A New Type of Supramolecular Assembly by Hydrogen Bond Templating: Identification of Rare Monodentate Acetate Coordination in $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot T\cdot ClO_4$ (T = 2,6-Diaminopyridinium Cation, $C_5H_8N_3$ and 2-Aminopyridinium Cation, $C_5H_7N_2$)

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In memory of Professor Bhaskar G. Maiya

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The complexes $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3\cdot ClO_4$ ($C_5H_8N_3$ = 2,6-diaminopyridinium cation) (**1**) and $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2\cdot ClO_4$ ($C_5H_7N_2$ = 2-aminopyridinium cation) (**2**) show novel self-assembled supramolecular structures in their crystals as elucidated by X-ray analysis. The structures contain $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ units as the building blocks. A detailed examination of the structures revealed that monodentate acetate, which is stabilised by a hydrogen-bond template T (2,6-diaminopyridinium cation in **1** and the 2-aminopyridinium cation in **2**), plays a directing role in forming these new types of hydrogen-bonded assemblies in **1** and **2**. Crystal data for **1** and **2** were determined by X-ray structure analysis.

Introduction

Oxo-bridged trinuclear iron clusters such as $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}RCOO)_6L_3]^{1+}$ (where L is a neutral monodentate ligand, e.g. H_2O and R is an alkyl or aryl group),[1] popularly known as "basic iron carboxylates", have been known for more than a century.[2] These trinuclear complexes are considered an important class of compounds because the $\{Fe_3(\mu_3{-}O)\}^{7+}$ unit has been proposed as the smallest building block for the formation of the iron core in ferritin, an iron storage protein.[3] However, examples of extended structures based on this building unit showing chain- or layer-like networks are scarce in the literature.[4,5] Recently, we reported a trinuclear iron(III) complex which aggregates to a 1D zig-zag chain-like structure through N−H···O hydrogen bonds.[5] In our continued efforts, we recently observed a new type of H-bonded supramolecular assembly in the complexes $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3\cdot ClO_4$ ($C_5H_8N_3$ = 2,6-diaminopyridinium cation) (**1**) and $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2\cdot ClO_4$ ($C_5H_7N_2$ = 2-aminopyridinium cation) (**2**). These species have $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ as a basic building block. The 2,6-diaminopyridinium cation (in **1**) and the 2-aminopyridinium cation (in **2**) play an important role in the templating of these H-bonded assemblies (Scheme 1) by stabilising a monodentate acetate coordinated to one of the iron centres in $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$. The stabilisation achieved here is through hydrogen bonding between the template (T) and monodentate acetate (Scheme 1). To the best of our knowledge, $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ is the first structurally characterised complex among "basic metal carboxylates" that has unusual monodentate acetate coordination.

Results and Discussion

Compounds **1** and **2** were isolated from aqueous solutions (pH 3.5) by dissolving ferric chloride, acetic acid, 2,6-diaminopyridine (for compound **1**) or 2-aminopyridine (for compound **2**) and sodium perchlorate. The neutral complex $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ cocrystallises with 2,6-diaminopyridinium and 2-aminopyridinium perchlorate in **1** and **2**, respectively. Protonation of 2,6-diaminopyridine or 2-aminopyridine in **1** and **2** is not surprising because the synthesis of these complexes were carried out at a low pH value. Compounds **1** and **2** were obtained in moderate yields and gave elemental analyses consistent with formulae $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3\cdot ClO_4$ (**1**) and $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2\cdot ClO_4$ (**2**). Interestingly, compounds **1** and **2** both always crystallise with only one molecule of the respective aminopyridine regardless of the amount of aminopyridine used in the synthesis.

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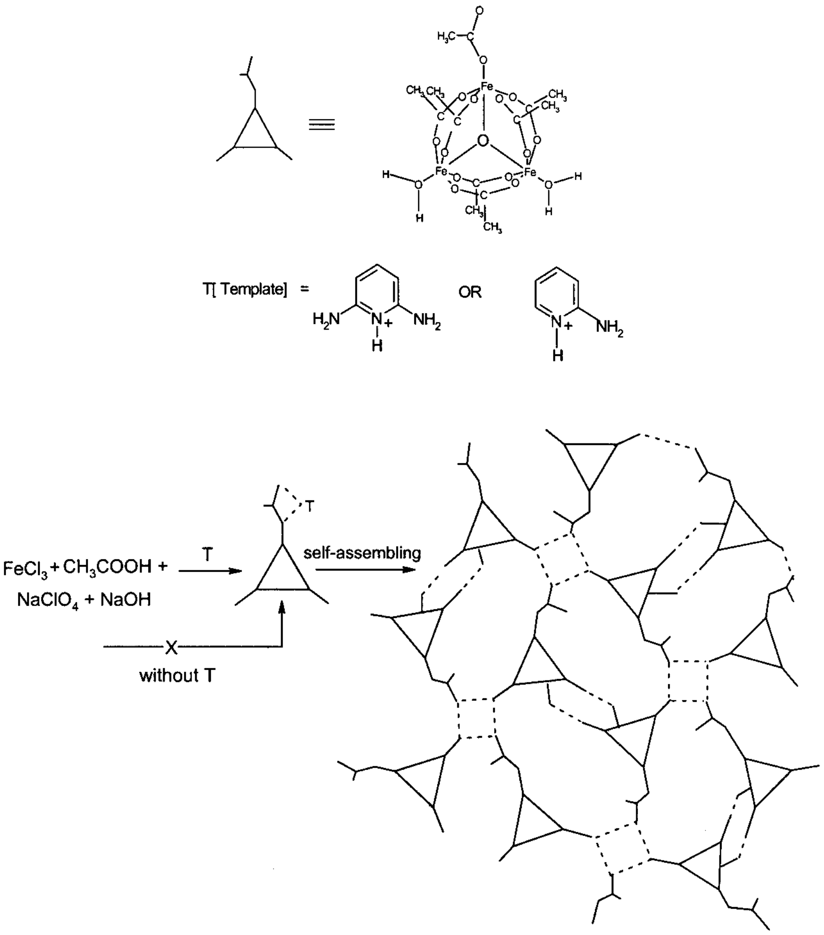

Scheme 1

Both the complexes crystallise in the monoclinic space group *P*2$_1$/*c*. The structural features of the [Fe$_3$(μ$_3$-O)(μ$_2$-CH$_3$COO)$_6$(H$_2$O)$_2$(CH$_3$COO)] motif in **1** and **2** are comparable. The thermal ellipsoid plots of [Fe$_3$(μ$_3$-O)(μ$_2$-CH$_3$COO)$_6$(H$_2$O)$_2$(CH$_3$COO)] in **1** and **2** are presented in Figure 1. Its overall structure is similar to that found in other trinuclear {M$_3$(μ$_3$-O)} compounds.[6] Unlike usual symmetric μ$_3$-oxotriiron(III) centres in basic metal carboxylates,[1] the unusual asymmetry in the present trinuclear structure [Fe$_3$(μ$_3$-O)(μ$_2$-CH$_3$COO)$_6$(H$_2$O)$_2$(CH$_3$COO)] (in **1** and **2**) arises from the differences in the coordination environments of the three metal ions. Whereas one of the iron centres is coordinated to a monodentate acetate ligand, the other two are bonded to two water molecules. Monodentate acetate coordination is not unusual in transition metal chemistry although it is rare in basic iron carboxylate chemistry.[1] Among the basic carboxylate complexes in which the carboxylate is reported to act as a monodentate ligand, the formato complex Fe$_3$O(OOCH)$_7$·5H$_2$O is the best known example. Here, one of the formate ligands has been described as being monodentate in nature.[7] [Fe$_3$(OH)(OOCCH$_3$)$_7$(NO$_3$)]·*n*H$_2$O is another such example.[2c] However, the ambiguity of whether the extra carboxylate remain as an adduct (coordinated ligand) or a solvated carboxylic acid has not resolved in both these cases due to the lack of unambiguous characterisation data for the complexes especially single-crystal structure analyses. The crystal structure of an analogous complex, [Cr$_2$Fe(μ$_3$-O)(μ$_2$-CH$_3$COO)$_6$(H$_2$O)$_3$] NO$_3$·CH$_3$COOH, in which the seventh carboxylate remains as a solvate of acetic acid, has been described.[8] The crystal structures of **1** and **2** thus represent the first examples of a structurally characterised {Fe$_3$(O)}$^{7+}$ complexes (Figure 1) having monodentate carboxylate coordination at one of the metal centres. Relevant crystallographic data for **1** and **2** are presented in Table 1 and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

At 298 K, the values of the effective magnetic moments for **1** and **2** were found to be 5.57 μ_B and 5.65 μ_B, respectively. These values are considerably smaller than the spin only value (10.25 μ_B) for a trinuclear cluster containing three high spin Fe^{III} ions (s = 5/2). This indicates an antiferromagnetic interaction between the three Fe^{III} centres in the trinuclear cluster. Similar antiferromagnetic interactions have been reported for [Fe$_3$(μ$_3$-O)(O$_2$CR)L$_3$]$^{1+}$ complexes (R = alkyl groups, L = monodentate ligands).[1c,5b]

Hydrogen Bond Templating and Supramolecular Structure

2,6-Diaminopyridine and 2-aminopyridine are present in monoprotonated forms in the crystal structures of **1** and **2**

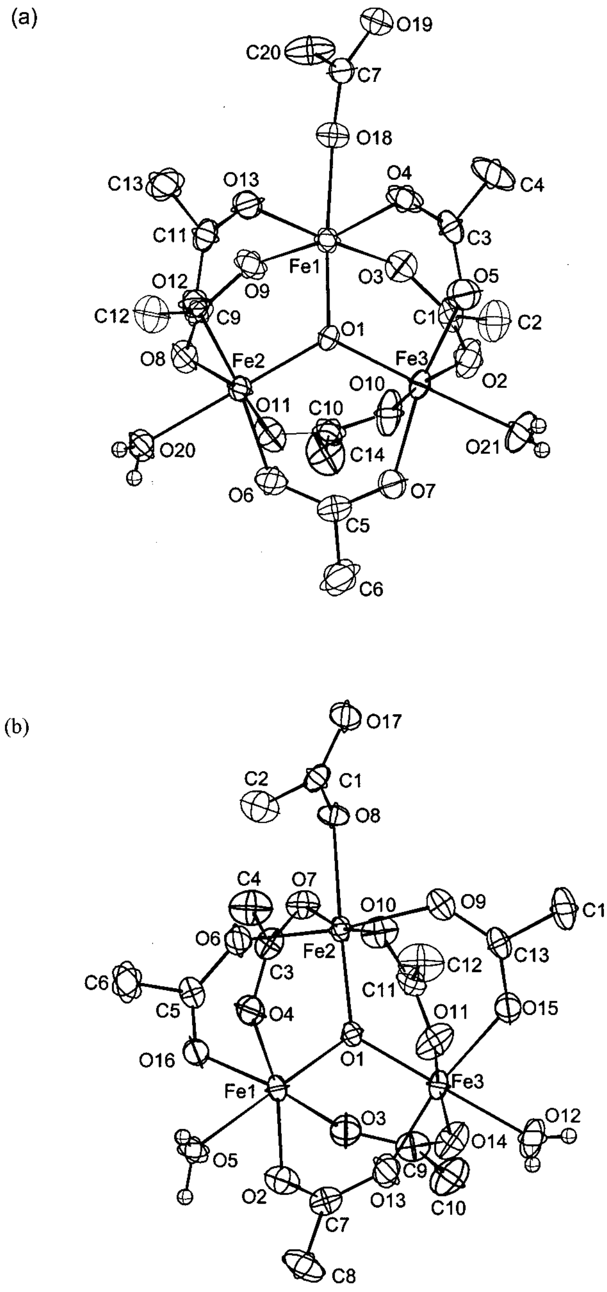

Figure 1. (a) Thermal ellipsoidal plot of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ in **1**; (b) thermal ellipsoidal plot of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ in **2**; acetate hydrogen atoms are omitted for clarity

Table 1. Crystallographic data for **1** and **2**

	1	**2**
Formula	$C_{19}H_{33}ClFe_3N_3O_{21}$	$C_{19}H_{32}ClFe_3N_2O_{21}$
Molecular mass	842.48	827.47
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
T (K)	293	293
a (Å)	10.992(10)	10.722(3)
b (Å)	18.711(13)	18.544(2)
c (Å)	16.564(11)	16.6100(15)
β (°)	106.35(7)	105.961(12)
Volume (Å^3)	3269(4)	3175.4(10)
Z	4	4
$D_{\text{calcd.}}$ (g cm^{-3})	1.712	1.731
Absorption coefficient (mm^{-1})	1.484	1.525
F(000)	1724	1692
λ (Å)	0.71073	0.71073
Crystal size (mm)	0.60 × 0.56 × 0.44	0.64 × 0.36 × 0.28
Theta range (°)	1.68/24.97	1.68/24.99
N	5736	5576
N_o [$I > 2\sigma(I)$]	3822	4548
R	0.0446	0.0394
wR	0.1027	0.1086
Largest diff. peak and hole (e Å^{-3})	0.654/ −0.539	0.934/−0.660

Table 2. Selected interatomic distances (Å) and angles (°) in $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3$ in **1**

Fe1−O1	1.909(3)	Fe1−O13	1.985(4)
Fe1−O3	2.018(4)	Fe1−O18	2.072(3)
Fe2−O1	1.888(3)	Fe2−O20	2.092(4)
Fe3−O1	1.897(3)	Fe3−O21	2.063(4)
O18−C7	1.267(5)	O3−C1	1.257(6)
C7−O19	1.255(6)	C7−C20	1.497(7)
N2−C19	1.345(8)	N2−C15	1.360(7)
C15−N4	1.331(8)	N3−C19	1.322(8)
C15−C16	1.381(8)	C19−C18	1.394(9)
O13−Fe1−O4	91.87(16)	O3−Fe1−O9	85.16(15)
O1−Fe1−O18	175.99(13)	O4−Fe1−O18	83.13(13)
O3−Fe1−O18	82.87(13)	O1−Fe2−O20	178.61(15)
O8−Fe2−O20	83.78(16)	O12−Fe2−O20	85.26(16)
O1−Fe3−O21	177.66(18)	Fe2−O1−Fe3	119.47(16)
Fe2−O1−Fe1	120.53(15)	Fe3−O1−Fe1	119.99(16)
C7−O18−Fe1	132.2(3)	O19−C7 −O18	121.0(5)
O19−C7−C20	118.0(4)	O12−C11−O13	124.4(4)
C19−N2−C15	124.3(5)	N4−C15−N2	118.7(5)
N4−C15−C16	124.0(6)	N2−C15−C16	117.3(6)
N3−C19−N2	117.6(5)	N3−C19−C18	124.5(7)
N2−C19−C18	117.9(7)	C17−C18−C19	119.0(7)

and are involved in noncovalent supramolecular interactions with monodentate acetates as depicted in Figure 2. We were unable to isolate $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ without adding 2,6-diaminopyridine or 2-aminopyridine (along with $NaClO_4$). This in itself suggests that these two amines are involved in the stabilisation of both the monodentate acetates which are coordinated to the {Fe$_3$} clusters and the extended structures (vide infra). Indeed, as seen in Figures 2 and 3, the unusual iron-coordinated monodentate acetate anion is hydrogen-bonded to protonated 2,6-diaminopyridine (in **1**) and 2-aminopyridine (in **2**) and is directly involved in the construction of a new type of supramolecular network. A closer look at the structures (see Figure 3) suggests that these hydrogen-bonding assemblies would not have formed without involvement of the monodentate acetates and that the monodentate acetate could not have been incorporated if it were not stabilised by the 2,6-diaminopyridinium or 2-aminopyridinium cation (Figure 2). In other words, the 2,6-diaminopyridinium or 2-aminopyridinium cation acts as a hydrogen bond template, stabilising the monodentate acet-

Table 3. Selected interatomic distances (Å) and angles (°) in $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2$ in **2**

Fe1−O1	1.889(2)	Fe1−O5	2.103(3)
Fe2−O1	1.911(3)	Fe2−O10	2.002(3)
Fe2−O7	2.013(3)	Fe2−O8	2.083(3)
Fe3−O1	1.892(3)	Fe3−O12	2.053(3)
O9−C13	1.253(5)	O8−C1	1.272(5)
O17−C1	1.249(5)	C13−C14	1.492(6)
C1−C2	1.502(6)	N1−C15	1.335(7)
N1−C19	1.356(8)	C15−N2	1.300(8)
C15−C16	1.433(7)	C19−C18	1.337(8)
O1−Fe1−O5	178.66(12)	O 4−Fe1−O5	84.23(12)
O16−Fe1−O5	85.00(12)	O1−Fe2−O9	93.72(12)
O1−Fe2−O7	96.04(11)	O1−Fe2−O8	176.56(11)
O10−Fe2 −O8	82.19(11)	O7−Fe2−O8	86.94(11)
O1−Fe3−O12	178.00(14)	O15−Fe3−O12	84.91(15)
O11−Fe3−O12	84.26(14)	Fe1−O1−Fe3	119.15(13)
Fe1−O1−Fe(2)	120.16(13)	Fe3−O1−Fe2	120.69(13)
C7−O13−Fe3	132.1(3)	C9−O3−Fe1	130.3(3)
O14−C9−O3	125.0(4)	O14−C9−C10	117.4(4)
O17−C1−O8	121.3(4)	O17−C1−C2	118.4(4)
O8−C1−C2	120.2(4)	O16−C5−C6	117.8(4)
C15−N1−C19	123.5(5)	N2−C15−N1	119.0(5)
N2−C15−C16	124.2(6)	N1−C15−C16	116.8(5)
C17−C16−C15	118.6(5)	C18−C19−N1	120.0(6)
C16−C17−C18	122.7(6)	C19−C18−C17	118.3(7)

ate anion which in turn is responsible for the formation of the novel layer-like hydrogen-bonded network of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$.

Description of the Supramolecular Networks

There are two different types of intermolecular hydrogen bonds in the layer-like, 2D assembly formed in **1** (Figure 3a and Figure 4). These can be described as follows: (i) Type I: each hydrogen atom belonging to the Fe(2)-coordinated water molecule O(20) makes a hydrogen bond with a Fe(1)-coordinated monodentate acetate oxygen O(19). This results in a tetramer consisting of two O(20) waters and two O(19) acetate oxygen atoms (Figure 3a and Figure 4). (ii) Type II: one hydrogen atom attached to O(21)water [which is coordinated to Fe(3)] undergoes bifurcated H-bonding interactions with O(5) and O(10) from two different bidentate acetate anions from an adjacent Fe_3 cluster and vice versa (Figure 3a and Figure 4). The geometrical parameters of the hydrogen bonds involved in constructing this 2D supramolecular assembly are listed in Table 4. Because of the equivalency of the all Fe_3 clusters in the whole crystal, it was possible to have these two types of hydrogen bonds to form an infinite 2D layer network. In the layer, each $\{Fe_3\}$ cluster is surrounded by six identical clusters and is interlinked by both types (I and II) of hydrogen bonding. Interestingly, in the supramolecular network, Fe(1) of an $\{Fe_3\}$ cluster faces Fe(1) of an adjacent $\{Fe_3\}$ cluster. Similarly, Fe(2) and Fe(3) of the same $\{Fe_3\}$ cluster face Fe(2) and Fe(3) from two different adjacent $\{Fe_3\}$ clusters, respectively.

In the crystal structure of **2**, a similar layer-like assembly is formed from intermolecular hydrogen bonding interactions of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ as shown in (see Figure 3b). The hydrogen atoms of O(5)water [coordinated to Fe(1)] are hydrogen bonded to two O(17) acetate oxygen atoms from two different adjacent $\{Fe_3\}$ clusters resulting in a supramolecular $\{O_4\}$ cluster which consists of two O(5) waters and two O(17) acetate oxygen atoms. This is similar to the type I hydrogen bonding interaction in compound **1**. One hydrogen atom of O(12)water [coordinated to Fe(3)] undergoes a hydrogen bonding interaction with O(11) belonging to a bidentate acetate ligand from an adjacent $\{Fe_3\}$ cluster and vice versa. Unlike the

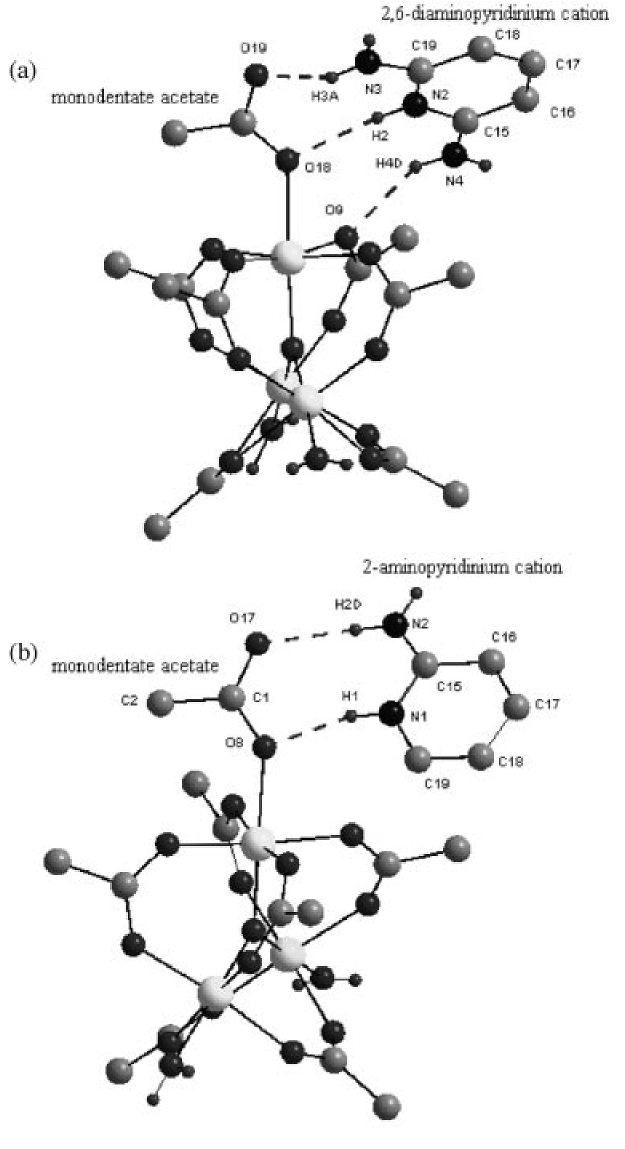

Figure 2. (a) Ball-and-stick representation of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3^+$ showing N−H···O hydrogen bonding interactions between the 2,6-diaminopyridinium cation and the coordinated monodentate acetate ligand in **1**; hydrogen bonding parameters (Å, °): N(3)−H(3A)···O(19), 0.86, 2.08, 2.849 (7), 148.4; N(2)−H(2)···O(18), 0.86, 2.19, 3.045(6), 173.2; N(4)−H(4D)···O(9), 0.86, 2.21, 2.988(7), 151.1; (b) ball-and-stick representation of $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2\text{-}(CH_3COO)]\cdot C_5H_7N_2^+$ showing N−H···O hydrogen bonding interactions between the 2-aminopyridinium cation and the coordinated monodentate acetate ligand in **2**; hydrogen bonding parameters (Å, °): N(2)−H(2D)···O(17), 0.86, 2.13, 2.932(6), 154.6; N(1)−H(1)···O(8), 0.86, 1.97, 2.804(5), 163.8

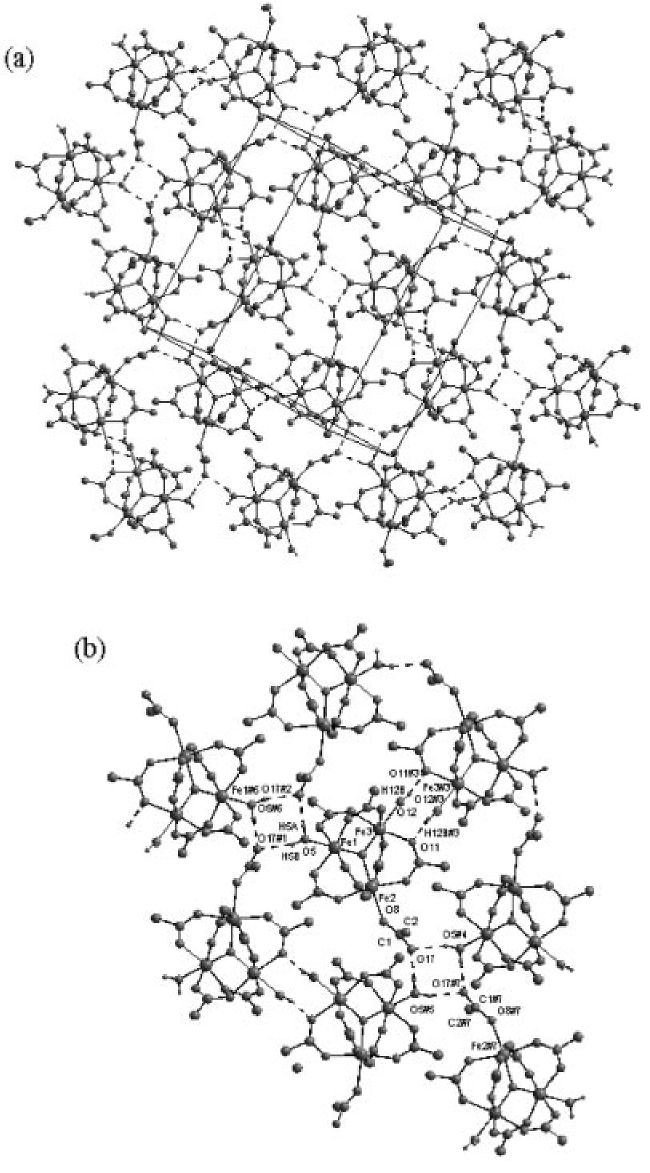

Figure 3. (a) 2D hydrogen-bonding supramolecular network present in **1** based on $Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ as a building block and involving coordinated water hydrogen atoms and acetate oxygen atoms; (b) intermolecular hydrogen bonds of $Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ in **2**; atoms with additional labels #1−#7 are related by symmetry transformations to generate equivalent atoms: #1: *x*, 1.5 − *y*, −0.5 + *z*; #2: 1 − *x*, 0.5 + *y*, 1.5 − *z*; #3: 1 − *x*, 2 − *y*, 2 − *z*; #4: *x*, 1.5 − *y*, 0.5 + *z*; #5: 1 − *x*, −0.5 + *y*, 1.5 − *z*; #6: 1 − *x*, 2 − *y*, 1 − *z*; #7: 1 − *x*, 1 − *y*, 2 − *z*

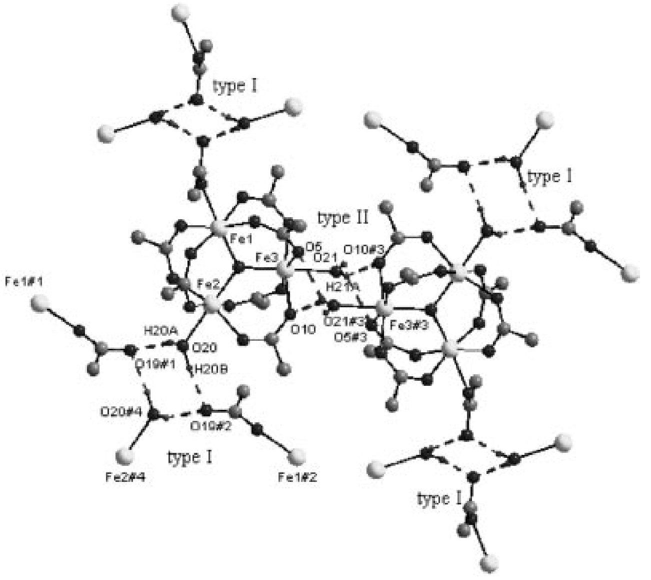

Figure 4. Drawing of two types of the intermolecular hydrogen bonds in **1** as shown in dashed lines; type I: O(20)−H(20A)···O(19); O(20)−H(20B)···O(19); type II: O(21)−H(21A)···O(5); O(21)−H(21A)···O(10); atoms with additional labels #1−#4 are related by symmetry transformations to generate equivalent atoms: #1: *x*, 0.5 − *y*, −0.5 + *z*; #2: 1 − *x*, −0.5 + *y*, 0.5 − *z*; #3: 1 − *x*, −*y*, 1 − *z*; #4: 1 − *x*, −*y*, −*z*

Table 4. Geometrical parameters of hydrogen bonds (Å, °) involved in the supramolecular construction (in **1**) as shown in Figures 3a and Figure 4; D = donor; A = acceptor; atoms with additional labels #1−#3 are related by symmetry operations specified in the caption of Figure 4

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(20)−H(20A)···O(19) # 1	0.65(6)	2.17(6)	2.795(6)	161(7)
O(20)−H(20B)···O(19) #2	0.94(7)	1.83(7)	2.755(5)	168(5)
O(21)−H(21A)···O(5) #3	0.66(7)	2.47(7)	3.021(7)	143(8)
O(21)−H(21A)···O(10) #3	0.66(7)	2.47(7)	3.064(7)	150(8)

Table 5. Geometrical parameters of hydrogen bonds (Å, °) involved in the supramolecular construction (in **2**) as shown in Figure 3b; D = donor; A = acceptor; atoms with additional labels #1−#3 are related by symmetry operations specified in the caption of Figure 3b

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(5)−H(5B)···O(17)# 1	0.83(5)	1.98(5)	2.785(4)	163(4)
O(5)−H(5A)···O(17) #2	0.87(4)	1.97(5)	2.832(4)	175(4)
O(12)−H(12B)···O(11) #3	0.84(7)	2.04(7)	2.858(5)	167(6)

type II hydrogen bonds in compound **1**, the hydrogen atom of O(12)water does not undergo bifurcated hydrogen bonding interactions in compound **2** (see Figure 3b). The relevant hydrogen bonding parameters in compound **2** are summarised in Table 5.

In the crystal structures of both compounds **1** and **2**, the supramolecular hydrogen bonding interactions result in the layer-like two-dimensional networks (Figure 3). In the three-dimensional structure, the packing of these two-dimensional layers gives rise to nano-sized channels when viewed down to crystallographic *a* axis (Figure 5). The layers are well-separated in this stacking (along crystallographic *a* axis) with inter-layer distance of about 11 Å.

Removal of Template

Thermogravimetric analysis (TGA) of **1** under nitrogen showed an initial weight loss of ca. 25% at 240°C due to loss of 2,6-diaminopyridinium perchlorate. The compound is unstable beyond 245°C losing iron coordinated acetates

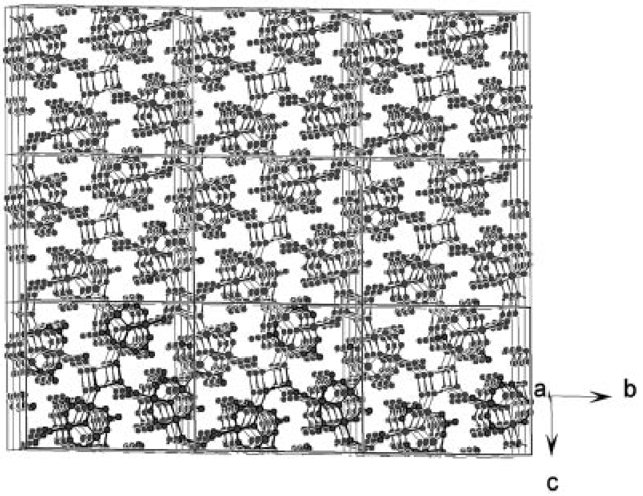

Figure 5. 3D structure of **1** (2,6-diaminopyridinium cation and perchlorate anion are not shown) showing the packing of the layers when viewed along the crystallographic *a* axis (3 × 3 × 3 cells)

including the (μ_3-O) atom with the decomposition of the trinuclear cluster (75.78% calcd, 75.44% obsd). As expected, the TGA curve of compound **2** is comparable with that of compound **1**. We wanted to check whether the template would be removed thermally but with retention of the supramolecular structure. The IR bands (700−850 cm^{-1}: γ-CH and pyridine ring bending bands, 2900−3350 cm^{-1}: N−H stretching vibrations) corresponding to the template gradually disappear on heating **1** and are completely lost when **1** is heated at 150°C for two hours. The resultant solid retains the $\{Fe_3(\mu_3\text{-O})\}$ cluster as supported by the presence of $\nu_{as}(Fe_3O)$ vibrations at 660 cm^{-1} and 625 cm^{-1} in the IR spectrum but the solid loses its crystallinity as evidenced by X-ray powder diffraction studies. We also attempted to remove the template by washing **1** or **2** with an organic solvent in which 2,6-diaminopyridine and 2-aminopyridine are soluble but **1** and **2** are insoluble. However, we were not successful in removing the templates of **1** and **2** whilst maintaining their supramolecular structures (see Exp. Sect.). The fact that the amino bases (templates) cannot be removed from the crystal structure without resorting to heating the sample is probably due to the strong hydrogen bonding interactions of the template with the host trinuclear iron cluster.

Conclusion

A new type of layer-like network, constructed from an unusual trinuclear iron cluster $[Fe_3(\mu_3\text{-})(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]$ using supramolecular interactions, has been presented. The building complex unit represents the first example of a structurally characterised $\{M_3(\mu_3\text{-O})\}$ cluster in which a carboxylate anion acts as a monodentate ligand. The 2,6-diaminopyridinium cation in **1** and the 2-aminopyridinium cation in **2** act as hydrogen bonding templates and stabilise the monodentate acetates which in turn result in the formation of novel supramolecular networks in **1** and **2**. Despite the amine groups of the template being free for metal coordination, the fact that the aminopyridines are not involved in the covalent bonding interactions is very significant. These results help the understanding of the basic principles of supramolecular chemistry.

Experimental Section

Chemicals and Reagents: Doubly distilled water was used throughout. All other chemical reagents were of analytical grade purity.

Physical Methods: TGA analyses of compounds **1** and **2** were performed with a Mettler Toledo Star System thermal analyser under nitrogen at a scan rate of 10°C min^{-1}. Powder X-ray diffraction data were collected with a Phillips PW 3710 diffractometer. Microanalytical (C, H, N) data were obtained with a Perkin−Elmer model 240C elemental analyser. The infrared spectra were recorded by using KBr pellets with a Jasco-5300 FT-IR spectrophotometer. Room temperature (298 K) solid state magnetic susceptibility was measured by using a Sherwood Scientific magnetic susceptibility balance. $Hg[Co(NCS)_4]$ was used as the standard. Diamagnetic corrections $\{-375 \times 10^{-6}$ cgsu for $[Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3\cdot ClO_4$ (**1**) and -366.5×10^{-6} cgsu for $[Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2\cdot ClO_4$ (**2**), calculated from Pascal's constants,[9] were used to obtain the molar paramagnetic susceptibilities.

Synthesis of $[Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_8N_3\cdot ClO_4$ (1): To a stirred aqueous solution (30 mL) of $FeCl_3$ (2 g, 12.33 mmol) were added CH_3COOH (10 mL), 2,6-diaminopyridine (9.16 mmol, 1 g) and $NaClO_4$ (36.75 mmol, 4.5 g), followed by drop wise addition of 1 M NaOH (until the pH of solution reached 3.5. Further addition of NaOH resulted in the formation of a precipitate). The resultant red solution was filtered into 100 mL beaker which was subsequently kept covered with perforated aluminium foil for a week at room temperature. The red crystals of **1** which formed during this time were separated by filtration, washed with cold water and dried at room temperature. Yield: 1.8 g (52% based on Fe). Selected data for **1**, IR (KBr pellet): $\tilde{\nu}$ = 3470 (w), 3350 (m), 3244 (w), 3013 (m), 2939 (m), 2471(w), 2378 (w), 1666 (s), 1601 (s), 1521 (s), 1442 (s), 1174 (m), 1101 (s), 939 (w), 817 (m), 775 (m), 717 (w), 661 (s), 619 cm^{-1} (s). $C_{19}H_{33}ClFe_3N_3O_{21}$ (842.48): calcd. C 27.09, H 3.95, N 4.99; found C 26.98, H 3.99, N 4.92.

Synthesis of $[Fe_3(\mu_3\text{-O})(\mu_2\text{-}CH_3COO)_6(H_2O)_2(CH_3COO)]\cdot C_5H_7N_2\cdot ClO_4$ (2): To a stirred aqueous solution (30 mL) of $FeCl_3$ (2 g, 12.33 mmol) were added CH_3COOH (10 mL), 2-aminopyridine (9.14 mmol, 0.861 g) and $NaClO_4$ (36.75 mmol, 4.5 g), followed by drop wise addition of 1 M NaOH (until the pH of solution reached 3.56. Further addition of NaOH resulted in formation of precipitate). The resultant red solution was filtered and was kept at room temperature for a week. The red crystals of compound **2** which formed during this time were separated by filtration, washed with cold water and dried at room temperature. Yield: 1.79 g (53% based on Fe). Selected data for **2**, IR (KBr pellet): $\tilde{\nu}$ = 3431 (w), 1670 (s), 1602 (s), 1446 (s), 1172 (m), 1103 (s), 773 (m), 659 (s), 615 (s), 522 cm^{-1} (m). $C_{19}H_{32}ClFe_3N_2O_{21}$ (827.47): calcd. C 27.58, H 3.89, N 3.38; found C 27.46, H 3.83, N 3.32.

Caution! *Although no problems were encountered in this work, care should be taken in the handling of perchlorate salts.*

Attempted Reaction for the Removal of the Template: Complex **1** (0.418 mmol, 0.352 g) was suspended in toluene (40 mL) and stirred for 24 h. The suspension was then filtered, washed with toluene and dried at room temperature in the air. The solid was identified as **1** by elemental analysis ($C_{19}H_{33}ClFe_3N_3O_{21}$: calcd. C 27.09, H 3.95, N 4.99; found C 27.15, H 3.89, N 4.93) and IR studies. Similar attempts with **2** for the removal of its template were also unsuccessful (both 2,6-diaminopyridine and 2-aminopyridine are soluble in toluene).

X-ray Crystallography: Data for **1** and **2** were collected at 293 K on an Enraf−Nonius Mach-3 diffractometer using graphite-monochromated Mo-K_α radiation. The structures were solved (SHELXS-97)[10] and refined over F^2 using the SHELXL-97 program.[11] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the 2,6-diaminopyridinium and 2-aminopyridinium cations and the acetate ligands were assigned their positions on the basis of geometrical considerations and were allowed to ride upon the respective carbon and nitrogen atoms. The hydrogen atoms of the coordinated water molecules were located in the differential Fourier maps and were refined using isotropic thermal parameters. CCDC-234723 and -234724 (for compounds **1** and **2** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html. [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk]

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