

# Synthesis, crystal structure and magnetic properties of three polynuclear manganese compounds bearing ferrocenecarboxylato ligands

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## Abstract

The reactions of sodium ferrocenecarboxylate ( $\text{FcCO}_2\text{Na}$ ) and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in methanol in the presence of ancillary ligands of 1,10-phenanthroline (phen) or 2,2'-bipyridine (2,2'-bpy) produce three discrete polynuclear complexes bearing ferrocenecarboxylato ligands:  $[\text{Mn}_2(\text{FcCO}_2)_3(\text{phen})_2](\text{ClO}_4) \cdot 2\text{CH}_2\text{Cl}_2$  (**1**),  $[\text{Mn}_3(\text{FcCO}_2)_6(2,2'\text{-bpy})_2] \cdot 2\text{H}_2\text{O}$  (**2**) and  $[\text{Mn}_4\text{O}_2(\text{FcCO}_2)_7(2,2'\text{-bpy})_2]\text{ClO}_4 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (**3**). It is shown that their composition and skeletons are tuned by the ancillary ligands and the ratios of starting materials. In dimanganese complex **1**, both Mn(II) ions are pentacoordinated in a distorted trigonal bipyramidal geometry and bridged by three ferrocenecarboxylato ligands in a distorted *syn-syn* bridging mode, which is rare in triply carboxylato-bridged dimanganese complexes. Compound **2** presents a linear trinuclear  $[\text{Mn}_3(\mu_2\text{-}\eta^1\text{:}\eta^1\text{-O}_2\text{CFC})_4(\mu_2\text{-}\eta^1\text{:}\eta^2\text{-O}_2\text{CFC})_2]$  core, in which six ferrocenecarboxylato ligands show two different bridging modes. The cationic  $\text{Mn}_4\text{O}_2$  core of **3** has a butterfly structure, in which two Mn(III) ions at “body” sites are bridged by an additional ferrocenecarboxylato ligand and they are further connected to the Mn(III) ions at “wing-tip” sites by ferrocenecarboxylato ligands. Magnetic susceptibilities of **1** and **2** were measured. Both of them mediate a weak antiferromagnetic coupling between the Mn(II) ions bridged by ferrocenecarboxylato ligands.

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**Keywords:** Manganese; Crystal structure; Ferrocenecarboxylato; Magnetic properties

## 1. Introduction

Organic carboxylato ligands have been extensively utilized in constructing functional infinite or discrete polynuclear compounds that have potential applications in hydrogen storage [1], catalysis [2], optic [3] and magnetic materials [4]. In contrast, organometallic carboxylic acids have been relatively rarely used, though this kind of ligand might induce unusual properties in the formed metal complexes due to the rich properties and the potential steric and electronic effect of the organometallic group [5]. Ferro-

cenecarboxylic acids, as ligands containing typical organometallic group that exhibits not only high thermal stability, but also excellent redox activity and attractive properties in respect of catalysis, magnetism and nonlinear optics [6], have attracted much interest in coordination chemistry in recent years. Some metal complexes with ferrocenecarboxylic acid ligand have been reported [7–12]. In this context, we have also reported recently two manganese complexes bearing ferrocenecarboxylato ligands [10]. The reaction of Mn(II) with ferrocenecarboxylate gave polymer  $[\text{Mn}_3(\text{FcCO}_2)_6(\text{CH}_3\text{OH})_4]_n$  in the absence of ancillary ligands, while that afforded  $[\text{Mn}_3(\text{FcCO}_2)_6(\text{H}_2\text{O})_2(4,4'\text{-bpy})_n]$  in the presence of bridging ancillary ligand of 4,4'-bipyridine. Both complexes contain the similar infinite chain constructed alternatively from mononuclear [Mn(II)] units

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and dinuclear  $[\text{Mn}_2(\text{FcCO}_2)_4]$  units via  $\mu_2$ -ferrocenecarboxylato-*O,O'* bridging and show antiferromagnetic interactions with an unprecedented  $J_1$ – $J_1$ – $J_2$  (AF1–AF1–AF2) repeating sequence [10]. Driven by these interesting results and as continuation of our interest in metal complexes of ferrocenecarboxylato ligands, we turn to use non-bridging ligands such as 2,2'-bipyridine and 1,10-phenanthroline as coligands to investigate their influence on the structures and properties of the complexes of Mn-ferrocenecarboxylato system, and herein we wish to report three discrete polynuclear manganese complexes bearing ferrocenecarboxylato ligands tuned by coligands and the stoichiometric ratio of the reactants. The use of phen as ancillary ligand led to the formation of a rarely reported triply carboxylato-bridged dimanganese(II) complex  $[\text{Mn}_2(\text{FcCO}_2)_3(\text{phen})_2](\text{ClO}_4) \cdot 2\text{CH}_2\text{Cl}_2$  (**1**) with two penta-coordinated Mn(II) ions. Using 2,2'-bpy as ancillary ligand and varying the stoichiometric ratio of the reactants, we obtained a linear trinuclear complex  $[\text{Mn}_3(\text{FcCO}_2)_6(2,2'\text{-bpy})_2] \cdot 2\text{H}_2\text{O}$  (**2**) and a butterfly-like tetranuclear complex  $[\text{Mn}_4\text{O}_2(\text{FcCO}_2)_7(2,2'\text{-bpy})_2] \cdot \text{ClO}_4 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (**3**). Magnetic susceptibilities of **1** and **2** were measured. Both of them exhibit a weak antiferromagnetic coupling between Mn(II) ions bridged by ferrocenecarboxylato ligand. To the best of our knowledge, only two cases of discrete polynuclear manganese complexes containing ferrocenecarboxylato ligands, that is, a dinuclear complex cation  $[\text{Mn}_2(\text{phen})_4(\text{FCA})_2]^{2+}$  (FCA = anion of 3-ferrocenyl-2-crotonic acid) [8] and a manganese supercubane  $[\text{Mn}_{13}\text{O}_8(\text{OCH}_3)_6(\text{fcdc})_6]$  (fcdc = 1,1'-ferrocenedicarboxylate) [11], have been reported in the literatures, and no magnetic properties of discrete polynuclear manganese-ferrocenecarboxylate complexes have ever been studied previously.

## 2. Results and discussion

### 2.1. Synthesis of complexes 1–3 and IR spectra

The reaction of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{FcCO}_2\text{Na}$  and phen in a ratio of 1:1:1 in MeOH at room temperature afforded a dinuclear Mn(II) complex of  $[\text{Mn}_2(\text{FcCO}_2)_3(\text{phen})_2](\text{ClO}_4) \cdot 2\text{CH}_2\text{Cl}_2$  (**1**). When phen was replaced by 2,2'-bpy and the ratio of the starting materials changed to 1:2:1, a trinuclear Mn(II) complex of  $[\text{Mn}_3(\text{FcCO}_2)_6(2,2'\text{-bpy})_2] \cdot 2\text{H}_2\text{O}$  (**2**) was obtained. Changing the stoichiometric ratio of the reactants from 1:2:1 to 1:1:1 in  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ - $\text{FcCO}_2\text{Na}$ -2,2'-bpy system, we could isolate a tetranuclear Mn(III) compound of  $[\text{Mn}_4\text{O}_2(\text{FcCO}_2)_7(2,2'\text{-bpy})_2] \cdot \text{ClO}_4 \cdot 2\text{CH}_2\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (**3**). The difference of complexes 1–3 in nuclearity indicates the chemical modification of the coligands and the reaction conditions on the composition and the structure of the final products. It is noteworthy that all manganese ions in **3** display III+ oxidation state, indicating that the formation of **3** was accompanied by an oxidation reaction of Mn(II) in reactant to Mn(III) in product. This oxidation reaction is probably accomplished by oxygen in air, but the mecha-

nism of the reaction is not clear at present, especially at the point that such a reaction was observed only under the conditions with 2,2'-bpy as coligand and in a specific stoichiometry of the reactants. From the sense of the manganese source for the synthesis, the isolation of **3** is very different from that for the reported  $[\text{Mn}_4\text{O}_2]$  complexes which were usually obtained from the conversion of trinuclear complexes  $[\text{Mn}_3\text{O}(\text{RCOO})_6\text{L}_3]^{0,+}$  (L = pyridine,  $\text{H}_2\text{O}$ ) or from the assembly reactions using  $\text{MnO}_4^-$  to oxidize Mn(II) [13].

The characteristic IR bands of the ferrocenyl group are observed at 3094 and 486  $\text{cm}^{-1}$  for **1**, 3098 and 490  $\text{cm}^{-1}$  for **2** and 3095 and 486  $\text{cm}^{-1}$  for **3**, respectively, which are close to those in the reported compounds [14,15]. The strong absorption bands at 1559–1582 and 1388–1392  $\text{cm}^{-1}$  ranges can be assigned to  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  vibrations, respectively, which is consistent with the known complexes [15]. The characteristic absorption of  $\text{ClO}_4^-$  appears at 1107 and 1106  $\text{cm}^{-1}$  for compounds **1** and **3**, respectively [16].

### 2.2. Description of the structure of complexes 1–3

The single crystal X-ray diffraction analysis of **1** revealed a dinuclear block  $[\text{Mn}_2(\text{FcCO}_2)_3(\text{phen})_2]^+$ , a  $\text{ClO}_4^-$  ion and two  $\text{CH}_2\text{Cl}_2$  molecules in the asymmetric unit. As shown in Fig. 1 each Mn(II) ion possesses a distorted trigonal bipyramidal geometry with the coordination of three oxygen atoms from three ferrocenecarboxylato ligands and two nitrogen atoms from one 1,10-phenanthroline molecule. One oxygen atom and one nitrogen atom occupy the axis sites and the other atoms occupy the equatorial sites. The Mn–O bond lengths are in the range of 2.068(5) to 2.124(5) Å and the Mn–N bond lengths range from

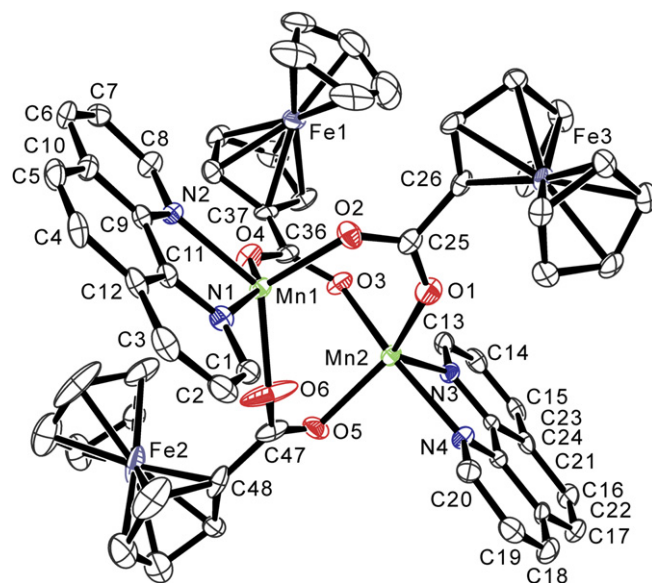


Fig. 1. ORTEP drawing of complex **1** showing 30% probability ellipsoids. For clarity, hydrogen atoms,  $\text{ClO}_4^-$  ion and  $\text{CH}_2\text{Cl}_2$  molecules are omitted and only selected atoms are labeled.

2.211(5) to 2.246(5) Å. The two Mn(II) ions of **1** are bridged by three ferrocenecarboxylato groups. The dihedral angles between the least-square plane of the bridging carboxylate [O,C,O] and the corresponding plane [Mn1,C<sub>carboxylato</sub>,Mn2] are 14.0°, 11.6°, and 23.6° for [O1,C25,O2] and [Mn1,C25,Mn2], [O3,C36,O4] and [Mn1,C36,O4], and [O5,C47,O6] and [Mn1,C47,Mn2], respectively. This gives a lightly distorted *syn-syn* bridging mode for the three ferrocenecarboxylato ligands and results in a Mn···Mn separation of 3.5594(3) Å, which is much shorter than those in reported dimers with three organic  $\mu_2$ -carboxylato-*O,O'* bridges [17,18]. This kind of triply carboxylato-bridged dimanganese(II) complexes with pentacoordinated Mn(II) geometry are rare. To the best of our knowledge, only dinuclear complex [Mn<sub>2</sub>(Ph<sub>2</sub>MeC-COO)<sub>3</sub>(2,2'-bpy)<sub>2</sub>]PF<sub>6</sub> was reported to have both three carboxylato bridges and pentacoordinated Mn(II) ions [19]. The pentacoordinated Mn(II) geometries in both cases seems to be attributed to the steric hindrance on the carboxylato groups. The dimeric Mn(II) complex in our case is different from the reported dimeric ferrocene containing carboxylato complex [Mn<sub>2</sub>(phen)<sub>4</sub>(FCA)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (FCA = anion of 3-ferrocenyl-2-crotonic acid) obtained from the reaction of Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O with FCA and phen in a ratio of 1:1:2 in ethanol–H<sub>2</sub>O solution [8]. In this complex, each six-coordinated Mn(II) ion is coordinated by two phen molecules and the Mn(II) ions are only bridged by two carboxylato groups. The group of Hou has ever made a similar reaction using Mn(OAc)<sub>2</sub>·2H<sub>2</sub>O to interact with a ferrocene-containing carboxylate (FcC<sub>6</sub>H<sub>4</sub>COONa) and phen in a ratio of 1:2:1 in methanol–H<sub>2</sub>O solution [9]. But it gave rise to a one-dimensional double bridged chain structure instead of a dimer structure.

It is shown in Fig. 2 that compound **2** has a discrete linear trinuclear structure with the Mn2 ion on the inversion center similar to the analogous complexes bearing organic carboxylato ligands [20–22]. The Mn2 ion is connected to Mn1 ion by three ferrocenecarboxylato groups with a Mn···Mn separation of 3.4289(1) Å, which is comparable to those reported with similar bridges [20,21,23]. Two of the three ferrocenecarboxylato ligands act as  $\mu_2$ - $\eta^1$ : $\eta^1$ -bridges. The other one behaves as a  $\mu_2$ - $\eta^1$ : $\eta^2$ -bridge. This means that it chelates to one Mn(II) ion using their two oxygen atoms and at the same time bridges another Mn(II) ion using one of the two carboxylato oxygen atoms. 2,2'-bipyridine adopts a chelating coordination mode. The central Mn2 ion is coordinated in an octahedral geometry by six oxygen atoms from six ferrocenecarboxylato ligands with the O–Mn–O angle in the range of 85.49(15) to 94.51(15) Å. The coordination of each terminal Mn(II) ion to two nitrogen atoms and four oxygen atoms from three ferrocenecarboxylato ligands leads to a distorted trigonal antiprism geometry with the O–Mn–N and O–Mn–O angles in the range of 56.31(11) to 162.32(14) Å.

The asymmetric unit of **3** contains a [Mn<sub>4</sub>O<sub>2</sub>(FcCO<sub>2</sub>)<sub>7</sub>(2,2'-bpy)<sub>2</sub>]<sup>+</sup>, a ClO<sub>4</sub><sup>−</sup>, two CH<sub>2</sub>Cl<sub>2</sub> molecules and seven H<sub>2</sub>O molecules. The cationic Mn<sub>4</sub>O<sub>2</sub> core has a

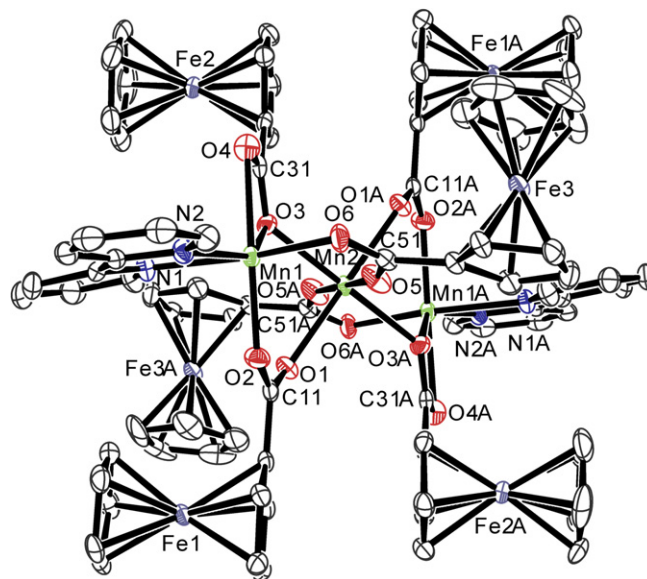


Fig. 2. ORTEP drawing of complex **2** showing 30% probability ellipsoids. For clarity, hydrogen atoms are omitted and only selected atoms are labeled. Symmetry operations: (A)  $-x + 1, -y + 2, -z$ .

butterfly structure with Mn3 and Mn4 occupying the “body” sites and Mn1 and Mn2 occupying the “wing-tip” sites as displayed in Fig. 3, which is similar to the reported cases bearing the Mn<sub>4</sub>O<sub>2</sub> core [13,24,25]. Each “wing-tip” Mn(III) ion is connected to the two “body” Mn(III) ions by a  $\mu_3$ -O atom to form a Mn<sub>3</sub> wing. Thus the cationic core can be considered as two edge-sharing Mn<sub>3</sub>O units with a dihedral angle of 135.886°. The  $\mu_3$ -O atoms do not lie in the Mn<sub>3</sub> planes, but slightly below the corresponding plane (0.3963 Å for O15, 0.3604 Å for O16). The two “body” Mn(III) ions (Mn3 and Mn4) are bridged by two  $\mu_3$ -O atoms and a  $\mu_2$ -ferrocenecarboxylato group with a Mn···Mn separation of 2.872(2) Å. Except a  $\mu_3$ -O bridge, the Mn1 atom is further bridged to Mn3 by a  $\mu_2$ -ferrocenecarboxylato group with a Mn···Mn separation of 3.4264(2) Å, and also to Mn4 by two  $\mu_2$ -ferrocenecarboxylato groups with a Mn···Mn separation of 3.2785(4) Å. Similar to Mn1, the Mn2 atom is also further bridged to Mn4 by an additional  $\mu_2$ -ferrocenecarboxylato group and to Mn3 by two additional  $\mu_2$ -ferrocenecarboxylato groups

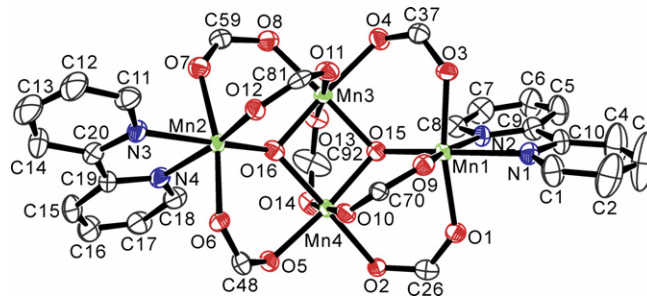


Fig. 3. ORTEP drawing of complex **3** showing 30% probability ellipsoids. Hydrogen atoms and ferrocene groups are omitted for clarity.

with a Mn···Mn separation of 3.4121(1) Å and 3.3015(3) Å, respectively. These Mn···Mn separations are comparable to those in the previously reported Mn<sub>4</sub>O<sub>2</sub> cores [13,24,25], which are in a nice agreement with the corresponding bridging modes and as well as the number of bridges. The seven ferrocenecarboxylato groups in the molecule of **3** behave as  $\mu_2$ -bridge using their two carboxylato oxygen atoms to connect two Mn(III) ions. The two 2,2'-bipyridine molecules chelate to two “wing-tip” Mn(III) ions. The cationic core [Mn<sub>4</sub>O<sub>2</sub>(FcCO<sub>2</sub>)<sub>7</sub>(2,2'-bpy)<sub>2</sub>]<sup>+</sup> has a C<sub>2</sub> symmetry. All of the Mn atoms in the cationic Mn<sub>4</sub>O<sub>2</sub> core are six-coordinated to form octahedral geometries with the Mn–O and Mn–N bond lengths in the range of 1.812(7) to 2.116(7) Å and 2.156(8) to 2.174(8) Å, respectively. The coordination around Mn3 and Mn4 at “body” sites shows clear evidence of a Jahn–Teller elongation, with O11, O13 (for Mn3) and O10, O14 (for Mn4) occupying axial positions. The situation at Mn1 and Mn2 is not so clear, probably due to the greater variety of ligation types resulting from the terminal 2,2'-bipy groups [25]. The presence of Jahn–Teller distortion confirms again the oxidation state of 3+ for the four manganese atoms in **3** derived from the consideration for charge balance.

Only a few work was carried out in infinite or discrete polynuclear manganese complexes using ferrocenecarboxylate as ligand [8–12]. Among them, only two cases reported by Tian et al. [8] and Kondo et al. [11] described the structures and the electrochemical properties of discrete polynuclear Mn(II) complexes with ferrocenecarboxylate ligands: a dimanganese complex cation [Mn<sub>2</sub>(phen)<sub>4</sub>(FCA)<sub>2</sub>]<sup>2+</sup> (FCA = dianion of 3-ferrocenyl-2-crotonic acid, phen = 1,10-phenanthroline) and a manganese supercubane [Mn<sub>13</sub>O<sub>8</sub>(OCH<sub>3</sub>)<sub>6</sub>(fcdc)<sub>6</sub>] · (fcdc = 1, 1'-ferrocenedicarboxylate). In this study, we isolated successfully three discrete polynuclear Mn-ferrocenecarboxylate complexes **1–3** using both different ancillary ligands and ratio of the starting materials to tune the nuclearities and structures of thus formed compounds. The presence of phen as ancillary ligands in the reaction of FcCO<sub>2</sub>Na and Mn(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O gave **1** which presents a rare triply carboxylato-bridged dimeric structure with both Mn(II) ions pentacoordinated. The reactions using 2,2'-bpy as ancillary ligand with different ratios of the starting materials gave compounds **2** and **3** with obviously different composition and skeletons, which is unprecedented in manganese complexes using ferrocene-involving carboxylate as ligands. It was shown that **2** has a linear trinuclear [Mn<sub>3</sub>( $\mu_2$ - $\eta^1$ : $\eta^1$ -O<sub>2</sub>CFC)<sub>4</sub>( $\mu_2$ - $\eta^1$ : $\eta^2$ -O<sub>2</sub>CFC)<sub>2</sub>] structure, in which six ferrocenecarboxylato ligands show two different bridging modes. The cationic Mn<sub>4</sub>O<sub>2</sub> core of **3** has a butterfly structure, in which two Mn(III) ions at “body” sites are bridged by an additional ferrocenecarboxylato ligand and they are further connected to the Mn(III) ions at “wing-tip” sites by ferrocenecarboxylato ligands. All of the ferrocenyl groups in complexes **1** and **2** adopt eclipsed conformations, however both eclipsed and staggered conformations are found in complex **3** due to the steric factor.

### 2.3. Magnetic properties

The magnetic properties of **1** and **2** were investigated by solid state magnetic susceptibility ( $\chi_m$ ) measurements in the 2.0–300 K range in a DC field of 2000 Oe; the resulting data are shown in Figs. 4 and 5 as  $\chi_m$  and  $\chi_m T$  vs  $T$  plots, respectively. The  $\chi_m$  in **1** increases as the temperature rises, reaching the maximum (0.12 cm<sup>3</sup> mol<sup>-1</sup>) at 20 K, then decreases. The  $\chi_m$  in **2** increases in a monotonous form. The  $\chi_m$  values at 300 K and 2 K are 0.02702 and 0.04773 cm<sup>3</sup> mol<sup>-1</sup> for compound **1**, and 0.04147 and 2.0699 cm<sup>3</sup> mol<sup>-1</sup> for compound **2**, respectively. The value of  $\chi_m T$  at 300 K for compound **1** and **2** is 8.11 and 12.46 cm<sup>3</sup> mol<sup>-1</sup> K, respectively, which is lower than that (8.75 and 13.13 cm<sup>3</sup> mol<sup>-1</sup> K) expected for two and three magnetically isolated high-spin Mn<sup>II</sup> ions, respectively. This indicates the presence of antiferromagnetic coupling. Decreasing the temperature the  $\chi_m T$  of **1** and **2** gradually

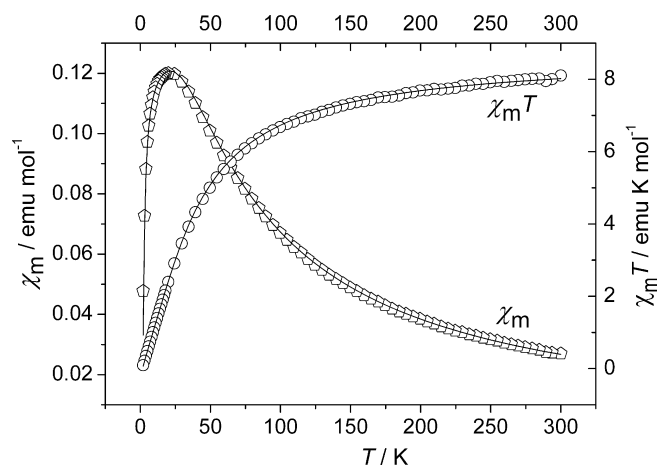


Fig. 4. Plot of  $\chi_m$  and  $\chi_m T$  vs  $T$  for **1**. Solid lines show the best fit of the data according to the proposed model.

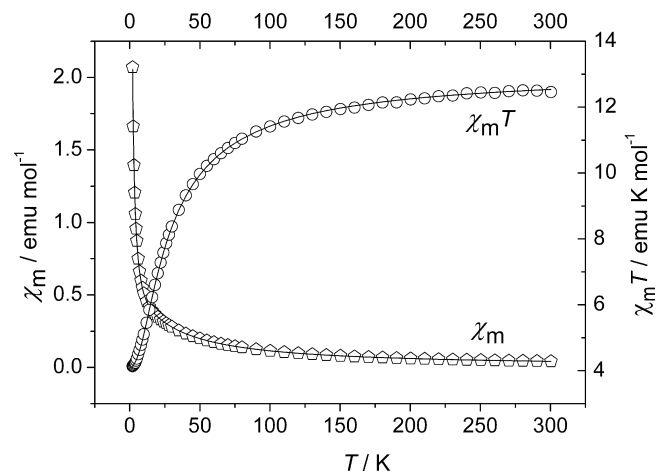


Fig. 5. Plot of  $\chi_m$  and  $\chi_m T$  vs  $T$  for **2**. Solid lines show the best fit of the data according to the proposed model.

decrease reaching 0.095 and 4.14096 cm<sup>3</sup> mol<sup>-1</sup> K at 2.0 K, respectively. The shape of these curves is also characteristic of the occurrence of weak antiferromagnetic interactions between the adjacent Mn(II) centers in both **1** and **2**.

Assuming isotropic exchange, the exchange Hamiltonians of **1** is  $H = -2JS_1S_2$  with  $S_1 = S_2 = 5/2$ , and the susceptibility per mole of the dimer is given by [26]:

$$\chi_{\text{dinuclear}} = \frac{2Ng^2\beta^2}{kT} \frac{x^2 + 5x^6 + 14x^{12} + 30x^{20} + 55x^{30}}{1 + 3x^2 + 5x^6 + 7x^{12} + 9x^{20} + 11x^{30}},$$

where  $x = \exp(J/kT)$ .

Molecular field approximation term [27]  $2zJ'$  was added to describe the inter-dimer Mn<sup>2+</sup> unit exchange interactions. The expression for the magnetic susceptibility becomes:

$$\chi_M = \frac{\chi_{\text{dinuclear}}}{1 - (2zJ'/Ng^2\beta^2)\chi_{\text{dinuclear}}}$$

The best fitting parameters obtained for **1** are  $J = -2.59$  cm<sup>-1</sup>,  $zJ' = -0.11$  cm<sup>-1</sup>, and  $g = 2.0$  with  $R = 6.39 \times 10^{-4}$ . This is consistent with the conclusion that the *syn-syn* carboxylato bridge usually induces an antiferromagnetic coupling between Mn(II) ions [28]. The  $J$  value of  $-2.59$  cm<sup>-1</sup> falls in the normal range for the Mn(II) dimer constructed by three *syn-syn* carboxylato bridges [18,29]. The much smaller  $zJ'$  value ( $-0.11$  cm<sup>-1</sup>) in comparison to the  $J$  value ( $-2.59$  cm<sup>-1</sup>) indicates a very weak exchange interaction between the adjacent dimers of **1**, which is actually negligible.

For the discrete linear trinuclear structure of **2** with a Mn(II) ion on the inversion center, the susceptibility data were thus analyzed by the following expression based on a Heisenberg Hamiltonian  $H = -2J(S_1S_2 + S_2S_{1A}) - 2J_{13}S_1S_3$  [21]. Considering the very small value of  $|J_{13}/J|$ , the  $J_{13}$  was fixed at 0 to calculate the susceptibility of **2**.

$$A = 1020x^{27.5} + 682.5x^{20} + 682.5x^{25} + 429x^{13.5} + 429x^{18.5} \\ + 429x^{22.5} + 247.5x^8 + 247.5x^{13} + 247.5x^{17} + 247.5x^{20} \\ + 126x^{3.5} + 126x^{8.5} + 126x^{12.5} + 126x^{15.5} + 126x^{17.5} \\ + 52.5 + 52.5x^5 + 52.5x^9 + 52.5x^{12} + 52.5x^{14} + 52.5x^{15} \\ + 15x^{2.5} + 15x^{6.5} + 15x^{9.5} + 15x^{11.5} + 1.5x^5 + 1.5x^8$$

$$B = 16x^{27.5} + 14x^{20} + 14x^{25} + 12x^{13.5} + 12x^{18.5} + 12x^{22.5} \\ + 10x^8 + 10x^{13} + 10x^{17} + 10x^{20} + 8x^{3.5} + 8x^{8.5} + 8x^{12.5} \\ + 8x^{15.5} + 8x^{17.5} + 6 + 6x^5 + 6x^9 + 6x^{12} + 6x^{14} + 6x^{15} \\ + 4x^{2.5} + 4x^{6.5} + 4x^{9.5} + 4x^{11.5} + 2x^5 + 2x^8$$

$$\chi_{\text{trinuclear}} = \frac{Ng^2\beta^2}{3kT} \frac{A}{B}$$

$$\chi_M = \frac{\chi_{\text{trinuclear}}}{1 - (2zJ'/Ng^2\beta^2)\chi_{\text{trinuclear}}}$$

where  $x = \exp(J/kT)$  and  $J$  is the coupling constant between the adjacent Mn(II) ions across three carboxylato bridges (two  $\mu_2\text{-}\eta^1\text{:}\eta^1$ -bridge and one  $\mu_2\text{-}\eta^1\text{:}\eta^2$ -bridge).  $N$ ,  $g$ ,  $\beta$  and  $k$  have their usual meanings,  $zJ'$  accounts for the intermolecular interactions. The best fitting parameters for **2** were found to be  $J = -2.38$  cm<sup>-1</sup>,  $zJ' = -0.015$  cm<sup>-1</sup>,  $g = 2.0$  with a nice agreement factor  $R = 1.85 \times 10^{-5}$ . The  $J$  value is comparable to that of the similar linear trinuclear Mn(II) complexes and suggests an antiferromagnetic coupling between Mn(II) ions [19,21,30]. The  $zJ'$  value ( $-0.015$  cm<sup>-1</sup>) is much smaller than the  $J$  value ( $-2.38$  cm<sup>-1</sup>), indicating an actually negligible weak exchange interaction between the adjacent trinuclear molecules of **2**.

### 3. Conclusions

In this study, we isolated successfully three discrete polynuclear compounds bearing organometallic carboxylato ligands from the reactions of FcCO<sub>2</sub>Na with Mn(ClO<sub>4</sub>)<sub>2</sub> · 6 H<sub>2</sub>O in the presence of 1,10-phenanthroline (phen) or 2,2'-bipyridine (2,2'-bpy) in methanol under the condition of different stoichiometric ratio of the reactants. Two pentacoordinated Mn(II) ions in **1** are bridged by three ferrocenecarboxylato ligands in a distorted *syn-syn* bridging mode, which is rare in triply carboxylato-bridged dimanganese(II) complexes. In the linear trinuclear compound **2** the neighboring Mn(II) ions are connected by two  $\mu_2\text{-}\eta^1\text{:}\eta^1\text{-O}_2\text{CFc}$  ligands and one  $\mu_2\text{-}\eta^1\text{:}\eta^2\text{-O}_2\text{CFc}$  ligand. The cationic Mn<sub>4</sub>O<sub>2</sub> core of **3** has a butterfly structure, in which two Mn(III) ions at “body” sites are bridged by an additional ferrocenecarboxylato ligand and both of them are further connected to the Mn(III) ions at “wing-tip” sites by ferrocenecarboxylato ligands. Magnetic susceptibility measurements of **1** and **2** revealed that both of them mediate a weak antiferromagnetic coupling between the Mn(II) ions bridged by ferrocenecarboxylato ligands.

### 4. Experimental

#### 4.1. General

Sodium ferrocenecarboxylate was prepared according to the literature method [31]. The other starting materials were commercially available and used without further purification. Elemental analyses (C, H, and N) were performed on a Vario EL analyzer. Infrared spectra were recorded as KBr pellet using a Nicolet 360 FT-IR spectrometer in the region of 400–4000 cm<sup>-1</sup>. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (MPMS XL-5) in the temperature range of 2–300 K with an applied magnetic field of 2000 Oe.

**Caution:** Although no problems were encountered in this work, the salt perchlorates are potentially explosive. They should be prepared in small quantities and handled with great care.

Table 1  
Crystal data and refinements details of complexes **1** and **2**

	<b>1</b>	<b>2</b>	<b>3</b>
Formula	C <sub>59</sub> H <sub>47</sub> Cl <sub>5</sub> Fe <sub>3</sub> Mn <sub>2</sub> N <sub>4</sub> O <sub>10</sub>	C <sub>86</sub> H <sub>74</sub> Fe <sub>6</sub> Mn <sub>3</sub> N <sub>4</sub> O <sub>14</sub>	C <sub>99</sub> H <sub>95</sub> Cl <sub>5</sub> Fe <sub>7</sub> Mn <sub>4</sub> N <sub>4</sub> O <sub>26</sub>
<i>Mr</i> (g mol <sup>-1</sup> )	1426.69	1887.41	2544.75
<i>T</i> (K)	173(2)	296(2)	183(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Trigonal	Triclinic	Monoclinic
Space group	<i>P</i> 3 <sub>2</sub>	<i>P</i> 1̄	<i>I</i> <sub>2a</sub>
<i>a</i> (Å)	11.4332(16)	11.4559(6)	33.908(3)
<i>b</i> (Å)	11.4332(16)	13.0128(7)	22.0836(10)
<i>c</i> (Å)	37.504(8)	14.8930(8)	34.991(3)
$\alpha$ (°)	90	109.4000(10)	90
$\beta$ (°)	90	111.7660(10)	112.371(9)
$\gamma$ (°)	120	97.4070(10)	90
<i>V</i> (Å <sup>3</sup> )	4245.7(12)	1862.53(17)	24229(3)
<i>Z</i>	3	1	8
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.674	1.683	1.395
$\mu$ , Mo K $\alpha$ (mm <sup>-1</sup> )	1.485	1.695	1.387
<i>F</i> (000)	2166	961	10336
Crystal size (mm)	0.40 × 0.37 × 0.37	0.27 × 0.11 × 0.08	0.29 × 0.27 × 0.25
$\Theta$ Range for data (°)	1.63–25.01	1.62–25.01	1.62–24
Reflections collected	30985	9548	76893
Unique reflections ( <i>R</i> <sub>int</sub> )	9971 (0.1406)	6472 (0.0741)	18875 (0.1126)
Completeness to $\theta_{\max}$ (%)	99.9.0	98.6	99.3
Maximum and minimum transmission	0.5791 and 0.5587	0.8763 and 0.6575	0.7230 and 0.6891
Data/restraints/parameters	9971/1/748	6472/3/517	18875/37/1216
Goodness of fit on <i>F</i> <sup>2</sup>	1.093	1.094	0.900
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0594	<i>R</i> <sub>1</sub> = 0.0572	0.0846
Final <i>wR</i> <sub>2</sub> indices	<i>wR</i> <sub>2</sub> = 0.1523	<i>wR</i> <sub>2</sub> = 0.1378	0.2148
Final <i>R</i> (for all data)	<i>R</i> <sub>1</sub> = 0.0611,	<i>R</i> <sub>1</sub> = 0.0640	0.1694
Final <i>wR</i> <sub>2</sub> (for all data)	<i>wR</i> <sub>2</sub> = 0.1537	<i>wR</i> <sub>2</sub> = 0.1422	0.2375
Largest difference in peak and hole (e Å <sup>-3</sup> )	1.943 and -1.509	0.846 and -0.498	1.739 and -1.140

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

Complex <b>1</b>					
Mn1–O2	2.068(5)	Mn1–N2	2.246(5)	Mn2–O5	2.124(5)
Mn1–O4	2.081(4)	Mn2–O1	2.053(5)	Mn2–N3	2.211(5)
Mn1–O6	2.085(6)	Mn2–O3	2.090(5)	Mn2–N4	2.241(5)
Mn1–N1	2.226(5)	O2–Mn1–N2	103.5(2)	O1–Mn2–N3	118.8(2)
O2–Mn1–O4	103.2(2)	O4–Mn1–N2	86.65(19)	O3–Mn2–N3	89.83(19)
O2–Mn1–O6	117.8(3)	O6–Mn1–N2	136.1(3)	O5–Mn2–N3	102.2(2)
O4–Mn1–O6	97.4(2)	N1–Mn1–N2	73.9(2)	O1–Mn2–N4	92.3(2)
O2–Mn1–N1	96.3(2)	O1–Mn2–O3	95.3(2)	O3–Mn2–N4	164.43(19)
O4–Mn1–N1	155.2(2)	O1–Mn2–O5	137.6(3)	O5–Mn2–N4	88.5(2)
O6–Mn1–N1	86.7(3)	O3–Mn2–O5	94.9(2)	N3–Mn2–N4	74.60(19)
Complex <b>2</b>					
Mn1–O2	2.081(3)	Mn1–N1	2.290(4)	Mn2–O3A	2.196(3)
Mn1–O6	2.163(3)	Mn1–O4	2.358(4)	Mn2–O3	2.196(3)
Mn1–N2	2.263(4)	Mn2–O5	2.130(3)	Mn2–O1A	2.209(3)
Mn1–O3	2.286(3)	Mn2–O5A	2.130(3)	Mn2–O1	2.209(3)
O2–Mn1–O6	98.09(14)	O2–Mn1–O4	161.23(13)	O3A–Mn2–O3	180.000(1)
O2–Mn1–N2	96.04(14)	O6–Mn1–O4	91.79(13)	O5–Mn2–O1A	90.53(13)
O6–Mn1–N2	91.27(14)	N2–Mn1–O4	99.67(13)	O5A–Mn2–O1A	89.47(13)
O2–Mn1–O3	105.07(13)	O3–Mn1–O4	56.31(11)	O3A–Mn2–O1A	89.11(12)
O6–Mn1–O3	110.87(13)	N1–Mn1–O4	88.89(14)	O3–Mn2–O1A	90.89(12)
N2–Mn1–O3	146.37(13)	O5–Mn2–O5A	180.0(2)	O5–Mn2–O1	89.47(13)
O2–Mn1–N1	86.49(15)	O5–Mn2–O3A	94.51(15)	O5A–Mn2–O1	90.53(13)
O6–Mn1–N1	162.32(14)	O5A–Mn2–O3A	85.49(15)	O3A–Mn2–O1	90.89(12)
N2–Mn1–N1	71.21(14)	O5–Mn2–O3	85.49(15)	O3–Mn2–O1	89.11(12)
O3–Mn1–N1	84.08(13)	O5A–Mn2–O3	94.51(15)	O1A–Mn2–O1	180.00(14)

## 4.2. Preparation of

 $[Mn_2(FeCO_2)_3(phen)_2](ClO_4) \cdot 2CH_2Cl_2$  (**1**)

To a methanol solution (20 mL) of  $FeCO_2Na$  (0.1255 g; 0.5 mmol) and phen (0.0901 g, 0.5 mmol) was added dropwise a methanol solution (10 mL) of  $Mn(ClO_4)_2 \cdot 6H_2O$  (0.1810 g; 0.5 mmol). The resulted mixture was stirred at room temperature for 1 h, giving some yellow precipitate which was collected by filtration and washed with methanol. The diffusion of *n*-hexane into a  $CH_2Cl_2$  solution of the precipitate gave yellow crystals. Yield: 0.1708 g (72%).  $C_{59}H_{47}Cl_5Fe_3Mn_2N_4O_{10}$ : Calc. C, 49.63; H, 3.29; N, 3.93. Found: C, 49.59; H, 3.46; N, 3.88%. IR (KBr): 3094(w), 1623(w), 1582(s), 1516(m), 1473(m), 1425(w), 1389(m), 1359(m), 1346(w), 1272(w), 1192(w), 1122(m), 1107(m), 1024(w), 1002(w), 921(w), 865(w), 850(m), 828(w), 800(w), 779(w), 729(m), 637(w), 623(w), 509(m), 486(w)  $cm^{-1}$ .

4.3. Preparation of  $[Mn_3(FeCO_2)_6(2,2'-bpy)_2] \cdot 2H_2O$ 

(2)

A methanol solution (5 mL) of 2,2'-bpy (0.0781 g, 0.5 mmol) was added to a methanol solution (5 mL) of

$Mn(ClO_4)_2 \cdot 6H_2O$  (0.1810 g; 0.5 mmol). Subsequently, a methanol solution (10 mL) containing  $FeCO_2Na$  (0.2510 g; 1 mmol) was added with stirring. The resulted mixture was stirred at room temperature for 5 h, producing some yellow precipitate which was collected by filtration and washed with methanol. Yellow crystals were obtained from the recrystallization of the precipitate in DMF. Yield: 0.1826 g (58%).  $C_{86}H_{74}Fe_6Mn_3N_4O_{14}$ : Calc. C, 54.68; H, 3.92, N, 2.97. Found: C, 54.56; H, 4.01; N, 2.89%. IR (KBr): 3445(br), 3098(w), 1594(m), 1560(s), 1473(s), 1441(m), 1392(s), 1359(s), 1346(m), 1318(w), 1248(w), 1192(w), 1103(m), 1020(m), 1001(w), 832(w), 810(m), 794(m), 781(m), 773(m), 738(w), 563(w), 512(m), 490(w), 480(w).

4.4. Preparation of  $[Mn_4O_2(FeCO_2)_7(2,2'$  $bpy)_2]ClO_4 \cdot 2CH_2Cl_2 \cdot 6H_2O$  (**3**)

A methanol solution (5 mL) of 2,2'-bpy (0.0781 g, 0.5 mmol) was added dropwise to a methanol solution (5 mL) of  $Mn(ClO_4)_2 \cdot 6H_2O$  (0.1810 g; 0.5 mmol). Subsequently, a methanol solution (5 mL) containing  $FeCO_2Na$  (0.1255 g; 0.5 mmol) was added dropwise with stirring. The resulted mixture was stirred at room temperature for 1 d,

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

Mn1–O15	1.833(6)	Mn2–O7	2.049(7)	Mn3–O13	2.116(7)
Mn1–O9	1.979(7)	Mn2–N3	2.159(9)	Mn3–Mn4	2.872(2)
Mn1–O3	2.012(7)	Mn2–N4	2.174(8)	Mn4–O15	1.922(6)
Mn1–O1	2.054(7)	Mn3–O16	1.924(6)	Mn4–O16	1.963(7)
Mn1–N1	2.156(8)	Mn3–O15	1.957(7)	Mn4–O5	1.992(6)
Mn1–N2	2.156(8)	Mn3–O8	2.007(7)	Mn4–O2	2.005(7)
Mn2–O16	1.812(7)	Mn3–O4	2.020(6)	Mn4–O14	2.080(7)
Mn2–O12	1.980(6)	Mn3–O11	2.102(7)	Mn4–O10	2.081(7)
Mn2–O6	2.047(7)				
O15–Mn1–O9	99.3(3)	O12–Mn2–N4	164.9(3)	O15–Mn4–O5	170.2(3)
O15–Mn1–O3	94.7(3)	O6–Mn2–N4	84.0(3)	O16–Mn4–O5	89.0(3)
O9–Mn1–O3	91.7(3)	O7–Mn2–N4	89.6(3)	O15–Mn4–O2	97.0(3)
O15–Mn1–O1	95.2(3)	N3–Mn2–N4	75.4(3)	O16–Mn4–O2	174.9(3)
O9–Mn1–O1	91.4(3)	O16–Mn3–O15	84.2(3)	O5–Mn4–O2	90.5(3)
O3–Mn1–O1	169.0(3)	O16–Mn3–O8	95.9(3)	O15–Mn4–O14	89.4(3)
O15–Mn1–N1	170.1(3)	O15–Mn3–O8	170.8(3)	O16–Mn4–O14	86.3(3)
O9–Mn1–N1	90.5(3)	O16–Mn3–O4	170.0(3)	O5–Mn4–O14	97.1(3)
O3–Mn1–N1	86.7(3)	O15–Mn3–O4	91.8(3)	O2–Mn4–O14	88.8(3)
O1–Mn1–N1	82.8(3)	O8–Mn3–O4	89.5(3)	O15–Mn4–O10	89.5(3)
O15–Mn1–N2	94.3(3)	O16–Mn3–O11	88.6(3)	O16–Mn4–O10	94.5(3)
O9–Mn1–N2	166.2(3)	O15–Mn3–O11	96.7(3)	O5–Mn4–O10	84.1(3)
O3–Mn1–N2	84.8(3)	O8–Mn3–O11	92.5(3)	O2–Mn4–O10	90.4(3)
O1–Mn1–N2	89.7(3)	O4–Mn3–O11	82.7(3)	O14–Mn4–O10	178.6(3)
N1–Mn1–N2	76.1(3)	O16–Mn3–O13	89.5(3)	O15–Mn4–Mn3	42.70(19)
O16–Mn2–O12	100.3(3)	O15–Mn3–O13	84.2(3)	O16–Mn4–Mn3	41.83(18)
O16–Mn2–O6	97.0(3)	O8–Mn3–O13	86.6(3)	O5–Mn4–Mn3	130.9(2)
O12–Mn2–O6	93.1(3)	O4–Mn3–O13	99.2(3)	O2–Mn4–Mn3	138.4(2)
O16–Mn2–O7	92.7(3)	O11–Mn3–O13	177.9(3)	O14–Mn4–Mn3	82.4(2)
O12–Mn2–O7	90.7(3)	O16–Mn3–Mn4	42.9(2)	O10–Mn4–Mn3	97.47(18)
O6–Mn2–O7	168.7(3)	O15–Mn3–Mn4	41.76(18)	Mn1–O15–Mn4	121.6(3)
O16–Mn2–N3	168.1(3)	O8–Mn3–Mn4	136.5(2)	Mn1–O15–Mn3	129.4(3)
O12–Mn2–N3	89.8(3)	O4–Mn3–Mn4	133.5(2)	Mn4–O15–Mn3	95.5(3)
O6–Mn2–N3	88.6(3)	O11–Mn3–Mn4	98.4(2)	Mn2–O16–Mn3	124.2(4)
O7–Mn2–N3	80.8(3)	O13–Mn3–Mn4	81.0(2)	Mn2–O16–Mn4	129.3(3)
O16–Mn2–N4	94.7(3)	O15–Mn4–O16	84.1(3)	Mn3–O16–Mn4	95.3(3)

giving some black brown precipitate which was collected by filtration and washed with methanol. The diffusion of *n*-hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the precipitate gave black brown crystals. Yield: 0.0273 g (15%). C<sub>97</sub>H<sub>91</sub>ClFe<sub>7</sub>Mn<sub>4</sub>N<sub>4</sub>O<sub>26</sub> (a form of **3** with CH<sub>2</sub>Cl<sub>2</sub> molecules removed under dryness): Calc. C, 49.06; H, 3.86; N, 2.36. Found: C, 49.36; H, 3.78; N, 2.63%. IR (KBr): 3443(br), 3095(w), 2953(w), 2924(w), 1599(w), 1559(m), 1474(s), 1444(m), 1388(s), 1359(m), 1194(w), 1121(m), 1106(m), 1057(w), 1025(m), 1002(w), 921(w), 819(w), 798(w), 772(m), 736(w), 653(w), 635(w), 623(w), 516(m), 486(w).

#### 4.5. X-ray crystallography

All data of **1–3** were collected on an APEX Bruker CCD diffractometer (**1** and **2**) or on a Stoe IPDS diffractometer (**3**) using graphite monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved by direct methods using the Program SHELXS-97 [32] and refined by the full-matrix least-squares methods on all  $F^2$  data with SHELXL-97 [33]. The perchlorate ion and water molecules of **3** were finally isotropically refined using distance restraints for the Cl–O, O $\cdots$ O, O–H, and H $\cdots$ H distances. Details of the structure solution and refinement are extensively described in the `_exptl_special_details` of the crystallographic information file (CIF) of **3**. The other non-hydrogen atoms in compounds **1** and **2** were refined anisotropically. Hydrogen atoms of water molecules were located in a difference Fourier map phased on the non-hydrogen atoms, and were refined isotropically in the final refinement cycles. H atoms on C atoms were placed in calculated positions and refined in a riding mode. The final cycles of full-matrix least-squares refinements were based on all unique reflections and variable parameters (Table 1). The molecular illustrations were drawn using the program XP [34]. The calculations of compounds **1** and **2** were performed using the WINGX System 1.64.05 [35]. Crystallographic data for compound **1–3** are given in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3.

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#### Appendix A. Supplementary material

CCDC 650367, 650368 and 650369 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Cryst-

tallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorgchem.2007.11.055](https://doi.org/10.1016/j.jorgchem.2007.11.055).

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