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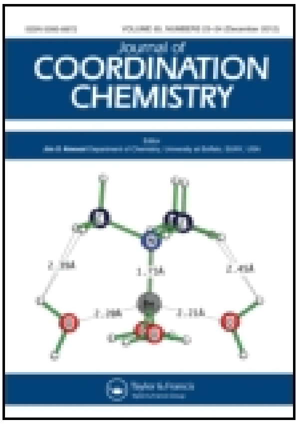

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Mononuclear manganese and tetranuclear copper compounds and their supramolecular networks constructed from hexafluoroglutaric acid and 2,2′-bipyridine

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Mononuclear manganese and tetranuclear copper compounds and their supramolecular networks constructed from hexafluoroglutaric acid and 2,2′-bipyridine

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$Mn(2,2'\text{-bpy})_2(HFGA)$ (**1**) and $[Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2(2,2'\text{-bpy})_4]\cdot 2HFGA\cdot 4H_2O$ (**2**) (H_2HFGA = hexafluoroglutaric acid and 2,2′-bpy = 2,2′-bipyridine) have been synthesized and characterized by X-ray structural analyses. **1** is a monomer with six-coordinate Mn^{2+} from two oxygens of HFGA and four nitrogens of two 2,2′-bpy. Complex **2** is tetranuclear with four Cu^{2+} ions bridged by triple-bridging μ_3-OH and double-bridging μ_2-OH. There are two crystallographically independent Cu^{2+} ions in different five-coordinate environments. Cu1 is coordinated by 2,2′-bpy and three OH ligands. Cu2 is coordinated by 2,2′-bpy, two μ_3-OH ligands, and one water molecule. The mononuclear and tetranuclear molecules as building blocks are connected to construct different 3-D supramolecular architectures *via* noncovalent interactions. Particularly, the lone pair (lp)–π ($F\cdots\pi$) interaction in **1** is observed. A hybrid water-anionic tape by linkage of $\{[(H_2O)_4(HFGA)]_2{}^{4-}\}_n$ fragments consisting of water dimers and HFGA anions in **2** is observed.

Keywords: Manganese; Copper; Hexafluoroglutaric acid; Crystal structure

1. Introduction

Crystal engineering of metal-organic supramolecules has attracted attention due to their fascinating architectures and potential applications in catalysis, magnetism, nonlinear optics, fluorescent sensing, etc. [1–6]. Noncovalent interactions are useful pathways for the design of supramolecular architectures from molecular building blocks, such as mononuclear, binuclear, and tetranuclear molecules or low-dimensional motifs, into structures of higher dimensionality [7–20]. Noncovalent interactions such as hydrogen bonds and π–π stacking are well-recognized in supramolecular chemistry [7–20]. A new type of supramolecular interaction, the lone pair (lp)–π, is an important topic for the past 5 years [21–29]. The importance of lp–π interaction is clearly evidenced in a number of biological systems [21–29].

Design and synthesis of metal–organic supramolecular networks based on carboxylates have attracted considerable attention [3–18]. Hexafluoroglutaric acid (H_2HFGA) is a fully fluorinated ligand containing two carboxylates and it may connect metal ions

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via various coordination fashions. Organic fluorines can give a variety of noncovalent interactions, such as C–H···F, C–F···π, and C–F···F, for crystal engineering [18, 21–23]. Metal complexes with H_2HFGA are infrequently reported [30, 31]. We synthesized two new complexes, Mn(2,2′-bpy)$_2$(HFGA) (**1**) and [$Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2$(2,2′-bpy)$_4$] · 2HFGA · $4H_2O$ (**2**) (H_2HFGA = hexafluoroglutaric acid and 2,2′-bpy = 2,2′-bipyridine). Complexes **1** and **2** are mononuclear and tetranuclear, respectively; discrete mononuclear and tetranuclear molecules based on carboxylates are less reported [12–16]. The organic fluorine plays a role in supramolecular crystal packing *via* F···π in **1** and C–H···F in **2**. 2,2′-Bipy is involved in π–π stacking interaction to stabilize the supramolecular structure. Attractive lp–π interaction (F···π) between HFGA and 2,2′-bpy is observed in **1**. The most interesting feature of **2** consists of the lattice water molecules and HFGA counterions with extensive hydrogen-bonding interactions, leading to the formation of a hybrid water-anionic polymeric assembly by the linkage of $\{[(H_2O)_4(HFGA)]_2{}^{4-}\}_n$ fragments. However, relatively less attention has been focused on hybrid hydrogen-bonded water assemblies with other solvents, small molecules, or counterions by hydrogen bonds [17–20]. We report the syntheses and structural characteristics of the two complexes.

2. Experimental

2.1. *Materials and physical measurements*

All analytical grade reagents and solvents were commercially available and used as received. Elemental analyses (C, H, N) were performed using an Elementar Vario EL analyzer. IR spectra (4000–400 cm^{-1}) were recorded on a Bruker EQUINOX-55 using KBr pellets. Thermogravimetric analyses (TGA) were performed on a WCT-1A Thermal Analyzer with a heating rate of 10°C min^{-1} from room temperature to 1000°C in air.

2.2. *Synthesis of the complexes*

2.2.1. Mn(2,2′-bpy)$_2$(HFGA) (1). A mixture of $MnSO_4 \cdot H_2O$ (0.0338 g, 0.2 mmol), hexafluoroglutaric acid (0.0480 g, 0.2 mmol), 2,2′-bipyridine (0.0312 g, 0.2 mmol), sodium hydroxide aqueous solution (2.0 mol L^{-1}, 0.30 mL), and deionized water (10 mL) in a 25 mL Teflon-lined stainless steel autoclave was heated under autogenous pressure at 140°C for 3 days, and then cooled to room temperature. The resulting solution was filtered and light-yellow block single crystals were obtained. Yield: 47% (based on Mn). Anal. Calcd (Found) for ($C_{25}H_{16}F_6N_4O_4Mn$) (%): C, 49.60 (49.32); H, 2.66 (2.59); N, 9.26 (9.40). Selected IR (KBr pellet, ν/cm^{-1}): 1683s, 1599m, 1494w, 1476w, 1442m, 1390m, 1142s, 768m, 738m, 416w.

2.2.2. [$Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2$(2,2′-bpy)$_4$] · 2HFGA · $4H_2O$ (2). The synthetic procedure of **2** was similar to that of **1** except that $MnSO_4 \cdot H_2O$ was replaced by $CuSO_4$ (0.0320 g, 0.2 mmol) and the amount of sodium hydroxide aqueous solution (2.0 mol L^{-1}, 0.25 mL). The resulting solution was filtered and blue block single crystals

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{25}H_{16}N_4O_4F_6Mn$	$C_{12.5}H_{11.5}N_2O_{4.5}F_3Cu$
Formula weight	605.36	382.28
Crystal system	Orthorhombic	Triclinic
Space group	*Pbcn*	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	14.6589(9)	14.6478(3)
b	10.7104(6)	14.6692(3)
c	15.6662(10)	14.8158(3)
α	90	101.0700(10)
β	90	104.7480(10)
γ	90	104.1010(10)
Volume (Å^3), Z	2459.6(3), 4	2874.24(10), 8
Calculated density (Mg m^{-3})	1.635	1.767
Absorption coefficient (mm^{-1})	0.624	1.587
F(000)	1220	1540
Crystal size (mm^3)	0.38 × 0.35 × 0.22	0.32 × 0.30 × 0.20
θ range for data collection (°)	2.36–25.49	1.75–27.97
Limiting indices	$-16 \le h \le 17$; $-12 \le k \le 9$; $-18 \le l \le 18$	$-19 \le h \le 19$; $-19 \le k \le 19$; $-19 \le l \le 19$
Reflections collected/unique	11773/2276 [R(int) = 0.0398]	50855/13681 [R(int) = 0.0245]
Data/restraints/parameters	2276/0/183	13681/4/845
Goodness-of-fit on F^2	1.031	1.018
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0510$, $wR_2 = 0.1458$	$R_1 = 0.0374$, $wR_2 = 0.1001$
R indices (all data)	$R_1 = 0.0718$, $wR_2 = 0.1686$	$R_1 = 0.0575$, $wR_2 = 0.1140$
Largest difference peak and hole (e Å^{-3})	0.913 and −0.344	0.692 and −0.420

were obtained from the mother liquid after several weeks. Yield: 17% (based on Cu). Anal. Calcd (Found) for $C_{12.5}H_{11.5}F_3N_2O_{4.5}Cu$ (%): C, 39.24 (39.12); H, 3.01 (3.16); N, 14.65 (14.47). Selected IR (KBr pellet, ν/cm^{-1}): 3441s, 1674s, 1603m, 1497w, 1477w, 1447m, 1385m, 1149m, 773m, 732w, 417w.

2.3. X-ray crystal structure determination. X-ray single-crystal data collections for the two complexes were performed on a Bruker Smart Apex II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. Semiempirical absorption correction was applied on the complex using the SADABS program. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using SHELXS 97 and SHELXL 97 programs [32, 33]. Crystallographic data and details of the structure refinements are listed in table 1. The selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Structural description of [Mn(2,2′-bpy)$_2$(HFGA)] (1)*

Complex **1** is mononuclear consisting of one Mn^{2+}, one HFGA anion, and two 2,2′-bpy (figure 1a). HFGA ligand coordinates to Mn^{2+} by rare bis(monodentate) fashion. The two 2,2′-bpy coordinate to Mn^{2+} bidentate with twisting angle of 88.9°. The Mn^{2+} is six

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Mn(1)–O(1)	2.114(2)	Mn(1)–O(1)A	2.114(2)
Mn(1)–N(1)	2.275(3)	Mn(1)–N(1)A	2.275(3)
Mn(1)–N(2)	2.278(3)	Mn(1)–N(2)A	2.278(3)
O(1)–Mn(1)–N(1)	92.73(10)	O(1)–Mn(1)–N(1)A	100.46(10)
O(1)–Mn(1)–N(2)	90.33(10)	O(1)–Mn(1)–N(2)A	164.45(10)
O(1)A–Mn(1)–O(1)	95.29(14)	O(1)A–Mn(1)–N(1)	100.46(10)
O(1)A–Mn(1)–N(1)A	92.73(10)	O(1)A–Mn(1)–N(2)	164.45(10)
O(1)A–Mn(1)–N(2)A	90.33(10)	N(1)–Mn(1)–N(1)A	160.43(14)
N(1)–Mn(1)–N(2)	93.74(10)	N(1)–Mn(1)–N(2)A	71.96(10)
N(1)A–Mn(1)–N(2)	71.96(10)	N(1)A–Mn(1)–N(2)A	93.74(10)
N(2)–Mn(1)–N(2)A	88.03(13)	–	–

Symmetry transformations used to generate equivalent atoms: A: $-x + 2$, y, $-z + 3/2$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Cu(1)–O(1)	2.3347(18)	Cu(1)–O(3)	1.9649(17)
Cu(1)–O(4)	1.9126(17)	Cu(1)–N(1)	2.001(2)
Cu(1)–N(2)	2.017(2)	Cu(2)–O(1)	1.9680(17)
Cu(2)–O(2)	1.9118(19)	Cu(2)–O6W	2.219(2)
Cu(2)–N(3)	2.016(2)	Cu(2)–N(4)	2.003(2)
Cu(3)–O(3)	1.9658(16)	Cu(3)–O(4)	1.9117(18)
Cu(3)–O5W	2.228(2)	Cu(3)–N(7)	2.005(2)
Cu(3)–N(8)	2.010(2)	Cu(4)–O(1)	1.9733(17)
Cu(4)–O(2)	1.9093(18)	Cu(4)–O(3)	2.2892(17)
Cu(4)–N(5)	2.018(2)	Cu(4)–N(6)	1.999(2)
O(3)–Cu(1)–O(1)	83.24(7)	O(3)–Cu(1)–N(1)	177.85(8)
O(3)–Cu(1)–N(2)	100.75(8)	O(4)–Cu(1)–O(1)	99.48(8)
O(4)–Cu(1)–O(3)	80.71(7)	O(4)–Cu(1)–N(1)	97.32(8)
O(4)–Cu(1)–N(2)	163.90(9)	N(1)–Cu(1)–N(2)	80.91(8)
N(1)–Cu(1)–O(1)	97.97(7)	N(2)–Cu(1)–O(1)	96.61(7)
O(1)–Cu(2)–O6W	101.11(9)	O(1)–Cu(2)–N(3)	157.07(8)
O(1)–Cu(2)–N(4)	99.73(8)	O(2)–Cu(2)–O(1)	81.36(7)
O(2)–Cu(2)–O6W	93.81(9)	O(2)–Cu(2)–N(3)	94.71(9)
O(2)–Cu(2)–N(4)	170.52(9)	N(3)–Cu(2)–O6W	101.68(9)
N(4)–Cu(2)–O6W	95.21(9)	N(4)–Cu(2)–N(3)	80.60(10)
O(3)–Cu(3)–O5W	96.42(8)	O(3)–Cu(3)–N(7)	99.48(8)
O(3)–Cu(3)–N(8)	155.01(8)	O(4)–Cu(3)–O(3)	80.70(7)
O(4)–Cu(3)–O5W	98.79(9)	O(4)–Cu(3)–N(7)	171.19(9)
O(4)–Cu(3)–N(8)	95.38(8)	N(7)–Cu(3)–O5W	89.96(9)
N(7)–Cu(3)–N(8)	80.71(9)	N(8)–Cu(3)–O5W	108.57(9)
O(1)–Cu(4)–O(3)	84.26(7)	O(1)–Cu(4)–N(5)	100.81(8)
O(1)–Cu(4)–N(6)	175.96(8)	O(2)–Cu(4)–O(1)	81.28(7)
O(2)–Cu(4)–O(3)	95.37(7)	O(2)–Cu(4)–N(5)	165.24(9)
O(2)–Cu(4)–N(6)	96.31(9)	N(5)–Cu(4)–O(3)	99.37(7)
N(6)–Cu(4)–O(3)	99.24(8)	N(6)–Cu(4)–N(5)	80.69(9)

coordinate in a distorted octahedron. O1, N1, N1A, and N2A occupy the equatorial plane with a mean deviation of 0.092 Å. While O1A and N2 occupy axial positions with O1A–Mn–N2 angle of 164.45(10)°. The bond angles of N1A–Mn–O1A and O1–Mn–N2 are 92.73(10)° and 90.33(10)°, respectively, close to 90°, indicating slight distortion. The average Mn–N and Mn–O bond distances are 2.276 and 2.114 Å, respectively.

Attractive lp–π interaction between fluorine of HFGA and the π-system of 2,2′-bpy is observed (figure 1b). The distance between F3 and the centroid of the aromatic ring (C6/C10, N2) is 3.291 Å. The shortest distance between F3 and the aromatic ring (C8) is 3.122 Å, close to the C + F (3.17 Å) van der Waals radii. The calculated energy

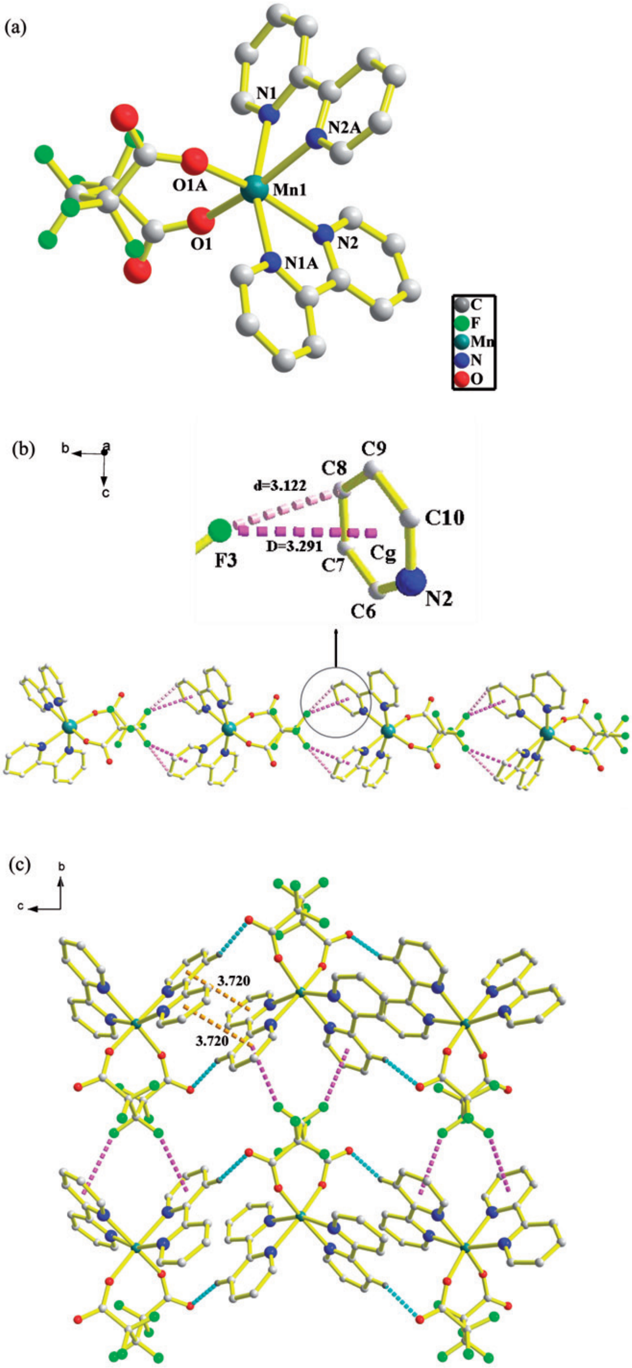

Figure 1. View of the structure of **1**: (a) Molecular structure. All hydrogens are omitted for clarity. Symmetry codes: A: $-x, y, -z + \frac{1}{2}$. (b) 1-D chain structure by F···π interactions and (c) 2-D supramolecular network.

minimum characterizing bonding between an lp and a single π ring often falls at a distance greater than the sum of the van der Waals′ radii, since too short contact distances result in repulsive interactions [21, 22]. 1-D chain structure is formed through F$\cdots\pi$ interactions along the *b*-axis (figure 1b). In addition, C–H $\cdots$ O and π–π stacking interactions are observed. C–H $\cdots$ O hydrogen bond arises from hydrogen of 2,2′-bpy and carboxyl, C9–H9$\cdots$O2 [$-x$, $1-y$, $1-z$], 3.297 Å, 160.18°. The $\pi\cdots\pi$ stacking interactions form between pyridine rings of adjacent molecules with centroid–centroid distance of 3.720 Å. These interactions give a 2-D supramolecular network (figure 1c).

3.2. *Structural description of [$Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2(2,2'\text{-}bpy)_4$] · 2HFGA · 4$H_2O$ (2)*

Complex **2** consists of $[Cu_4(\mu_2\text{-OH})_2(\mu_3\text{-OH})_2(H_2O)_2(2,2'\text{-bpy})_4]^{4+}$ -$\{Cu_4\}^{4+}$, two free HFGA anions, and four free water molecules (figure 2a). The four Cu^{2+} ions are bridged by triple-bridging μ_3-OH and double-bridging μ_2-OH to form a tetranuclear unit with chair-like stepped structure. Cu1 and Cu2, Cu3 and Cu4 are linked by one μ_3-OH ligand. Cu1 and Cu3, Cu2 and Cu4 are linked by one μ_3-OH and one μ_2-OH. There are two types of Cu$\cdots$Cu distances. The slightly longer Cu$\cdots$Cu distances are 3.489(2) and 3.515(2) Å when bridged by one OH^-; short Cu$\cdots$Cu distances are 2.931(2) and 2.908(2) Å when bridged by two OH^-. There are two crystallographically independent Cu^{2+} in different five-coordinate environments. Cu1 is coordinated by a 2,2′-bpy [d(Cu1–N) = 2.001(2) and 2.017(2) Å], two μ_3-OH [d(Cu1–O) = 1.9649(17) and 2.3347(18) Å], and one μ_2-OH [d(Cu1–O) = 1.9126(17) Å]. The coordination environment for Cu2 is a 2,2′-bpy [d(Cu2–N) = 2.003(2) and 2.016(2) Å], one μ_3-OH [d(Cu2–O) = 1.9680(17) Å], one μ_2–OH [d(Cu2–O) = 1.9118(19) Å], and one water molecule [d(Cu2–O6W) = 2.219(2) Å]. Cu1 and Cu2 have similar square-pyramidal coordination. Two nitrogens and two OH^- form the equatorial planes around Cu1 and Cu2 with mean deviation from planes of 0.1269 and 0.1209 Å, respectively, but the axial sites are occupied by O1 for Cu1 and by O6w for Cu2. The coordination environments of Cu4 and Cu3 are similar to those of Cu1 and Cu2, respectively.

Free water molecules form hydrogen bonds with oxygens of HFGA, resulting in a unique hybrid water-HFGA anionic tape generated by linkage of $\{[(H_2O)_4(HFGA)]_2{}^{4-}\}_n$ fragments (figure 2b). Within the chain, the water dimer (O3W$\cdots$O4W) with distance of 2.719 Å is found. The OW$\cdots$O(HFGA) distances range from 2.744 to 2.798 Å. The coordinated water molecules (O5W and O6W) form hydrogen bonds with crystal water to form water trimers, O2W$\cdots$O5W$\cdots$O1W and O6W$\cdots$O3W$\cdots$O4W with O$\cdots$O distances ranging from 2.651 to 2.736 Å. Hydroxo groups (O1, O2, O3, and O4) form hydrogen bonds with oxygens of HFGA, and the O$\cdots$O distances range from 2.795 to 2.911 Å. So, $\{Cu_4\}^{4+}$ cationic units are connected to the hybrid water-HFGA anionic tape *via* hydrogen bonds, resulting in a 2-D supramolecular network (figure 2c). In addition, the C–H$\cdots$F hydrogen bonds with C$\cdots$F separations of 3.158–3.348 Å form between 2,2′-bpy and HFGA. The O–H$\cdots$F hydrogen bond forms between free water (O1W) and the HFGA with O1W$\cdots$F distance of 3.095 Å. In the tetranuclear unit, four 2,2′-bpy molecules are almost parallel to each other with dihedral angles 3.1°–11.4° between them. There are intermolecular π–π stacking interactions between 2,2′-bpy molecules from adjacent tetranuclear units with a face-to-face distance of 3.578 Å. Taking into account these noncovalent contacts,

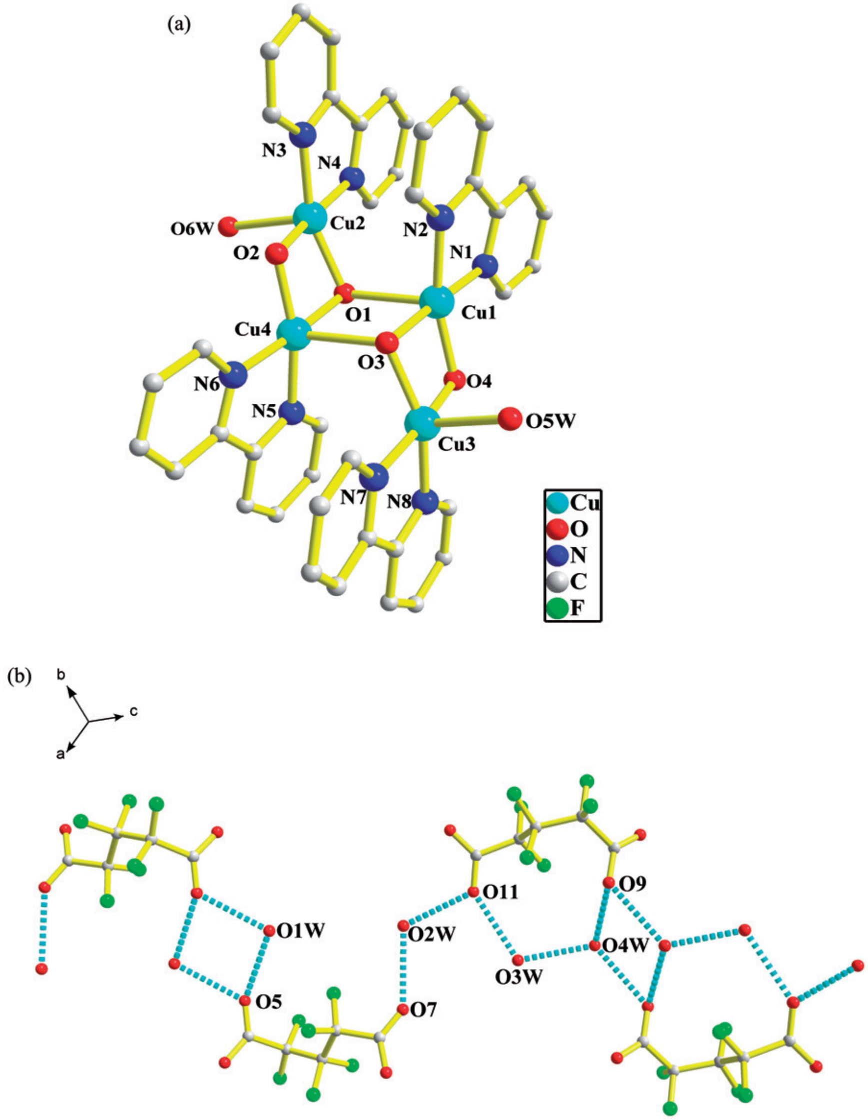

Figure 2. View of the structure of **2**: (a) Molecular structure. All hydrogens, uncoordinated water and HFGA are omitted for clarity. (b) 1-D water-HFGA hybrid anionic chain, (c) 2-D supramolecular network. 2,2′-bipy are omitted for clarity, and (d) 3-D supramolecular network.

a 3-D supramolecular structure is formed (figure 2d, hydrogen-bonding parameters are listed in table S1).

3.3. *Thermogravimetric analysis*

The TGA-DTA analyses of **1** and **2** were studied from room temperature to 1000°C (Supplementary material). Complex **1** is thermally stable up to 209°C, then decomposes

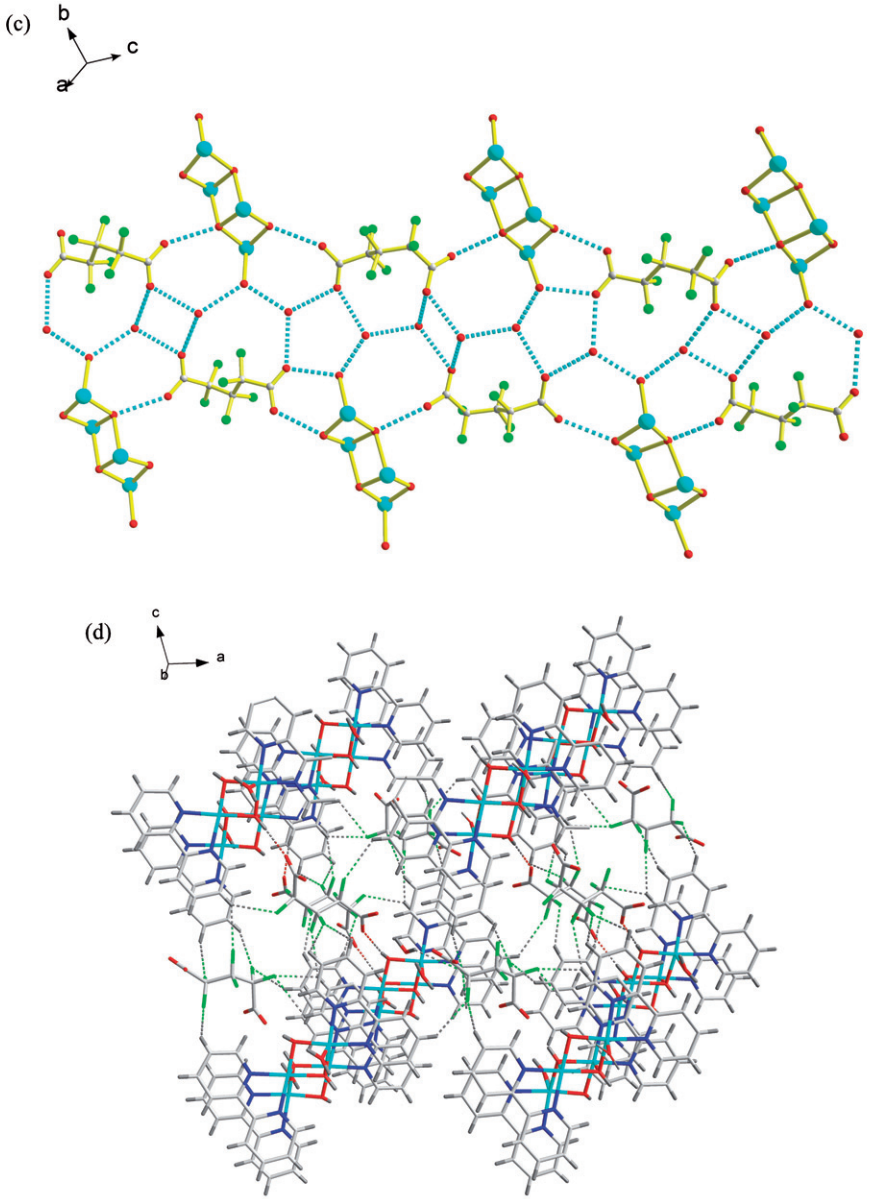

Figure 2. Continued.

from 209°C to 501°C to yield MnO_2 as the final residue. The total weight loss is 88.71% (Calcd 88.28%). For **2**, the first weight loss of 4.93% occurs at 57–87°C from loss of free water (Calcd 4.71%). Decomposition of organic ligands takes place from 200°C to 418°C. The total weight loss of 74.65% suggests decomposition leaving CuO as the final product (Calcd 79.07%).

4. Conclusion

The reactions of $MnCl_2/CuSO_4$ with hexafluoroglutaric acid (HFGA) and 2,2′-bipy gave mononuclear $Mn(2,2'\text{-bpy})_2(HFGA)$ (**1**) and tetranuclear $[Cu_4(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)_2(H_2O)_2(2,2'\text{-bpy})_4]\cdot 2HFGA\cdot 4H_2O$ (**2**). In the field of metal complexes based on carboxylates, discrete mononuclear, and tetranuclear molecules are little known. Noncovalent interactions assemble the discrete molecules into higher dimensional architectures. F–π, C–H$\cdots$O, and $\pi\cdots\pi$ stacking interactions in **1** are observed; O–H$\cdots$O, O–H$\cdots$F, C–H$\cdots$F, and $\pi\cdots\pi$ stacking interactions in **2** are observed. These interactions give 3-D supramolecular networks of **1** and **2** from molecular building blocks. The lp–π interaction in **1** and the hybrid water-anionic tape in **2** are unusual.

Supplementary material

The crystallographic data of **1** (CCDC-796331) and **2** (CCDC-730734) can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk/deposit.

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