Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2012, **22**, 323–324

Mendeleev Communications

A new metal-organic framework of Mn^{II}–chelidamic acid consolidated by octamer water clusters

Hossein Eshtiagh-Hosseini and Masoud Mirzaei

Department of Chemistry, Ferdowsi University of Mashhad, 91779-1436 Mashhad, Iran.
E-mail: heshtiagh@um.ac.ir; mirzaeesh@um.ac.ir

DOI: 10.1016/j.mencom.2012.11.015

A 1D metal-organic framework with two symmetry-independent heptacoordinated Mn^{II} atoms stitched by centrosymmetric octamer water clusters is reported.

The most commonly used strategies in the extension of supramolecular structures are van der Waals, ion pairing and hydrogen bonding interactions and face to face π–π stacking and edge to face C–H···π, C–O···π, N–H···π, S–O···π, Ti···π, Hg–Cl···π, S···S interactions.[1,2] Metal-organic frameworks are interesting due to their fascinating topological architectures and useful properties. Dicarboxylic acids are usually water-soluble, commercially available, cheap and versatile N,O-chelators possessing diverse coordination modes with a recognized biological function in the body metabolism and as enzyme inhibitors, plant preservatives and food sanitizers. The complexation of transition metal ions from dipicolinic acid has been reported. The reasons for this interest are the ability of the ligands so it gave stable chelates with different coordination modes, affinity to form strong hydrogen bonds and its biological activity in human metabolism. The dipicolinate complexes of transition metals and main groups are known.[1–4] However, the coordination chemistry of chelidamic acid is less developed and relevant structural information is relatively scarce. The main reason is that dicarboxylic acids generally tend to react with metal salts to yield insoluble polymeric materials, which can be difficult to characterize and almost impossible to crystallize. We have shown that reaction of metal salts with functionalized carboxylic and dicarboxylic acids using a proton transfer mechanism leads to the isolation of soluble materials. The contribution of proton transfer complexes also expands the knowledge of the coordination chemistry of chemically/biologically important carboxylate ligands, further interest is derived from their potential applications. A wide range of Mn^{II} carboxylate complexes exhibit excellent catalytic activity towards the disproportionation of hydrogen peroxide. Such compounds are of interest not only because they mimic the activity of the biologically important mangano-catalysts but also since a number of them catalyze the low temperature peroxide bleaching of fabrics.[5–8]

Here, we report the crystal structure of the Mn complexes of chelidamic acid as the heterocyclic carboxylic acids by the help of proton transfer from chelidamic acid to the present chloride anion and/or 2-aminopyrimidine in the solution. The title compound is a 1D coordination polymer with two symmetry-independent heptacoordinated (distorted pentagonal bipyramid) Mn atoms. Both 4-hydroxy-2,6-dicarboxylatopyridine moieties and water molecules act as bridging ligands. The staircase-like geometry of the coordination polymer is stabilized by π-stacking. A centrosymmetric octamer of noncoordinated water molecules fills the voids in the crystal packing.

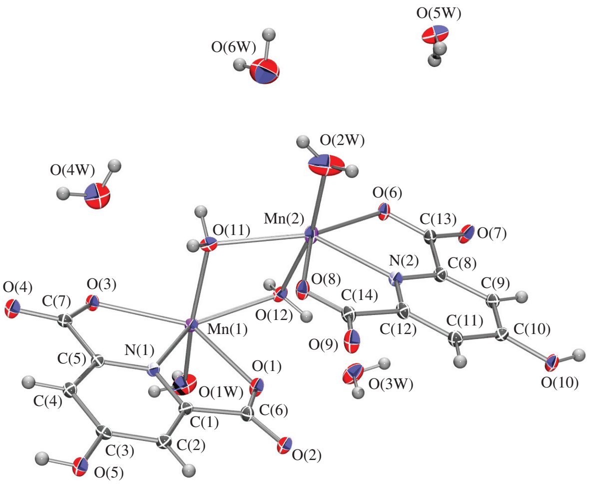

Figure 1 ORTEP-3 drawing of the asymmetric unit of **1**. Displacement ellipsoids are drawn for a probability of 50% and hydrogen atoms are shown as spheres of arbitrary radii.

Compound **1**[†] (Figure 1)[‡] is similar to decaaquabis(μ_3-4-hydroxypyridine-2,6-dicarboxylato)bis(4-hydroxypyridine-2,6-dicarboxylato)tetramanganese(II) **2**.[6] Molecular graphs of both compounds are similar, with two symmetry-independent manganese atoms. The metal centres are all heptacoordinated, in the form of a distorted pentagonal bipyramid (Figure 1S, see Online Supplementary Materials). The main difference between compounds **1** and **2** consists in coordinated water molecules, which bridge two symmetry-independent Mn atoms in **1**. Three water molecules are coordinated to each Mn(1), two of which act as bridging ligands. The coordination polyhedron around Mn(1) is completed by tridentate 4-hydroxy-2,6-dicarboxylatopyridine and an O atom from a carboxylate group from another 4-hydroxy-2,6-dicarboxylatopyridine, which then acts as a bridging bidentate ligand [it acts as a tridentate ligand to another, inversion-related Mn(1)]. Therefore, the coordination polyhedra of Mn(1) and Mn(2) are almost identical (their geometrical parameters are very similar,

---

[†] Commercial chemicals were used without further purification. A Buck-500 scientific spectrometer was employed to record the IR spectrum of **1**. Elemental analysis was performed on a Thermo Finnigan Flash-1112EA microanalyzer.

General procedure for the preparation of compound **1**. The reaction of $MnCl_2 \cdot 2H_2O$ (12 mg, 0.075 mmol), 2-aminopyrimidine (30 mg, 0.31 mmol), and H_3cda (30 mg, 0.15 mmol) in deionized water (10 ml) afforded colourless prism crystals of the compound (35% yield, based on H_3cda) upon slow evaporation of the reaction mixture at room temperature. IR (KBr, ν/cm^{-1}): 3410 (m), 2960 (m), 1645 (m), 1525 (m), 1470 (m), 1435 (m), 1177 (m). Found (%): C, 27.22; H, 3.66; N, 4.67. Calc. for $C_{14}H_{14}Mn_2N_2O_{14} \cdot 4H_2O$ (%): C, 27.27; H, 3.57; N, 4.54.

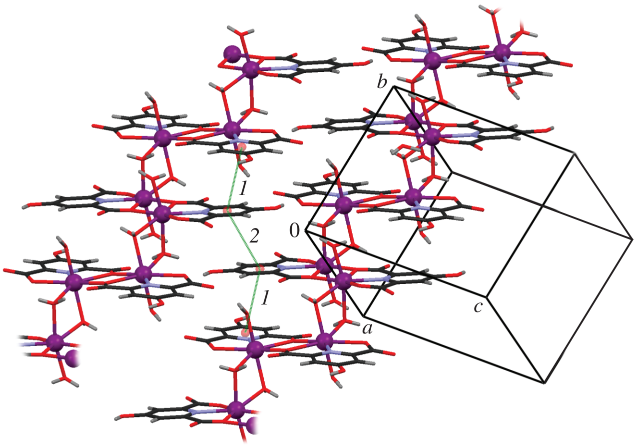

Figure 2 (*1*) Intra- and (*2*) intermolecular π-stacking in the crystal packing of **1**. Manganese atoms are shown as spheres of arbitrary radii. Geometric parameters: (*1*) $d(C_g\cdots C_g)$ = 3.6899 (17) Å, angle between ring planes 5.81(14)°, interplanar distance 3.3166(12) Å, offset 1.617 Å; (*2*) $d(C_g\cdots C_g)$ = = 3.7244(15) Å, angle between ring planes 0°, interplanar distance 3.3241(11) Å, offset 1.680 Å.

Figure 1S, Table 3S), although they are symmetry-independent. Unlike **2**, which comprises discrete planar units, **1** forms staircase-like chains (Figure 2S) extending in the direction [010]. Each ‘step’ comprises a pair of inversion-related Mn atoms (Figure 2S). The staircase-like structure is further stabilized by intra- and intermolecular π-stacking (Figure 2): there are finite motives comprising two intramolecular interactions [between N(1)···C(6) and N(2)···C(12) rings, marked as *1* in Figure 2] and one intermolecular interaction [between inversion-related N(1)···C(6) rings, marked as *2* in Figure 2]. There are four non-coordinated water molecules in the asymmetric unit (Figure 1), two of them being disordered over two positions. They are arrayed into an eight-membered centrosymmetric chain with two central, inversion-related, water molecules [O(6W)] in a disorder fashion (Figure 3). Such octamers fill the voids and connect the polymeric chains through hydrogen bonds.

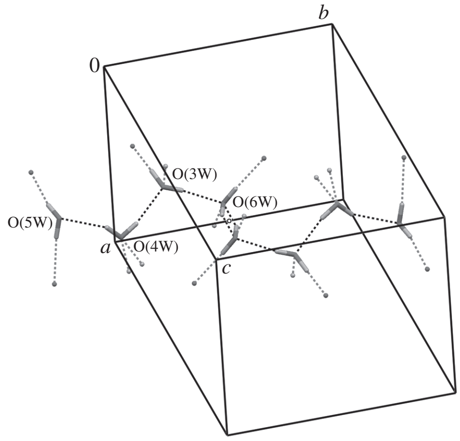

Figure 3 A centrosymmetric chain of water molecules with the central pair of O(6W) molecules disordered. Crystallographic inversion centre is indicated as an open circle. Hydrogen bonds between water molecules are shown as black dashed lines, while those between water and coordination polyhedra (omitted for clarity) are shown as grey dashed lines.

This work was supported by the Ferdowsi University of Mashhad (grant no. 21304/2).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.11.015.

References

1 M. Mirzaei, H. Aghabozorg and H. Eshtiagh-Hosseini, *J. Iran. Chem. Soc.*, 2011, **8**, 580.
2 M. Mirzaei, H. Eshtiagh-Hosseini, M. Chahkandi, N. Alfi, A. Shokrollahi, N. Shokrollahi and A. Janiak, *CrystEngComm*, 2012, DOI: 10.1039/C2CE26442K.
3 Y. Kazuhiro, Y. Noriko and F. Tadayasu, *Eur. Patent EP0603-165*, 1994.
4 K. Murakami, Y. Tanemura and M.Yoshino, *J. Nutr. Biochem.*, 2003, **14**, 99.
5 M. Devereux, M. McCann, V. Leon, V. McKee and R. J. Ball, *Polyhedron*, 2002, **21**, 1063.
6 M. Mirzaei, V. Lippolis, H. Eshtiagh-Hosseini and M. Mahjoobizadeh, *Acta Crystallogr.*, 2012, **C68**, m7.
7 S. K. Ghosh, J. Ribas, M. Salah El Fallah and P. K. Bharadwaj, *Inorg. Chem.*, 2005, **44**, 3856.
8 J.-P. Zou, X.-M. Liu, L.-S. Yan, A.-M. Deng, Q.-J. Xing and M.-H. Chen, *J. Coord. Chem.*, 2010, **63**, 56.

Received: 19th July 2012; Com. 12/3958

---

‡ *Crystal data for* **1**. Crystals of $C_{14}H_{22}Mn_2N_2O_{18}$ (M = 616.22) are triclinic, space group $P\bar{1}$, at 100 K: $a = 9.4351(5)$, $b = 10.8065(6)$ and $c =$ $= 11.1035(6)$ Å, $\alpha = 87.8480(10)°$, $\beta = 74.0430(10)°$, $\gamma = 80.0070(10)°$, $Z = 2$, $V = 1071.92(10)$ Å^3, $d_{calc} = 1.909$ g cm^{-3}, μ(MoKα) = 1.276 mm^{-1}. Data were collected on a colourless prismatic crystal mounted and centered on a Bruker SMART APEX2 CCD area detector diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The final unit cell was determined from 5180 reflections in the range of $1.9° < \theta < 28.0°$. The data were integrated using the SAINT suite of software and corrected for the effects of absorption using SADABS. The structure was solved by direct methods and refined iteratively *via* full-matrix least-squares and difference Fourier analysis using the SHELX-97 suite of software. The hydrogen atoms of OH groups and those of water molecules were found in the difference Fourier synthesis and normalized at the standard X-ray value of 0.85 /A. The H(C) atom positions were calculated. All the hydrogen atoms were refined in isotropic approximation within the riding model with the U_{iso}(H) parameters equal to $1.2U_{eq}(C_i)$ and $1.5U_{eq}(O_j)$, where $U(C_i)$ are the equivalent thermal parameters of the carbon atoms, $U(O_j)$ are the equivalent thermal parameters of the oxygen atoms to which the corresponding H atoms are bonded. Two water molecules O(5W) and O(6W) are disordered over two positions with the occupancies 3:1. Their minor components were refined isotropically. For more details, see Online Supplementary Materials.

CCDC 889442 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2012.