两个基于混酸配体的十二核锰配合物的合成和结构

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摘要：应用乙酸锰、高锰酸钾和丙酸(或氯乙酸)混酸体系合成，得到了 2 个基于 $Mn_{12}O_{12}$ 核心的十二核锰配合物，分子式分别为 $[Mn_{12}O_{12}(O_2CMe)_8(O_2CEt)_8(H_2O)_4]\cdot 2H_2O$ (**1**)和$[Mn_{12}O_{12}(O_2CMe)_{12}(O_2CCl_3)_4(H_2O)_4]\cdot 4MeCO_2H\cdot 8H_2O$ (**2**)。X 射线单晶衍射分析表明配合物 **1** 结晶于四方晶系 $I\bar{4}$ 空间群，晶胞参数为：$a=b=2.650\ 5(3)$ nm，$c=1.349\ 7(3)$ nm，$Z=4$；配合物 **2** 结晶于四方晶系 $I4_1/acd$ 空间群，晶胞参数为：$a=b=2.7067(1)$ nm，$c=2.5880(2)$ nm，$Z=8$。这 2 个配合物结构都具备 $Mn_{12}O_{12}$ 核心，与其他经典 Mn_{12} 明星分子的核心相似。中心的 Mn_4O_4 立方核通过 μ_3-氧桥被非共面的 Mn_8O_8 环聚集在一起，而 16 个 η^2-μ-混合羧酸以不同方向在外围充当连接桥，同时提供了酸性环境。文中还分析了混酸体系的 pKa 值对配合物结构形成的影响。

关键词：十二核锰；簇合物；丙酸；氯乙酸
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Synthesis and Structure of Two Dodecanuclear Manganese Clusters Based on Mixed Acids

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Abstract: Two new $Mn_{12}O_{12}$ cores based dodecanuclear manganese complexes formulated with $[Mn_{12}O_{12}(O_2CMe)_8(O_2CEt)_8(H_2O)_4]\cdot 2H_2O$ (**1**) and $[Mn_{12}O_{12}(O_2CMe)_{12}(O_2CCl_3)_4(H_2O)_4]\cdot 4MeCO_2H\cdot 8H_2O$ (**2**) have been synthesized by the reaction of $Mn(O_2CMe)_2\cdot 4H_2O$, $KMnO_4$ and mixed acid of RCO_2H and $MeCO_2H$ (R=Et (**1**), Cl_3CCO_2H (**2**)) in acidic conditions. X-ray diffraction crystal structure analysis shows that the complex **1** crystallizes in the tetragonal space group $I\bar{4}$ has $a=b=2.650\ 5(3)$ nm, $c=1.349\ 7(3)$ nm and $Z=4$. The complex **2** crystallizes in tetragonal space group $I4_1/acd$ has $a=b=2.706\ 7(1)$ nm, $c=2.588\ 0(2)$ nm and $Z=8$. In the two complexes, the structure of the $Mn_{12}O_{12}$ core is similar to that found in all classic Mn_{12} derivatives and comprises a central Mn_4O_4 cubane core surrounded by a nonplanar Mn_8O_8 ring held together with μ_3-oxo bridges, while the peripheric bridging is ensured by sixteen η^2-μ-mixed carboxylate anions in different orientations which provide an acidic condition. The effect of pKa data in each mixed acid system for obtaining the two complexes are also investigated in this article. CCDC: 847334, **1**; 847335, **2**.

Key words: dodenuclear manganese, cluster; propionic acid; chloroethanoic acid

0　Introduction

The synthesis of discrete polymetallic complexes has been driving the last twenty years by the discovery that molecules with large numbers of unpaired electrons can behave as single-molecule magnets (SMMs)[1]. SMMs exhibit peculiar slow magnetic relaxation and quantum tunneling of magnetization below a blocking temperature similar to those observed in classical magnets[2]. Study of their unusual magnetic behavior will be not only beneficial for both physics and chemistry, but also potentially used in high-density information storage devices for quantum computing. Gradually, the vast majority of SMMs reported have contained manganese[3], cobalt[4], iron[5-6], nickel[7], chromium[8] or rare earth[9]. Each of these SMMs has been synthesized using appropriate metal and coordinative flexible organic ligands. Their magnetic properties may be altered depending on the intriguing superexchange coupling interaction propagated through the bridging bonds. It is known that the first SMM, $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] \cdot MeCO_2H \cdot 3H_2O$ (complex 3, omitted as Mn_{12}-OAc), was obtained and acetic acid in the system is not only a bridging ligand but a solvent with acidic conditions[10]. At this time of day, there is a continuing need for new synthetic methods that can achieve novel SMMs. Following the above consideration, we choose mixed acid as solvents to provide acidic conditions and act as bridged ligands. In particular, adjusting the appropriate equivalence relation of the two acids, we obtained two discrete polymetallic complexes with $Mn_{12}O_{12}$ core, formulated as $[Mn_{12}O_{12}(O_2CMe)_8(O_2CEt)_8(H_2O)_4] \cdot 2H_2O$ (1) and $[Mn_{12}O_{12}(O_2CMe)_{12}(O_2CCCl_3)_4(H_2O)_4] \cdot 4MeCO_2H \cdot 8H_2O$ (2).

1　Experimental

1.1　Materials and physical measurements

All chemicals and solvents were used as received; all preparations and manipulations were performed under aerobic conditions. The C, H, microanalyses were carried out with a Elementar Various-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4 000~400 cm^{-1} on a Bruker-EQUINOX 55 FT-IR spectrometer.

1.2　Synthesis of complexes 1 and 2

$[Mn_{12}O_{12}(O_2CMe)_8(O_2CEt)_8(H_2O)_4] \cdot 2H_2O$ (1): $Mn(O_2CMe)_2 \cdot 4H_2O$ (0.245 g, 1 mmol) was dissolved in a mixture of 10 mL propionate acid and 5 mL acetic acid and treated with a fine powder of $KMnO_4$ (0.060 g, 0.38 mmol) with vigorous stirring to afford a dark brown solution. After 12 h of additional stirring, the impurities were removed by filtration. The filtrate was left undisturbed at room temperature in vacuum for several weeks. Large black cubic crystals of the product were obtained with a yield of 72% after being washed with hexanes and dried in the vacuum. Anal. Calcd. for $C_{40}H_{76}Mn_{12}O_{50}$(%): C, 23.75; H, 3.72. Found (%): C, 23.83; H, 3.80. FT-IR (KBr, cm^{-1}): 3 375.6 (w), 2 975.5 (m), 2 939.8 (m), 2 881.6 (w), 1 562.3 (vs), 1 466.2 (s), 1 425.8 (vs), 1 297.9 (s), 1 079.6 (w), 1 012.2 (w), 888.3 (w), 813.2 (w), 564.1 (vs), 447.9 (m).

$[Mn_{12}O_{12}(O_2CMe)_{12}(O_2CCCl_3)_4(H_2O)_4] \cdot 4MeCO_2H \cdot 8H_2O$ (2): To a solution of Cl_3CCO_2H (2.608 g, 16 mmol) in 20 mL acetic acid was added $Mn(O_2CMe)_2 \cdot 4H_2O$ (1.000 g, 4.082 mmol). The reaction mixture was stirred for two hours. Then the solution was added $KMnO_4$ (0.240 g, 1.519 mmol) and was stirred for another few hours. The result black solution was filtered and the filtrate was stored for a few days at room temperature. Rectangle black block crystals of the product were obtained with a yield of 82% after recrystalized in CH_2Cl_2. Anal. Calcd. for $C_{40}H_{76}Mn_{12}O_{64}Cl_{12}$(%): C, 18.00; H, 2.79. Found(%): C, 18.02; H, 2.87. FT-IR (KBr, cm^{-1}): 3 389.8 (w), 2 937.9 (w), 1 754.3 (w), 1 718.4 (w), 1 656.9 (s), 1 571.5 (s), 1 502.9 (s), 1 446.7 (vs), 1 376.1 (s), 1 353.3 (s), 1 328.5 (s), 1 240.8 (w), 1 028.9 (w), 960.6 (w), 841.4 (s), 746.8 (m), 716.8 (w), 675.3 (s), 646.7 (s), 608.1 (s), 566.2 (w), 541.4 (w), 446.3 (w).

1.3　X-ray crystallography

The diffraction data of 1 and 2 were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293 K. The data integration and reduction were processed with SAINT software. An empirical absorption

Table 1　Crystal Data and structure refinement for complex 1 and 2

	1	2
Empirical formula	$C_{40}H_{76}Mn_{12}O_{50}$	$C_{40}H_{76}Cl_{12}Mn_{12}O_{64}$
Formula weight	2 016.29	2 649.56
Wavelength / nm	0.071 073	0.071 073
Crystal system	Tetragonal	Tetragonal
Space group	$I\bar{4}$	$I4_1/acd$
a / nm	2.650 5(3)	2.706 7(1)
b / nm	2.650 5(3)	2.706 7(1)
c / nm	1.349 7(3)	2.588 0(2)
V / nm^3	9.482(3)	18.961(1)
Z	4	8
D_c / (g·cm^{-3})	1.412	1.856
μ / mm^{-1}	1.619	1.981
Reflns collected	10 920	64 372
Unique reflns	7 687	4 675
R_{int}	0.045 3	0.044 3
S	1.023	1.067
R_1 ($I>2\sigma(I)$)	0.088 7	0.052 6
wR_2 (all data)	0.261 6	0.153 6

$^a R_1=\sum ||F_o|-|F_c||/\sum |F_o|$; $^b wR_2=[\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

correction was applied to the collected reflections with SADABS[11]. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 using the SHELXTL program package[12]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The organic hydrogen atoms were generated geometrically (C-H, 0.096 nm); the aqua hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. The details of crystallographic data is provided in Table 1.

CCDC: 847334, **1**; 847335, **2**.

2　Results and discussion

2.1　Synthesis

Enormous elaboration is being focused on constructing dodecanuclear manganese complexes by choosing simplex carboxylate ligands or non-organic bridging ligands to completely replace the O_2CMe^- ligands of first SMM $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot MeCO_2H\cdot3H_2O$ (omitted as Mn_{12}-OAc). In this case, the previous reported synthetic strategies to achieve Mn_{12} complexes are using RCO_2^- to reaction with Mn12-OAc in polar and anhydrous solvents, such as MeCN, EtOH, CH_2Cl_2, $CHCl_3$, and so on[13-19]. In our investigation, however, two new derivatives **1** and **2** of the Mn_{12} family were prepared by the partial substitution of O_2CMe^- with $EtCO_2^-$ and $Cl_3CCO_2^-$, respectively. Encouraged by our preliminary experimentation, the satisfying molar ratios of the Mn^{II}:Mn^{VII} have been found to give consistently pure and high yield products. Moreover, small changes to the Mn^{II}:Mn^{VII} ratios have no noticeable effect on the identity of the products and yields. A Mn^{II}:Mn^{VII} ratio of 3.67:1.33 has become our routinely used stoichiometry and has provided access to complexe **1** and **2**. The ratio provides theoretically an average metal oxidation of +3.33. Potassium permanganate in our experiments commonly has been a little excessive comparative to the ratios in theory.

Previous development and use of ligand substitution reactions on Mn_{12}-OAc complex have access to many $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ derivatives with a large variety of R groups [2,5,13-21]. The ligand substitution reaction according to eq. (**1**) needs a carboxylic acid with a lower pK_a and an excessive amount to remove the acetic acid.

$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]+16RCO_2H=$

$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]+16MeCO_2H$ (1)
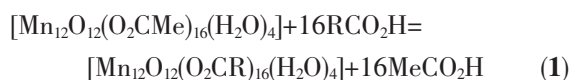
When a conjugate acid of the carboxylate group owns a pK_a comparable to, or even higher than that of acetic acid (pK_a=4.76), such as $EtCO_2H$ (pK_a=4.88), it is difficult to complete substitution reactions. And even if a carboxylic acid with a much lower pK_a, Cl_3CCO_2H (pK_a =0.65), cannot obtain the complete substitution products without removing the acetic acid. That is, above two strategies usually need to be taken into account at the same time. In complex **1**, $EtCO_2H$ and $MeCO_2H$ have a similar pK_a and both they are liquid. Therefore, they have similar chances and finally only partial replacements of acetate groups. Excess acid could not be added. We attempted double propanoic acid dosage than that of in Experimental Section and the similar result was obtained. For complex **2**, four to eight double in the Cl_3CCO_2H dosage got the same product and only the yield had little difference. The procedures described in Experimental Section have been found to give consistently pure and high yield products. We haven′t explored all possible solvents, reagent ration and stoichiometric relation, so do not claim that procedures optimization. Both the two compounds are soluble in acetone, MeCN, EtOH, $CHCl_3$ and CH_2Cl_2.

## 2.2　Description of structures

Labelled ORTEP plots of **1** and **2** are given in Fig.1 and Fig.2. Crystallographic information for **1** and **2** is given in Table 1.

Complex **1** crystallized in the tetragonal space group $I\bar{4}$ with the asymmetric unit containing two 0.25 Mn_{12} molecules of the formula unit, which are related by a crystallographically inversion center, and two
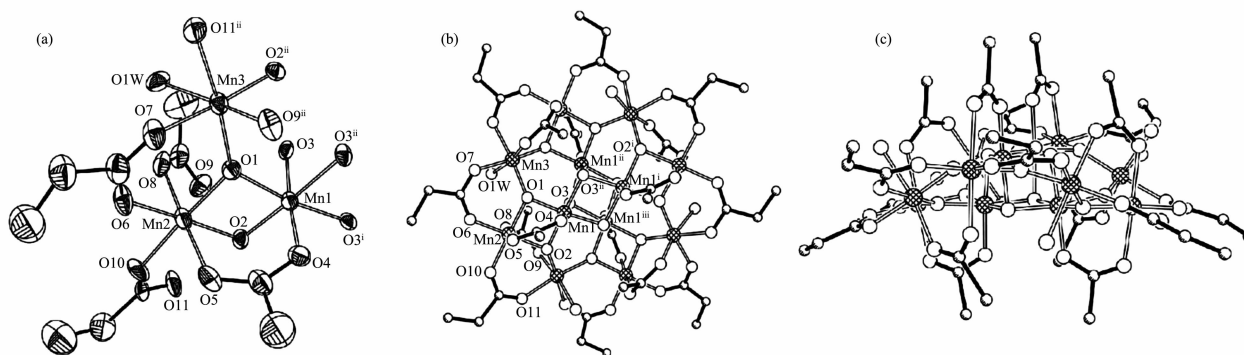
Some equivalent atoms have been generated to complete the Mn coordination, H atom omitted for clarity; Symmetry codes: ^{i} $-y+1/2$, $x-1/2$, $-z+3/2$; ^{ii} $y+1/2$, $-x+1/2$, $-z+3/2$; ^{iii} $-x+1$, $-y$, z

Fig.1 (a) Coordination environments of Mn atoms in **1** with thermal ellipsoids at 30%; (b) View along the c axis of the Mn_{12} molecule in **1**; (c) Side view of the Mn_{12} molecular in **1**
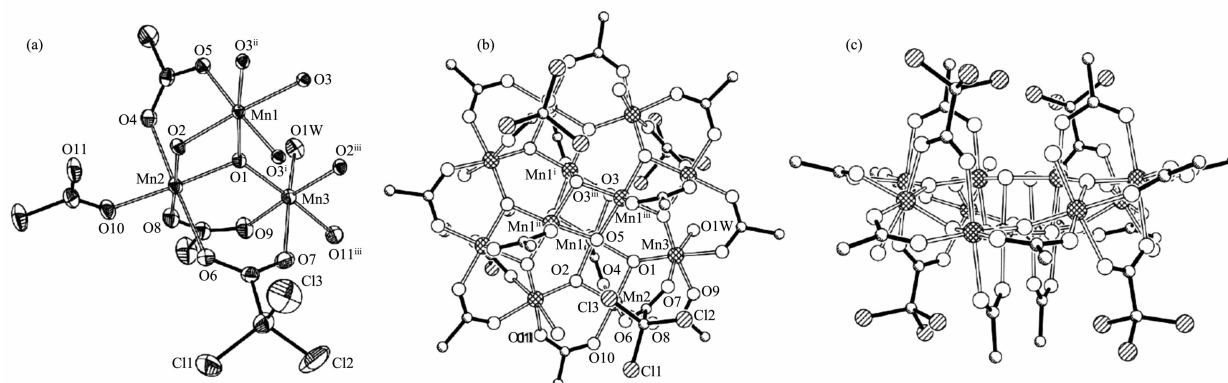
Some equivalent atoms have been generated to complete the Mn coordination, H atom omitted for clarity; Symmetry codes: ^{i} $y-3/4$, $-x+3/4$, $-z+1/4$; ^{ii} $-x$, $-y+3/2$, z; ^{iii} $-y+3/4$, $x+3/4$, $-z+1/4$

Fig.2 (a) Coordination environments of Mn atoms in **2** with thermal ellipsoids at 30%; (b) View along the c axis of the Mn_{12} molecule in **2**; (c) Side view of the Mn_{12} molecular in **2**

half-occupancy water guest molecules. The two Mn_{12} molecules in **1** are structurally equivalent, so that only one of them is described here. Fig.1 shows a perspective view of one Mn_{12} molecule with atom labeling. The Mn_{12} molecule consists of a central $[Mn_4^{IV}O_4]$ cubane surrounded by a nonplanar Mn_8O_8 ring, which are bridged by and connected to the cube via μ_3-O^{2-} ions similar to complex **2** which crystallized in the tetragonal space group $I4_1/acd$ (Fig.2). As we know, they have the same $Mn_{12}O_{12}$ core, which are also found in other reported Mn12 clusters. The Mn-O bond distances make it clear that all of the atoms in the central cube are Mn^{IV}, and the Mn_8O_8 ring consists of eight Mn^{III}. These assignments are supported by marked Jahn-Teller elongation in the axial Mn-O acetates bonds (0.2037~0.2216 nm) in complex **1**. From Fig.1b, we can see that eight propionate ligands are all at the equatorial Mn^{III}-Mn^{III} carboxylate sides while the remaining eight axial Mn^{III}-Mn^{III} sites are occupied by acetates. So it possesses a structure similar to that reported in the literature [13]. The occupation of the axial positions by the $MeCO_2^-$ rather than the $EtCO_2^-$ groups is rationalized on the basis of relative basicities. The acetate acid has a lower pK_a (4.76) while $EtCO_2H$ has a higher pK_a (4.88). The more basic, stronger donor $EtCO_2^-$ ligands favor occupation of the equatorial sites where shorter and stronger Mn-O bonds can be formed[13,18]. Moreover, the $MeCO_2^-$ groups are all bridging Mn^{III}/Mn^{IV} pairs with only one O atom on a Jahn-Teller (JT) elongation site, and these are the (Mn1/Mn2, Mn1^i/Mn2^i, Mn1^{ii}/Mn2^{ii}, Mn1^{iii}/Mn2^{iii}, Mn2/Mn3, Mn2^i/Mn3^i, Mn2^{ii}/Mn3^{ii} and Mn2^{iii}/Mn3^{iii}) pairs, respectively (Fig.1b), which are different from those reported in literature[18]. In complex **2**, only four $Cl_3CCO_2^-$ groups replace the $MeCO_2^-$ site in Mn_{12}-OAc in the four of

eight axial sites and they are all bridging Mn^{III}/Mn^{III} pairs, which are analogical to NO_3^- groups in complexes reported by literature[16]. Similarly, the pK_a of Cl_3CCO_2H (0.65) is close to that of inorganic acid (pK_a is lower than 2), for example HNO_3, which is much lower than that of $Bu^tCH_2CO_2H$ (pK_a is higher or equal to 5). Therefore, in **2** the remaining four axial Mn^{III}-Mn^{III} and the eight equatorial Mn^{III}-Mn^{III} carboxylate sites are occupied by acetates (Fig.2b), resulting in a $[Mn_{12}O_{12}]^{16+}$ core similar to that of **1** and with a significant distortion reflecting the increase of bond distances equal to 0.0289 nm (longer than the standard distance, 0.01 nm), even longer than that of Mn_{12}-O_2CEt (complex **4**) and all of the Mn^{III}-Mn^{III} distances in **2** (Table 2). Compared to complex **1**, Jahn-Teller elonga-tion axes are even longer and all the Mn^{III}-O bonds in the $Cl_3CCO_2^-$ groups and four of the Mn^{III}-O bonds in the $MeCO_2^-$ which are bridging Mn^{III}/Mn^{IV} pairs are showing strong Jahn-Teller elongation in complex **2**. There are 0.028 9 nm longer for Jahn-Teller axes on average than Mn^{III}-O bonds without Jahn-Teller effects. Besides of these, Mn⋯Mn bond distances in complex **2** are longer than that of **1**, which means there is an apparent distortion in $[Mn_{12}O_{12}]^{16+}$ ring for **2**. Additional differences are reflected in the linearity of the Mn4 units that span the core of the cluster, with **1** and **2** having angles of the type Mn^{III}⋯Mn^{IV}⋯Mn^{IV} equal to almost 180° while the corresponding angle in Mn12-OAc is only/171°. However, the angles of the type Mn^{III}⋯Mn^{IV}⋯Mn^{IV} in complex **3** are in the range of 173.81° ~177.88° (Table 2). That is to say, the plates consist of the $[Mn_{12}O_{12}]^{16+}$ rings in complexes **1**, **2**, and **4** are not so more turn up than complex **3**. The similarity of complexes **1** and **2**, and the difference between them and complex **3** are likely reflective of the distribution

Table 2 Comparison of Mn^{III}-O bond lengths and selected Mn^{III}⋯Mn^{IV}⋯Mn^{IV} angles in complex 1~4

Complex	Bond distance / nm			Angles / (°)
	Mn^{IV}-O^{2-} (Inner core)	Mn^{IV}-O^{2-} (outer core)	Mn^{III}-O (JT axial elongation)	Mn^{III}⋯Mn^{IV}⋯Mn^{IV}
1	0.191 4~0.193 2	0.186 8~0.193 0	0.216 9~0.221 6	176.89~178.0
2	0.190 0~0.192 4	0.187 2~0.191 1	0.214 6~0.226 4	177.78
3	0.189 0~0.196 0	0.1863		171.4
4	0.189 7~0.192 0	0.184 3~0.188 1	0.213 3~0.221 8	173.81~177.88
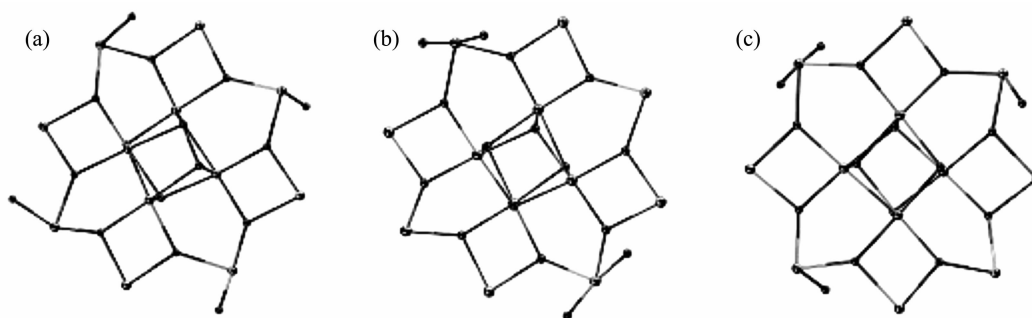
Fig.3　(a), (b) and (c) are the three types of the coordinated H_2O molecules in the $[Mn_{12}O_{12}(O_2CR)_x((O_2CR')_{16-x}(H_2O)_4)]$ (from literatures)

of ligands around the cluster. Furthermore, there are three styles of the four coordinated H_2O being arranged to coordinate to Mn^{III} ions (Fig.3). In the type of (a), each H_2O ligand bonds to a Mn^{III} ions[5,15]; in the type of (b), each two H_2O ligands bond to a Mn^{III} ion and them have been arranged between the plate of $[Mn_{12}O_{12}]^{16+}$ [17]; and the type of (c), has two H_2O ligands bonded to one Mn^{III} ion and one H_2O ligand on each of two other Mn^{III} ions[2]. Both the cores of $[Mn_{12}O_{12}]^{16+}$ in complexes **1** and **2** are belong to the type of (a), and here the pK_a of the substitution acid, RCO_2H maybe play an important role.

In conclusion, we synthesized two complexes, compound **1** and **2**, involve two mixed bridging ligands. The different strategy in our synthesis is that we choose mixed acid as the solvents to provide acid condition, which change the idea that replace the $MeCO_2^-$ group in the Mn_{12}-OAc with other groups and its condition of non-acid organic solvents.

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