Synthesis, Structure and Characterization of a Novel Two-Dimensional Supramolecular Mn(II) Coordination Polymer Constructed from a 1,10-Phenanthroline Derivative and a Flexible Dicarboxylate

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The title complex, $[Mn_2(glu)(L)_2(HL)_2]\cdot 0.5H_2O$ (H_2glu = glutaric acid, HL = 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) has been synthesized using a hydrothermal method and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Crystal data: $C_{162}H_{88}Cl_8F_8Mn_4N_{32}O_9$, triclinic, space group $P\bar{1}$, a = 14.932(5), b = 16.414(5), c = 17.891(5) Å, α = 115.851(5), β = 91.288(5), γ = 112.894(5)°, V = 3536.4(19) Å^3, Z = 1. Compound **1** exhibits 1D chains which are further stacked by C–H$\cdots\pi$ interactions to give two-dimensional supramolecular layers.

Key words: Coordination Polymer, Crystal Structure, Glutaric Acid, 1,10-Phenanthroline Derivative

Introduction

The rational design and the synthesis of coordination polymers have attracted considerable current attention due to the interesting topologies and potential applications of the products in nonlinear optics, magnetism, molecular recognition, gas adsorption, *etc.* [1 – 3]. Generally, the diversity in the framework structures greatly depends on the selection of the ligand, the metal, the inorganic counterion, the solvent system, and sometimes the metal-to-ligand ratio [4]. Among these, the selection of the ligand is an important factor that may be utilized in determining the framework topology [5]. In this regard, organic ligands with aromatic polycarboxylate groups are especially attractive because the carboxyl group can bridge two or more metal centers to produce polymers with versatile structural motifs [6]. So far, rigid aromatic polycarboxylic acids such as benzenedicarboxylic acids, 1,3,5-benzenetricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid *etc.*, belong to the important family of polycarboxylate *O*-donor ligands, which have been extensively used to prepare coordination polymers [7]. However, the coordination chemistry of flexible glutaric acid has not been widely studied, especially in the presence of secondary *N*-donor ligands.

1,10-Phenanthroline (phen) has been widely used to build supramolecular architectures because of its excellent coordinating ability and large conjugated system that can easily form π-π interactions [8]. However, its derivative 2-(2-chloro-6-fluorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) (HL), has not been well studied in coordination chemistry [9 – 12]. Here, we selected the glutarate dianion (glu) as an organic linker and HL as an *N*-donor chelating ligand, generating a new two-dimensional supramolecular coordination polymer, $[Mn_2(glu)(L)_2(HL)_2]\cdot 0.5H_2O$.

Results and Discussion

Structure description

The X-ray crystallographic study has revealed that the compound **1** has a two-dimensional supramolecular structure. As shown in Fig. 1, the asymmetric unit of **1** contains two Mn(II) cations, one glu^{2-} dianion, two HL ligands, two L^{-1} anions, and one uncoordinated water molecule with half occupancy. Each Mn(II) atom is six-coordinated in a distorted octahedral environment surrounded by two carboxylate oxygen atoms from two different glu^{2-} dianions and four nitrogen atoms from one HL and one L^{-1}. For Mn1, the O3, N1, N5, and N6 atoms comprise the basal plane, while the O4A and N2 atoms occupy the axial positions. For Mn2, the O2, N3, N4, and N9 atoms comprise the basal plane, while the O1A and N10 atoms occupy the axial positions. The Mn–O and Mn–N distances in **1** (Table 1) are comparable to those observed for Mn(bpy)(glu) (bipy = 4,4'-bipyridine) [13]. The two oxygen atoms at each Mn center are *cis*. As depicted in Fig. 2, each Mn(II) atom is bridged by the glu^{2-} dianions to give a one-dimensional chain structure with the Mn1$\cdots$Mn2 distance of 10.976(5) Å The polymeric chain structure is brought about by the carboxylate groups of the glu^{2-} dianions which act as bridging ligands to two Mn centers each. Thereby eight-membered

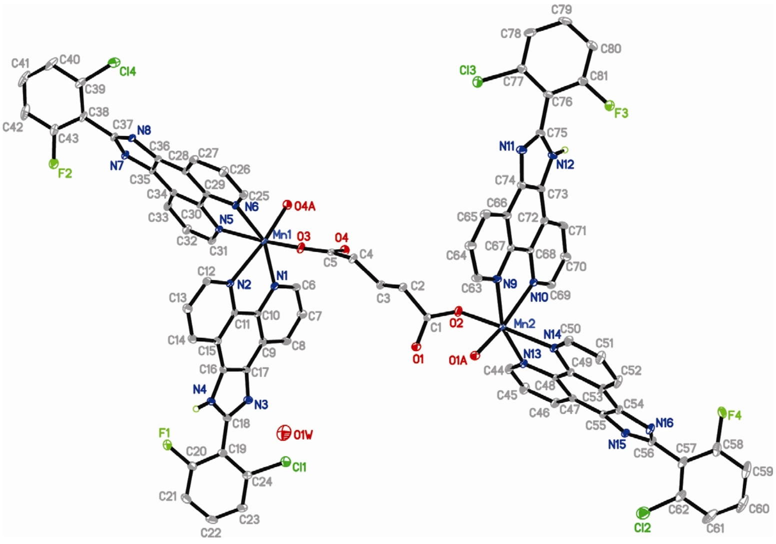

Fig. 1 (color online). The coordination environments of the Mn atoms in $[Mn_2(glu)(L)_2(HL)_2]\cdot 0.5H_2O$.

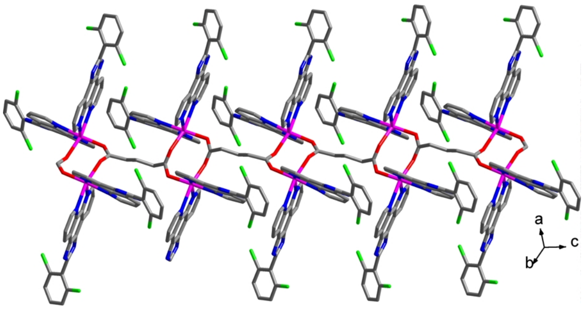

Fig. 2 (color online). View of the one-dimensional chain structure of $[Mn_2(glu)(L)_2(HL)_2]\cdot 0.5H_2O$.

(OCOMnOCOMn) rings with crystallographic inversion symmetry are formed (Fig. 2) which interconnect the formula units in the asymmetric unit as depicted in Fig. 1.

The L^{-1} and HL ligands are attached on both sides of the chain structure and play important roles in the formation of the chain structure. Two of their N atoms occupy coordination positions at the Mn(II) atom, whereas the remaining coordination positions are available for glu^{2-} dianions, allowing the formation of the chain structure It is noteworthy that the adjacent chains are connected through C–H$\cdots\pi$ interactions (3.385 Å) between an imidazole ring (C35–C37, N7, N8) of L^{-1} and C71A (symmetric code A: x, $y-1$, $z-1$) of HL, resulting in a two-dimensional supramolecular layer structure containing hydrophilic and hydrophobic strands running parallel (Fig. 3).

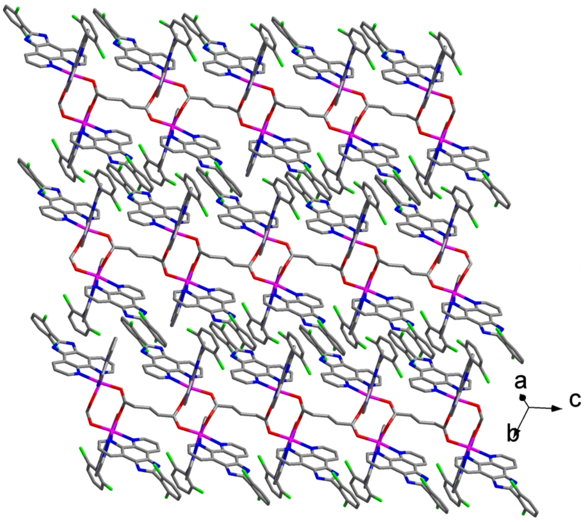

Fig. 3 (color online). Supramolecular layer structure of $[Mn_2(glu)(L)_2(HL)_2]\cdot 0.5H_2O$ constructed by C–H$\cdots\pi$ interactions.

It is noteworthy that the structure of **1** presented here is clearly different from that of the previously reported compound [Cd(1,2-bdc)(L)(H_2O)] (1,2-bdc = 1,2-benzenedicarboxylate) [12]. In the latter compound, the Cd(II) center is seven-coordinated by two nitrogen atoms from one L^{-1} ligand, one water oxygen atom, and four carboxylate oxygen atoms from two different 1,2-bdc ligands, in a distorted pentagonal bipyramid. Each pair of adjacent Cd(II) atoms are bridged by two 1,2-bdc ligands to form a dimeric structure.

Experimental Section

Generals

All the materials were of analytical reagent grade and used as received without further purification. The IR spectrum was obtained on a Perkin-Elmer 2400LSII spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer.

*Synthesis of compound **1***

The pH value of a mixture of $MnCl_2 \cdot 4H_2O$ (1 mmol), H_2glu (1 mmol) and HL (1 mmol) in 10 mL of distilled water was adjusted between 5 and 6 by adding triethylamine. The resultant solution was heated at 458 K in a Teflon-lined stainless-steel autoclave for 3 d. The reaction mixture was then slowly cooled to room temperature. Pale-yellow crystals suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield: 42 % based on Mn(II). – Anal. for $C_{162}H_{88}Cl_8F_8Mn_4N_{32}O_9$ (%): calcd. C 59.23, H 2.68, N 13.65; found C 59.47, H 2.52, N 13.37. – IR (KBr, cm^{-1}): ν = 3274w, 3051w, 1709w, 1615m, 1584s, 1578m, 1455s, 1424w, 1365w, 1345s, 844w.

X-Ray structure determination

Single-crystal X-ray diffraction data for complex **1** were recorded at T = 273(2) K on an Oxford Diffraction Gemini R Ultra diffractometer, using the ω scan technique with MoK_α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods with SHELXS-97 [14] and refined by full-matrix least-squares techniques using SHELXL-97 [15]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as rigid groups. The hydrogen atoms associated with the water molecules were not located from difference Fourier maps. Crystal data, data collection parameters and details of the structure refinement are given in Table 1, selected bond lengths and angles in Table 2.

CCDC 771311 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.

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Table 1. Crystal structure data for **1**.

Formula	$C_{81}H_{44}Cl_4F_4Mn_2N_{16}O_{4.5}$
M_r	1641.00
Crystal size, mm^3	0.22 × 0.21 × 0.16
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	14.932(5)
b, Å	16.414(5)
c, Å	17.891(5)
α, deg	115.851(5)
β, deg	91.288(5)
γ, deg	112.894(5)
V, $Å^3$	3536.4(19)
Z	2
D_{calcd}, g cm^{-3}	1.54
μ(MoK_α), cm^{-1}	0.6
F(000), e	1664
hkl range	$-19 \le h \le 16$; $-15 \le k \le 22$; $-22 \le l \le 17$
θ range, deg	2.22 – 29.35
Refl. collect. / unique / R_{int}	27180 / 9225 / 0.033
Data / ref. parameters	9225 / 1009
$R1$ / $wR2$ [$I \ge 2\sigma(I)$]	0.0630 / 0.1648
$R1$ / $wR2$ (all data)	0.1075 / 0.1789
GoF (F^2)	1.069
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e $Å^{-3}$	1.35 / −0.81

Table 2. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **1** with estimated standard deviations in parentheses[a].

Mn(1)–O(3)	2.1159(18)	Mn(1)–O(4)#1	2.148(2)
Mn(1)–N(6)	2.234(2)	Mn(1)–N(1)	2.253(2)
Mn(1)–N(5)	2.286(2)	Mn(1)–N(2)	2.358(2)
Mn(2)–O(1)#2	2.129(2)	Mn(2)–O(2)	2.1195(18)
Mn(2)–N(9)	2.252(2)	Mn(2)–N(13)	2.252(2)
Mn(2)–N(14)	2.266(2)	Mn(2)–N(10)	2.341(2)
O(3)–Mn(1)–O(4)#1	99.70(8)	O(4)#1–Mn(1)–N(6)	94.23(9)
O(3)–Mn(1)–N(6)	92.47(8)	O(4)#1–Mn(1)–N(1)	103.21(9)
O(3)–Mn(1)–N(1)	97.18(8)	O(3)–Mn(1)–N(5)	165.99(8)
N(6)–Mn(1)–N(1)	158.28(9)	N(6)–Mn(1)–N(5)	74.19(8)
O(4)#1–Mn(1)–N(5)	85.80(8)	O(3)–Mn(1)–N(2)	93.44(8)
N(1)–Mn(1)–N(5)	94.05(8)	N(6)–Mn(1)–N(2)	88.12(8)
O(4)#1–Mn(1)–N(2)	166.53(7)	N(5)–Mn(1)–N(2)	82.07(8)
N(1)–Mn(1)–N(2)	71.96(8)	O(2)–Mn(2)–N(9)	90.11(9)
O(2)–Mn(2)–O(1)#2	97.43(7)	O(2)–Mn(2)–N(13)	97.66(8)
O(1)#2–Mn(2)–N(9)	86.13(8)	N(9)–Mn(2)–N(13)	160.60(8)
O(1)#2–Mn(2)–N(13)	110.27(9)	O(1)#2–Mn(2)–N(14)	87.93(8)
O(2)–Mn(2)–N(14)	171.01(8)	N(13)–Mn(2)–N(14)	73.64(8)
N(9)–Mn(2)–N(14)	97.48(8)	O(1)#2–Mn(2)–N(10)	157.38(8)
O(2)–Mn(2)–N(10)	89.54(7)	N(13)–Mn(2)–N(10)	89.93(8)
N(9)–Mn(2)–N(10)	72.31(8)	N(14)–Mn(2)–N(10)	88.19(8)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z-1$; #2 $-x+1, -y, -z$.

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