [Mn·(COO)$_3$]·(Hdma) [**1**; Hdma = protonated dimethylamine (Me$_2$NH$_2$)].

The chemicals with reagent-grade quality were purchased from commercial sources and used without purification.

Preparation of compound: The mixture of Mn(NO$_3$)$_2$·6H$_2$O (0.2000 g, 0.35 mmol), (±)-2-methylpiperazine (0.02 g 0.20 mmol), 4-carboxyphenyl-boronic acid (0.0746 g, 0.45 mmol), L(+)-tartaric acid (0.0829 g 0.55 mmol), methanol (2.0 mL) and *N,N*-dimethylformamide (DMF, 6.0 mL) was packed into a 23 mL Teflon-lined stainless steel vessel, heated up to 120 ºC and kept at this temperature for 96 h and then cooled to room temperature. As a result, the brown transparent crystals were obtained.

X-crystallography: Suitable single crystals of [Mn·(COO)$_3$]·(Hdma) (**1**) were carefully selected under an optical microscope and glued to thin glass fibers. Whereafter, single-crystal X-ray diffraction analyses were performed on a computer-controlled XCalibur E CCD diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda_{MoK\alpha}$= 0.71073 Å) at T = 293.2 K. Empirical absorption corrections were made using the SADABS program[9]. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined using the SHELXTL software package[10]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms on the ligand were placed in idealized positions and refined using a riding model.

Structure description: A single-crystal X-ray crystallographic study reveals that [Mn·(COO)$_3$]·(Hdma) crystallizes in a noncentrosymetrical hexagonal space group of R-3c. The asymmetric unit contains one manganese atom, three protonated formic acids from the decomposition of DMF solvent *in situ* and one dissociative charge-balancing protonated dimethylamine from the decomposition of DMF solvent in situ, too (Fig. 1a). Manganese atom is six-coordinated with six oxygen atoms from three carboxylic groups. The two manganese atoms are connected by a μ_2-bridging formic acid resulting in one-dimensional chain (Fig. 1b). These one-dimensional chains are further linked *via* formic acid forming 4-connected two-dimensional layer (Fig. 1c). These layers are pillared by formic acid adopting μ_2-bridging mode, leading to a 6-connected three-dimensional framework (Fig. 1d).

REFERENCES

1. B.F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **111**, 5962 (1989).
2. O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi and J. Kim, *Nature*, **423**, 705 (2003).
3. S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).

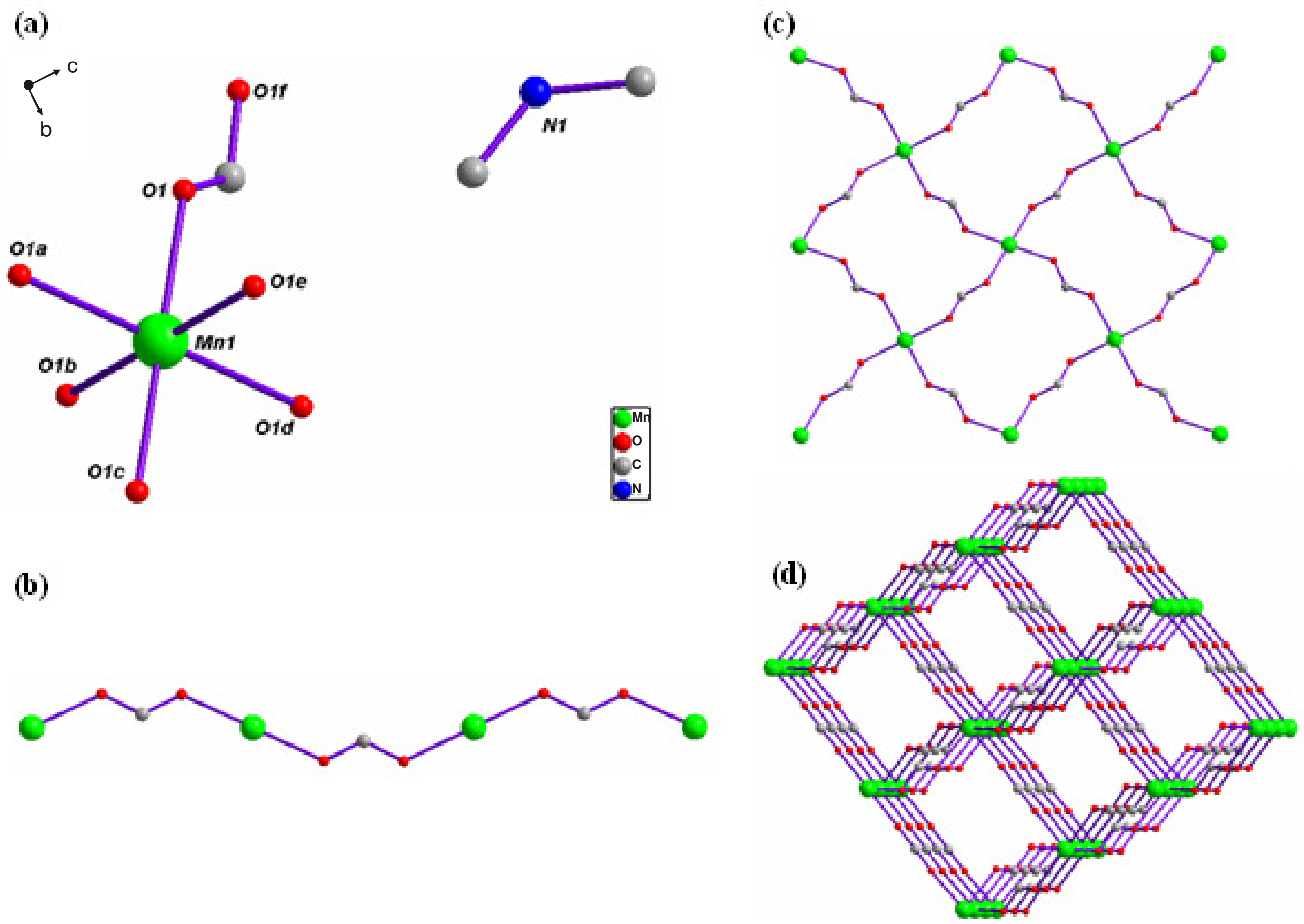


Fig. 1. (a) Coordination environment around the Mn atom in compound **1**; (b) The 1D chains in compound **1**; (c) Perspective view of the two-dimensional layer of compound **1**; (d) View of the 3D network of compound **1**. Hydrogen atoms are omitted for clarity

4. M.J. Rosseinsky, *Micropor. Mesopor. Mater.*, **73**, 15 (2004).
5. G. Ferey, C. Mellot-Draznieks, C. Serre and F. Millange, *Acc. Chem. Res.*, **38**, 217 (2005).
6. K.O. Kongshaug and H. Fjellvag, *Polyhedron*, **26**, 5113 (2007).
7. X.M. Lu, P.Z. Li, X.T. Wang, S. Gao, X.J. Wang, S. Wang, Y.H. Deng, Y.J. Zhang and L. Zhou, *Polyhedron*, **27**, 2402 (2008).
8. C.B. Tian, Z.Z. He, Z.H. Li, P. Lin and S.W. Du, *Cryst. Eng. Comm.*, **13**, 3080 (2011).
9. G.M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction; Institute for Inorganic Chemistry, University of Göttingen: Göttingen, Germany (1996).
10. G.M. Sheldrick, SHELXL-97, Program for Solution of Crystal Structures; University of Göttingen: Göttingen, Germany (1997).