‘Ionic crystals’ consisting of trinuclear macrocations and polyoxometalate anions exhibiting single crystal to single crystal transformation: breathing of crystals[†]

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Abstract. Ion pairing of trinuclear macrocation cluster (known as basic carboxylate), $[M_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]^{1+}$ and a Keggin type polyoxometalate cluster anion $[SiW_{12}O_{40}]^{4-}$ is stabilized with a number of crystal water molecules in composite type compounds $[M_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4[SiW_{12}O_{40}] \cdot xH_2O \cdot 2ClCH_2COOH$ [$M = Fe^{3+}$, $x = 18$ (**1**); $M = Cr^{3+}$, $x = 14$ (**2**)]. When the crystals of **1** are heated at 85°C and 135°C for 3.5 hours in an open atmospheric condition, it goes to $[Fe_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4[SiW_{12}O_{40}] \cdot 10H_2O \cdot 2ClCH_2COOH$ (**dehydrated 1-85°** $\equiv$ **1'**), and $[Fe_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4[SiW_{12}O_{40}] \cdot 8H_2O \cdot 2ClCH_2COOH$ (**dehydrated 1-135°** $\equiv$ **1''**) respectively with the loss of considerable amount of lattice water molecules retaining their single crystallinity. On the other hand, the single crystals of compound **2**, upon heating at 85°C or 135°C for 3.5 hours, undergo ‘crystal-to-crystal transformation’ to the single crystals of $[Cr_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4[SiW_{12}O_{40}] \cdot 8H_2O \cdot 2ClCH_2COOH$ (**dehydrated 2** $\equiv$ **2'**). Crystal structure analyses show that the parent compounds **1** and **2** undergo molecular rearrangement (molecular motion in the solid state) in respective dehydrated compounds. Remarkably, these dehydrated crystals (**1'**, **1''** and **2'**), upon exposure to water vapor at an ambient condition, regenerate the crystals of parent compounds **1** and **2**, respectively.

Keywords. Iron and chromium basic carboxylates; silicotungstate Keggin cluster anion; ion pairing into ionic crystals; single crystal to single crystal transformations; dehydration; rehydration.

1. Introduction

Transition metal carboxylate chemistry, in particular, trinuclear oxo-centered macrocation, generally formulated as $[M_3O(OOCR)_6L_3]^+$ (where $M = Fe^{3+}$, Cr^{3+} , *etc.*, $R = H$, CH_3 , CH_2Cl , *etc.*, $L =$ neutral ligands, such as, H_2O , pyridine, *etc.*), has played vital role in the development of modern inorganic chemistry.^{1–5} The $\{\mu_3-O\}$ -centered trinuclear metal complexes are also known as ‘basic’ metal carboxylate complexes. Two basic carboxylate complexes, $[Fe_3(\mu_3-O)(OOCCH_3)_6(H_2O)_3]Cl \cdot 6H_2O$ and $[Cr_3(\mu_3-O)(OOCCH_3)_6(H_2O)_3]Cl \cdot 6H_2O$, whose physical properties have been exhaustively studied, are known for

over 50 years.⁶ An interesting feature of a homonuclear ‘basic carboxylate complex’ (when the concerned metal centers are paramagnetic) is that the complex nearly always fails to adopt the expected 3-fold symmetry.^{6–8} It has been argued that net antiferromagnetic coupling distorts spontaneously to a non-3-fold symmetry as a result of spin frustration (also known as “magnetic Jahn Teller effect”).⁹ We have been working on basic trinuclear cluster containing compounds and exploiting their solid state properties to obtain new materials in application point of view. Recently, we have demonstrated that the basic iron trinuclear (μ_3-O) cluster-containing compound is capable of sensing methanol in a single crystal to single crystal transformation study.¹⁰ We have also shown that the same iron basic carboxylate can recognize pyridine molecule from its vapor state in a gas-solid reaction.¹¹ Generally, basic trinuclear

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[†]Dedicated to Professor K. C. Kumara Swamy on the occasion of his 60th birth anniversary.

Table 1. Crystal Data and Structural Refinement Parameters for Compound **1**, **dehydrated 1'** and **dehydrated 1''**.

	1	1'	1''
Empirical formula	C ₅₂ H ₁₁₄ Cl ₂₆ Fe ₁₂ O ₁₂₆ SiW ₁₂	C ₅₂ H ₉₈ Cl ₂₆ Fe ₁₂ O ₁₁₈ SiW ₁₂	C ₅₂ H ₉₄ Cl ₂₆ Fe ₁₂ O ₁₁₆ SiW ₁₂
Formula weight	6581.62	6437.49	6401.46
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
<i>a</i> [Å]	30.283(9)	30.607(8)	30.507(13)
<i>b</i> [Å]	17.759(5)	17.805(5)	17.764(7)
<i>c</i> [Å]	32.435(9)	30.083(8)	29.939(12)
α [deg]	90.0000	90.000	90.000
β [deg]	101.292(4)	113.060(4)	112.941(7)
γ [deg]	90.0000	90.000	90.000
<i>V</i> [Å ³]	17106(8)	15084(7)	14941(11)
<i>Z</i>	4	4	4
<i>D</i> _{calc} [Mg m ⁻³]	2.556	2.835	2.846
μ [mm ⁻¹]	9.536	10.806	10.908
<i>F</i> (000)	12360	12040	11960
Crystal size [mm ³]	0.36 × 0.08 × 0.06	0.28 × 0.16 × 0.04	0.18 × 0.10 × 0.06
θ range for data collection [deg]	1.28 to 26.00	1.35 to 28.37	1.40 to 26.16
Reflections Collected/unique	87670/16902	85120/17989	74774/14813
<i>R</i> [int]	0.0570	0.0676	0.1314
Refinement method	Full-matrix least-squares on <i>F</i> ²		
Data/restraints/parameters	16902/0/1009	17989/0/1015	14813/0/ 953
Goodness-of-fit on <i>F</i> ²	1.164	1.076	0.963
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0503/0.1216	0.0512/0.0991	0.0531/0.1149
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0596/0.1278	0.0706/0.1056	0.1028/0.1333
Largest diff. Peak/hole [e Å ⁻³]	1.978/-2.314	1.862/-1.668	2.074/-1.46

Figure 1. UV-Visible absorbance spectra of, (left) [Fe₃(μ_3 -O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 18H₂O · 2ClCH₂COOH (**1**) and (right) [Cr₃(μ_3 -O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 14H₂O · 2ClCH₂COOH (**2**) in 1 × 10⁻⁴ M. in methanol solution. For compound **1**: $\lambda_{\max}$ (nm) = 460, 420 and 270 and corresponding $\epsilon_{\max}$ (M⁻¹cm⁻¹) = 924, 1326 and 14510, respectively. For compound **2**: $\lambda_{\max}$ (nm) = 599, 450 and 268 and corresponding $\epsilon_{\max}$ (M⁻¹cm⁻¹) = 242, 211 and 11660, respectively.

(μ_3 -O)-bridged transition metal carboxylate clusters are well documented in the literature in three different contexts: (i) discrete (μ_3 -O) clusters, that are classified either under neutral mixed metal-(μ_3 -O) clusters or discrete cationic (μ_3 -O) clusters.⁶ These basic trin-

uclear clusters are considered as important subclass of inorganic trinuclear compounds because of their numerous applications such as, majority of higher nuclear clusters {e.g., Fe₁₀ wheel type clusters} are generated from these starting precursors.^{12,13} This class of com-

Figure 2. PXRD patterns of basic carboxylate-Keggin based ionic crystals. left: compounds **1**, **1'** and regenerated **1**; right: **2**, **2'** (dehydrated at 85°C) and regenerated **2**.

Figure 3. TGA/Mass plot of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2 \text{ClCH}_2\text{COOH}$ (**1**) (left); TGA/Mass plot of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1'**) (right).

pounds are also important in terms of magnetism,¹⁴ and catalysis.¹⁵

(ii) Open metal-organic framework materials (MOFs), in which trinuclear ($\mu_3\text{-O}$)-clusters, acting as building units, are interconnected by organic linkers using covalent bonds in the relevant crystal lattice having well-defined pores and cavities.¹⁶ (iii) Ionic crystals,

in which 's' block metal ions (e.g., Na^+ , K^+ , Rb^+ , Cs^+ ions), trinuclear macrocations, polyoxometalate anions and solvent molecules are accommodated in the crystal lattice and stabilized by electrostatic interactions.^{17–25}

Polyoxometalates are metal-oxide based molecular clusters, generally observed in anionic forms, that

Figure 4. TGA/Mass plot of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1''**) (left); TGA/Mass plot of water regenerated compound (**regenerated 1**) (right).

Figure 5. TGA/Mass plot of $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2**) (left); TGA/Mass plot of $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2'**) (right).

Figure 6. TGA/Mass plot of water regenerated compound (**regenerated 2**).

are isolated as crystalline materials with appropriate cations.²⁶ The interest in this class of polyoxometalate based 'ionic crystals' has opened up a new field of

research and enormous work has been done by Mizuno and co-workers, especially in terms of their applications in selective sorption and desorption of small molecules.^{17–25} They found that the systems showing this selective host-guest chemistry have the maximum macrocation/polyoxometalate ratio of 2:1, where the remaining negative charges are generally counterbalanced by alkali metal ions. In this contribution, we have discussed a series of ionic crystals consisting of macrocation/polyoxoanion ratio of 4:1 without the presence of alkali metal cations. We have described here the synthesis and structural characterization of the compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**) (ratio of macrocation/polyoxoanions is 4:1). Compound **1**, on heating at 85°C for 3.5 hours in an open oil bath, undergoes single crystal to single crystal transformation resulting in a dehydrated compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1'**). When the crystals of compound **1** are heated at 135°C for 3.5 hours in an open oil bath, relatively more dehydrated compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1''**) is obtained.

Figure 7. (a) Thermal ellipsoidal representation (50% probability level) of the asymmetric unit of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**) excluding lattice solvent water and chloroacetic acid and hydrogen atoms. (b) The molecular structure of compound **1**, excluding lattice water and chloroacetic acid molecules. Color code: Mo, yellow; Si, cyan; O, red; Fe, dark green; C, gray; Cl, light green; H, purple.

$\text{O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1''**) is obtained. Both these dehydrated compounds (**1'** and **1''**) have been characterized by single crystal X-ray structure determination. One of these dehydrated compounds, **1'** on exposing to water vapor for one week regenerates to compound **1** (**regenerated 1**). The single crystals of **regenerated 1** exhibited similar cell parameters as those of parent **1** (the single crystal structure of **regenerated 1** could not be determined due to its poor data quality). The crystals of **regenerated 1** were further characterized by routine spectroscopic analysis, TGA-Mass studies and powder X-ray diffraction studies. We have shown similar crystal to crystal transformations mediated by chromium analogue compounds as shown below (unlike compound **1**, chromium

analogue **2** resulted in the same dehydrated compound, **2'**, even when **2** was heated at 85°C as well as 135°C). That is,

We have thus demonstrated here a reversible crystal to crystal transformation mediated by compounds **1** and **2** through exclusion and inclusion of water molecules in

Figure 8. (a) The unit cell packing diagram of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**) which shows the arrangement of lattice water molecules in hydrophilic channels; (b) The unit cell packing diagram of $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (dehydrated **1-85°**) which shows the arrangement of lattice water molecules in hydrophilic channels.

respective ionic crystals. The parent compounds **1** and **2**, and their dehydrated forms, **1'**, **1''** and **2'** are unambiguously characterized by single crystal X-ray crystallography. The regenerated **1** and **2** are characterized by determining their unit cell parameters and comparing these unit cell parameters with those of the parent compounds **1** and **2**. All these compounds are additionally characterized by IR and UV-visible spectra, powder X-ray diffraction (PXRD) studies and their TGA analyses.

2. Experimental

2.1 Materials

All the chemicals were reagent grade and used without any further purification. The distilled water was used throughout the work. $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, hydrochloric acid and anhydrous FeCl_3 were acquired from Merck. ClCH_2COOH was received from S. D. Fine Chemicals. $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was obtained from Loba Chemicals.

2.2 Physical measurements

Infrared spectra of solid samples were obtained as KBr pellets on a JASCO-5300 FT-IR spectrophotometer. A Cary 100 Bio UV/vis spectrophotometer was used to record the electronic

absorption spectra. Thermogravimetric analyses were carried out on a STA 409 PC analyzer and corresponding masses were analyzed by QMS 403 C mass analyzer, under the flow of N_2 gas with a heating rate of 5°C min^{-1} , in the temperature range of 30–1100°C. The Powder X-ray diffraction patterns were recorded using Cu-K α ($\lambda = 1.54 \text{ \AA}$) radiation on a Phillips PW 3710 diffractometer at a scanning speed of 3° min^{-1} .

2.3 Synthesis and characterization

2.3a $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**): To a 100 mL of water, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (0.5 g, 0.17 mmol), 5 mL of 2.3 M HCl were added, followed by the addition of ClCH_2COOH (5.5 g, 58.20 mmol). The pH of the resulting reaction mixture was adjusted to 2.0 by 5 M NaOH solution. To this solution, FeCl_3 (0.34 g, 2.10 mmol) was added and the resulting solution was stirred for an hour, then filtered and the filtrate was kept open at room temperature. After one week, settled red colored crystals were collected, dried at room temperature and used for further studies. Yield: 0.45 g (39% based on W). IR (KBr pellet): (ν/cm^{-1}): 3342, 2945, 1734, 1614 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1431, 1392 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1259, 1016, 974 (s, $\nu_{\text{asym}}(\text{W=O})$), 920 (br, $\nu_{\text{asym}}(\text{Si-O})$), 798 (br, $\nu_{\text{asym}}(\text{W-Oc-W})$), 692 (m, $\nu_{\text{asym}}(\text{Fe}_3\text{-O})$), 574, 507. Anal. calcd. for $\text{C}_{52}\text{H}_{114}\text{Cl}_{26}\text{Fe}_{12}\text{O}_{126}\text{SiW}_{12}$: C, 9.49; H, 1.75%. Found: C, 9.88; H, 2.01%.

Figure 9. (a) C–H···O hydrogen bonding interactions in $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**). (b) C–H···O hydrogen bonding interactions with relevant symmetry codes in compound **1**. (c) O–H···O hydrogen bonding interactions in compound **1**. (d) O–H···O hydrogen bonding interactions with relevant symmetry codes in compound **1**. Color code: W, yellow; O, red; Fe, dark green; Cl, light green; C, gray; H, purple; $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]^{1+}$ cluster, purple polyhedra; $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster, golden yellow polyhedra; C–H···O hydrogen bonding interactions, brown dotted lines; O–H···O hydrogen bonding interactions green dotted lines.

2.3b $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1'**): Compound **1**, on heating in the temperature range of 80–85°C for 3.5 h, produced **1'**. IR (KBr pellet): (ν/cm^{-1}): 3296, 2945, 1728, 1610 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1431, 1394 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1259, 1016, 974 (s, $\nu_{\text{asym}}(\text{W=O})$), 918 (br, $\nu_{\text{asym}}(\text{Si-O})$), 798 (br, $\nu_{\text{asym}}(\text{W-Oc-W})$), 690 (m, $\nu_{\text{asym}}(\text{Fe}_3\text{-O})$), 578, 509. Anal. calcd. for $\text{C}_{52}\text{H}_{98}\text{Cl}_{26}\text{Fe}_{12}\text{O}_{116}$ O₁₁₈SiW₁₂: C, 9.70; H, 1.53%. Found: C, 10.11; H, 1.49%.

2.3c $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1''**): Compound **1**, on heating in the temperature range of 130–140°C for 3.5 h, produced **1''**. IR (KBr pellet): (ν/cm^{-1}): 3306, 2949, 2334, 1738, 1614 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1550, 1429, 1398 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1259, 1016, 974 (s, $\nu_{\text{asym}}(\text{W=O})$), 918 (br,

$\nu_{\text{asym}}(\text{Si-O})$), 800 (br, $\nu_{\text{asym}}(\text{W-Oc-W})$), 690 (m, $\nu_{\text{asym}}(\text{Fe}_3\text{-O})$), 578, 511. Anal. calcd. for $\text{C}_{52}\text{H}_{94}\text{Cl}_{26}\text{Fe}_{12}\text{O}_{116}$ SiW₁₂: C, 9.76; H, 1.48%. Found: C, 9.59; H, 1.55%.

2.3d $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (regenerated **1**): **1'**, on exposure to water vapor for the period of one week produced **regenerated 1**, and was characterized by IR, PXRD and TGA/Mass analysis and by comparing unit cell parameters of the regenerated one with those of parent **1**.

2.3e $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2**): To 100 mL of water, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (0.5 g, 0.17 mmol), 5 mL of 2.3 M HCl were added followed by the addition of ClCH_2COOH (5.5 g, 58.20 mmol). The pH of the resulting reaction mixture

Table 2. Geometrical parameters of the C–H ···O hydrogen bonds (Å,°) involved in supramolecular network of compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**), where D=donor; A=acceptor.

D–H ··· A	d(D ··· H)	d(H ··· A)	d(D ··· A)	∠(DHA)
C2–H2A....O54	0.97	2.59	3.558(19)	174.6
C2–H2B....O9#1	0.97	2.61	3.315(15)	129.9
C2–H2B....O17#2	0.97	2.56	3.349(14)	138.7
C4–H4B....O41#3	0.97	2.80	3.500(16)	129.8
C6–H6A....O11#1	0.97	2.63	3.506(17)	150.0
C10–H10A...O4#4	0.97	3.02	3.569(15)	117.2
C10–H10A....O6#4	0.97	2.81	3.494(15)	128.6
C10–H10A....O13#4	0.97	2.62	3.428(14)	141.4
C10–H10A....O49#5	0.97	2.60	3.412(13)	141.0
C12–H12B....O8#6	0.97	2.40	3.368(13)	178.4
C12–H12A....O39#7	0.97	2.67	3.541(14)	150.2
C14–H14A...O8#1	0.97	2.56	3.366(13)	140.6
C20–H20A....O47#8	0.97	2.59	3.378(15)	138.2
C22–H22A....O9#9	0.97	2.88	3.471(12)	120.0
C22–H22B...O34#10	0.97	2.65	3.272(12)	122.6
C24–H24B...O11#9	0.97	2.71	3.318(16)	121.3
C24–H24B...O12#9	0.97	2.67	3.530(15)	148.3

Symmetric transformations used to generate equivalent atoms: #1 x, 1-y, 0.5+z; #2 -x, 1-y, 1-z; #3 0.5-x, 1.5-y, 2-z; #4 0.5-x, 0.5-y, 1-z; #5 x, -1+y, z; #6 0.5-x, 0.5-y, 1-z; #7 0.5-x, -0.5+y, 1.5-z; #8 1-x, 2-y, 2-z; #9 0.5-x, 1.5-y, 1-z; #10 x, 1+y, z; #11 0.5-x, 0.5+y, 1.5-z; #12 x, 1+y, 1+z.

Table 3. Geometrical parameters of the O–H ···O hydrogen bonds (Å) involved in supramolecular network of compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**).

O(16)–O(27)#2	3.019(10)	O(16)–O(29)#2	3.039(11)
O(18)–O(54)#2	3.071(14)	O(13)–O(48)#9	2.898(10)
O(11)–O(49)#9	2.906(10)	O(11)–O(50)#9	2.909(10)
O(9)–O(34)#4	2.723(9)	O(2)–O(24)#4	2.909(10)
O(24)–O(57)	2.636(18)	O(24)–O(2)#4	2.909(10)
O(34)–O(9)#4	2.723(9)	O(34)–O(56)#7	2.738(11)
O(29)–O(16)#2	3.039(11)	O(29)–O(55)	2.686(18)
O(33)–O(38)#7	2.867(10)	O(27)–O(16)#2	3.019(10)
O(38)–O(56)	2.709(12)	O(38)–O(33)#11	2.867(10)
O(48)–O(13)#9	2.898(10)	O(48)–O(62)#12	3.000(9)
O(43)–O(54)#3	2.775(15)	O(49)–O(11)#9	2.909(10)
O(53)–O(58)#7	2.820(3)	O(54)–O(18)#2	3.071(14)
O(54)–O(43)#3	2.775(15)	O(55)–O(29)	2.686(18)
O(56)–O(34)#11	2.738(11)	O(56)–O(38)	2.709(12)
O(56)–O(58)	2.910(3)	O(57)–O(24)	2.636(18)
O(57)–O(60)	3.030(5)	O(58)–O(53)#11	2.820(3)

Symmetric codes are already specified in the footnote of Table 2.

was adjusted to 2.0 by 5 M NaOH solution. To this solution, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 g, 2.50 mmol) was added and the resulting solution was stirred for an hour, then filtered and the filtrate was kept open at room temperature. After one week,

settled green colored crystals were filtered, dried in room temperature and used for further studies. Yield: 0.52 g (46% based on W). IR (KBr pellet): (ν/cm^{-1}): 3557, 3335, 2949, 1643 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1440, 1406 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1263,

Figure 10. A perspective view of packing diagram along the crystallographic *b* axis: (a) $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1**) and (b) $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**1'**); Color code: $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]^{1+}$ cluster, purple polyhedra; $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster, golden yellow polyhedra; non-coordinated water molecules, blue; Cl, light green.

Table 4. The inter nuclear distances between two $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster anions along crystallographic *c* axis in compound **1** and **1'**.

$[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (1) Internuclear distance (Å) between two $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster anions		$[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (1') Internuclear distance (Å) between two $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster anions	
Si – Si	17.78	Si – Si	15.35
W1 – W1	13.15	W1A – W1A	11.31
W1 – W1	20.31	W1A – W1B	19.53
W2 – W2	14.02	W2A – W2A	13.67
W2 – W2	19.76	W2A – W2B	17.98
W3 – W3	18.37	W3 – W3	14.92
W3 – W3	19.67	W3 – W3	18.55
W4 – W4	17.66	W4A – W4A	13.63
W4 – W4	23.81	W4B – W4A	21.12
W5 – W5	18.14	W5A – W5B	15.34
W5 – W5	23.44	W5A – W5B	19.95
W6 – W6	11.91	W6A – W6A	9.05
W6 – W6	24.43	W6A – W6B	22.18

974 (s, $\nu_{\text{asym}}(\text{W}=\text{O})$), 920 (br, $\nu_{\text{asym}}(\text{Si}-\text{O})$), 800 (br, $\nu_{\text{asym}}(\text{W}-\text{O}-\text{W})$), 706, 659 (m, $\nu_{\text{asym}}(\text{Cr}_3-\text{O})$), 441. Anal. calcd. for $\text{C}_{52}\text{H}_{106}\text{Cl}_{26}\text{Cr}_{12}\text{O}_{122}\text{SiW}_{12}$: C, 9.66; H, 1.65%. Found: C, 9.76; H, 1.58%.

2.3f $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2'**): A bunch of crystalline compound **2**, on heating in the temperature range of 135°C for 3.5 h or 85°C for 3.5 h, produced same **2'** compound. IR (KBr pellet): (ν/cm^{-1}): 3557, 3342, 2953, 1643 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1440, 1410 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1261, 1016, 972 (s, $\nu_{\text{asym}}(\text{W}=\text{O})$), 920 (br, $\nu_{\text{asym}}(\text{Si}-\text{O})$), 802 (br, $\nu_{\text{asym}}(\text{W}-\text{O}-\text{W})$), 706, 655 (m, $\nu_{\text{asym}}(\text{Cr}_3-\text{O})$), 588, 439. Anal. calcd.

for $\text{C}_{52}\text{H}_{94}\text{Cl}_{26}\text{Cr}_{12}\text{O}_{116}\text{SiW}_{12}$: C, 9.82; H, 1.49%. Found: C, 10.06; H, 1.55%.

2.3g $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (regenerated **2**): Compound **2'**, on exposure to water vapor for the period of one week, produced **regenerated 2**. It was characterized by IR, PXRD and TGA/Mass analysis. IR (KBr pellet): (ν/cm^{-1}): 3314, 2951, 1792, 1643 (vs, $\nu_{\text{asym}}(\text{OCO})$), 1440, 1406 (vs, $\nu_{\text{sym}}(\text{OCO})$), 1263, 1016, 974 (s, $\nu_{\text{asym}}(\text{W}=\text{O})$), 920 (br, $\nu_{\text{asym}}(\text{Si}-\text{O})$), 800 (br, $\nu_{\text{asym}}(\text{W}-\text{O}-\text{W})$), 706, 655 (m, $\nu_{\text{asym}}(\text{Cr}_3-\text{O})$), 588, 532, 428. It was also characterized by comparing unit cell parameters of the regenerated one with those of parent **2**.

Table 5. Geometrical parameters of the C–H···O hydrogen bonds (Å, °) involved in supramolecular network of compound [Fe₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 10H₂O · 2ClCH₂COOH (**1'**), where D=donor; A=acceptor.

D–H···A	d(D···H)	d(H···A)	d(D···A)	∠(DHA)
C2–H2A....O8	0.97	2.47	3.442(13)	179.1
C4–H4B....O6	0.97	2.82	3.480(12)	126.1
C4–H4B....O15	0.97	2.57	3.395(11)	142.9
C6–H6A....O12#1	0.97	2.58	3.444(15)	148.0
C6–H6B....O57	0.97	2.71	3.410(3)	129.9
C10–H10A...O9#1	0.97	2.31	3.122(13)	140.3
C10–H10A....O10#1	0.97	2.75	3.387(12)	123.6
C14–H14A....O7	0.97	2.53	3.401(15)	150.2
C16–H16B....O52#2	0.97	2.69	3.510(2)	143.2
C18–H18A....O8#3	0.97	2.83	3.554(12)	131.8
C20–H20A....O42#2	0.97	2.57	3.492(15)	158.2
C22–H22A...O9#4	0.97	2.95	3.588(12)	124.3
C22–H22A....O11#4	0.97	2.61	3.522(11)	157.5
C22–H22B....O29#4	0.97	2.79	3.364(11)	119.0
C24–H24B...O13#4	0.97	2.44	3.409(11)	173.9
C24–H24B...O44#2	0.97	2.87	3.442(13)	118.5
C24–H24A...O47#2	0.97	2.55	3.509(13)	170.2

Symmetry transformations used to generate equivalent atoms: #1 0.5-x, -0.5+y, 0.5-z; #2 -x, -y, 1-z; #3 0.5-x, 0.5-y, 1-z; #4 x, 1-y, 0.5+z; #5 -1+x, y, z; #6 x, 1-y, -0.5+z; #7 0.5+x, 0.5+y, z; #8 0.5+x, -0.5+y, z; #9 0.5-x, 0.5+y, 0.5-z; #10 x, y, -1+z; #11 -x, y, 0.5-z; #12 x, y, 1+z; #13 1+x, y, z.

Table 6. Geometrical parameters of the O–H···O hydrogen bonds (Å) involved in supramolecular network of compound [Fe₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 10H₂O · 2ClCH₂COOH (**1'**).

O(2)–O(24)	2.886(9)	O(2)–O(55)#5	3.098(13)
O(9)–O(29)	2.733(9)	O(12)–O(38)#6	2.913(9)
O(12)–O(39)#6	3.026(10)	O(15)–O(40)#6	2.753(8)
O(17)–O(34)#7	2.840(9)	O(17)–O(35)#7	3.052(9)
O(22)–O(54)#1	3.079(11)	O(24)–O(56)	2.738(10)
O(29)–O(54)	2.773(10)	O(30)–O(50)#3	2.878(9)
O(34)–O(17)#8	2.840(9)	O(34)–O(45)#9	3.061(10)
O(34)–O(53)#10	2.560(18)	O(35)–O(17)#8	3.052(9)
O(38)–O(12)#4	2.913(9)	O(39)–O(12)#4	3.026(10)
O(40)–O(15)#4	2.753(8)	O(40)–O(56)#11	2.746(9)
O(45)–O(34)#1	3.061(10)	O(50)–O(54)#3	2.793(10)
O(53)–O(34)#12	2.560(18)	O(54)–O(22)#9	3.079(11)
O(55)–O(2)#13	3.098(13)	O(5)–O(56)#13	2.702(15)
O(56)–O(55)#5	2.702(15)		

Symmetry codes are already specified in the footnote Table 5.

at 450 nm and at around 600 nm, found in the absorption spectrum (Figure 1, right) of compound **2**, can be attributed to possible weak spin-forbidden d-d transition in iron³² and to the d-d transition for the central Cr³⁺ ion, respectively. The corresponding UV-visible absorption spectra are presented in Figure 1.

3.2 Powder X-ray diffraction (PXRD)

The powder X-ray diffraction (PXRD) patterns (Figure 2) of parent compound **1**, **1'** and **regenerated 1** did not show any notable change. This may be because of the following reasons: the heated crystals, **1'** and **1''** did

Intentionally, we have avoided higher temperature (for dehydration), because iron-coordinated water molecules are known to leave the crystal lattice resulting in the loss of crystalline state.^{33,34} Similarly, PXRD patterns of compound **2**, **2'** and **regenerated 2** are also recorded, and as expected, they have identical powder patterns as shown in Figure 2 (right).

The thermogravimetric analyses of all the compounds were performed in flowing N₂ with a heating rate of 5°C min⁻¹ in the temperature range of 30–1100°C.

3.3a $[Fe_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4$
 $[SiW_{12}O_{40}] \cdot 18H_2O \cdot 2ClCH_2COOH(1)$: TGA curve of compound **1** is divided into four sets. The first weight loss is 4.18% that corresponds to the loss of fifteen lattice water molecules per formula unit in the temperature range of 50–120°C (calculated mass loss for fifteen water molecules is 4.18%). The second weight loss is 3.80%, which corresponds to the loss of fourteen water molecules in the temperature range of 120–170°C (calculated mass loss for fourteen water molecules is 3.83%). The major mass loss of 37.04% was observed in the temperature range of 170–585°C due to the decomposition of the cluster. The evolution of water molecules (from the lattice and iron coordination sites) and carbon dioxide gas molecules are evidenced by the TGA / Mass curves, which are shown in blue and purple color respectively in Figure 3 (left).

Table 7. Geometrical parameters of the C–H···O hydrogen bonds (Å, °) involved in supramolecular network of compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH} (\mathbf{1}'')$. D=donor; A=acceptor.

D–H···A	d(D···H)	d(H···A)	d(D···A)	∠(DHA)
C2–H2B...O17#1	0.97	2.52	3.400(2)	151.5
C6–H6B...O9	0.97	2.64	3.545(16)	156.3
C6–H6A...O40#4	0.97	2.79	3.358(18)	118.0
C8–H8A...O3#3	0.97	2.41	3.375(16)	173.2
C8–H8B...O23#2	0.97	2.54	3.498(19)	170.5
C8–H8B...O25#2	0.97	2.84	3.410(19)	118.1
C14–H14B...O19#7	0.97	2.82	3.480(17)	125.6
C14–H14B...O1#7	0.97	2.56	3.385(17)	143.5
C14–H14A...O30#5	0.97	2.57	3.328(16)	134.7
C16–H16A...O12#5	0.97	2.47	3.438(17)	177.8
C18–H18B...O20#6	0.97	2.61	3.221(18)	120.7
C20–H20A...O10	0.97	2.29	3.116(17)	142.1
C20–H20A...O8	0.97	2.73	3.387(16)	125.5
C24–H24A...O2#3	0.97	2.63	3.490(2)	147.8

Symmetry transformations used to generate equivalent atoms: #1 $x, -y, 0.5+z$; #2 $1-x, 1-y, 1-z$; #3 $1-x, y, 0.5-z$; #4 $0.5-x, -0.5+y, 0.5-z$; #5 $0.5-x, 0.5+y, 0.5-z$; #6 $0.5-x, 0.5-y, -z$; #7 $-0.5+x, 0.5+y, z$; #8 $x, 1-y, 0.5+z$; #9 $0.5+x, 0.5-y, 0.5+z$; #10 $x, 1-y, -0.5+z$; #11 $x, y, -1+z$; #12 $x, y, 1+z$; #13 $-0.5+x, 0.5-y, -0.5+z$; #14 $-1+x, y, z$; #15 $1+x, y, z$.

Table 8. Geometrical parameters of the O–H···O hydrogen bonds (Å) involved in supramolecular network of compound $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH} (\mathbf{1}'')$.

O(2)–O(30)#3	2.900(12)	O(2)–O(31)#3	3.035(14)
O(1)–O(29)#3	2.727(12)	O(5)–O(49)	3.087(13)
O(5)–O(50)	2.849(13)	O(10)–O(40)#4	2.734(12)
O(14)–O(45)#4	2.898(12)	O(20)–O(53)#6	3.069(14)
O(24)–O(50)#8	3.038(14)	O(29)–O(53)#9	2.733(13)
O(34)–O(39)	2.866(14)	O(34)–O(54)	2.773(14)
O(40)–O(10)#5	2.734(12)	O(40)–O(54)	2.768(14)
O(45)–O(14)#5	2.898(12)	O(45)–O(53)	2.717(14)
O(47)–O(54)#4	3.048(14)	O(50)–O(24)#10	3.038(14)
O(50)–O(55)#11	2.500(3)	O(55)–O(50)#12	2.500(3)
O(53)–O(29)#13	2.733(13)	O(53)–O(56)#14	2.710(2)
O(54)–O(47)#5	3.048(14)	O(56)–O(53)#15	2.710(2)

Symmetric codes are already specified in the footnote of Table 7.

3.3b $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 10\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH} (\mathbf{1}')$: TGA curve (Figure 3, right) of compound $\mathbf{1}'$ is divided into three sets. The first weight loss 1.90%, which corresponds to the loss of seven lattice water molecules per formula unit in the temperature range of 50–140°C (calculated mass loss for seven water molecules is 1.96%). The second weight loss is 3.96% corresponding to the loss of fourteen water molecules in the temperature range of 140–201°C (calculated mass loss for fourteen

water molecules is 3.91%). The major mass loss of 38.67% was observed in the temperature range of 201–748°C due to the collapse of the structure of the cluster. The evolution of water molecules and carbon dioxide gas molecules are evidenced by the TGA / Mass curves, which are shown in blue and purple color respectively in the Figure 3, right ($\mathbf{1}'$).

3.3c $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH} (\mathbf{1}'')$: TGA curve

Table 9. Crystal Data and Structural Refinement for Compounds **2**, **dehydrated 2-85° (2')** and **dehydrated 2-135° (2')**.

	2	2 dehydrated 2-85°2'	dehydrated 2-135° 2'
Empirical formula	C ₅₂ H ₁₀₆ Cl ₂₆ Cr ₁₂ O ₁₂₂ SiW ₁₂	C ₅₂ H ₉₄ Cl ₂₆ Cr ₁₂ O ₁₁₆ SiW ₁₂	C ₅₂ H ₉₄ Cl ₂₆ Cr ₁₂ O ₁₁₆ SiW ₁₂
Formula weight	6463.36	6355.26	6355.26
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
a [Å]	30.1958(17)	30.539(6)	30.569(8)
b [Å]	17.7025(10)	17.777(3)	17.778(4)
c [Å]	32.2944(18)	29.880(6)	29.823(7)
α [deg]	90.0000	90.000	90.000
β [deg]	101.6470(10)	112.962(3)	112.809(4)
γ [deg]	90.0000	90.000	90.000
V [Å ³]	16907.2(16)	14936(5)	14940(6)
Z	4	4	4
D _{calc} [Mg m ⁻³]	2.539	2.826	2.825
μ [mm ⁻¹]	9.386	10.619	10.616
F(000)	12104	11864	11864
Crystal size [mm ³]	0.26 × 0.10 × 0.06	0.22 × 0.10 × 0.06	0.30 × 0.10 × 0.02
θ range for data collection [deg]	1.34 to 26.05	1.48 to 28.36	1.45 to 26.54
Reflections			
Collected/unique	87235/16671	85248/17891	69592/14651
R [int]	0.0473	0.0674	0.1329
Refinement method	Full-matrix least-squares on F ²		
Data/restraints/parameters	16671 / 0 / 1029	17891 / 0 / 964	14651 / 0 / 953
Goodness-of-fit on F ²	1.048	1.182	0.962
R ₁ /wR ₂ [I > 2 σ(I)]	0.0354/0.0911	0.0619/0.1226	0.0470/0.0946
R ₁ /wR ₂ (all data)	0.0452/0.0959	0.0779/0.1286	0.0809/0.1048
Largest diff. Peak/hole [e Å ⁻³]	2.125/-1.308	2.711/-2.473	2.038/-1.843

of **dehydrated 1''** can be divided into four sets. The first weight loss of 2.08% corresponds to the loss of seven lattice water molecules per formula unit in the temperature range of 50–140°C (calculated mass loss for seven water molecules is 1.97%). The second weight loss of 3.62% corresponds to the loss of thirteen water molecules in the temperature range of 140–201°C (calculated mass loss for thirteen water molecules is 3.66%). Two major mass losses (27.22% and 7.77%) are observed in the temperature range of 207–598°C, due to the decomposition of the structure of the trinuclear iron cluster. The evolution of water molecules and carbon dioxide gas molecules are shown by the TGA / Mass curves, which are shown in blue and purple color, respectively in the Figure 4, left.

3.3d [Fe₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]₄
[SiW₁₂O₄₀]-18H₂O-2ClCH₂COOH (**regenerated 1**):
The bunch of crystals of **regenerated 1** was dried in

room temperature and then loaded in to thermogravimetric crucible for TGA/Mass analysis. The typical TGA curve has been divided into three groups. The first weight loss of 2.89% corresponds to the loss of eleven lattice water molecules per formula unit in the temperature range of 50–120°C (calculated mass loss for eleven water molecules is 3.01%). The water mass loss in this stage is significantly less than the expected 4.18% (from parent compound **1**, Figure 3(1)). This might be due to the removal of some water molecules (approximately four water molecules) during the drying process of the relevant crystals at room temperature. The second weight loss of 3.78% corresponds to the loss of fourteen water molecules in the temperature range of 120–181°C (calculated mass loss for fourteen water molecules is 3.83%). The major mass loss (35.02%) is observed in the temperature range of 181–506°C due to the decomposition of the pertinent cluster. The evolution of water molecules and carbon dioxide gas molecules

Figure 13. Thermal ellipsoidal plot of the asymmetric unit of compound **2** (50% probability). Hydrogen atoms, lattice water molecules and lattice chloroacetic acid were omitted for clarity.

are observed by the TGA/Mass curves which are shown in blue and purple color respectively in the Figure 4, right.

3.3e $[Cr_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4 [SiW_{12}O_{40}] \cdot 14H_2O \cdot 2ClCH_2COOH$ (**2**): TGA curve (Figure 5, left) of compound **2** is divided into three sets. The first weight loss of 2.63% corresponds to the loss of nine lattice water molecules per formula unit in the temperature range of 50–130°C (calculated mass loss for nine water molecules is 2.51%). The second weight loss of 3.51%, which corresponds to the loss of thirteen water molecules (five water molecules from lattice and eight water molecules from iron coordination sites), occurred in the temperature range of 130–220°C (calculated mass loss for fifteen water molecules is 3.62%). The major weight loss of 37.60% was observed in the temperature range of 220–670°C showing the decomposition of the concerned cluster. The evolution of water molecules and carbon dioxide gas molecules are evidenced by the TGA/Mass curves, which are shown in blue and purple color respectively in the Figure 5, left.

3.3f $[Cr_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4 [SiW_{12}O_{40}] \cdot 8H_2O \cdot 2ClCH_2COOH$ (**dehydrated 2**–85°C/135°C≡**2'**): TGA curve (Figure 5, right) of **2'** is divided into four portions. The first weight loss of 1.83%, which corresponds to the loss of six lattice water

molecules per formula unit, occurred in the temperature range of 50–130°C (calculated mass loss for six water molecules is 1.70%). The second weight loss of 3.87% corresponds to the loss of fourteen water molecules (eight water molecules from lattice and six water molecules from iron coordination sites) in the temperature range of 142–191°C (calculated mass loss for fourteen water molecules is 3.97%). Two major weight losses (28.71% and 11.54%) were observed in the temperature range of 240–1017°C due to decomposition of the cluster. The evolution of water molecules and carbon dioxide gas molecules are evidenced in the TGA/Mass curves that are shown in blue and purple colors respectively as shown in the Figure 5, right.

3.3g $[Cr_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4$

$[SiW_{12}O_{40}] \cdot 14H_2O \cdot 2ClCH_2COOH$ (**regenerated 2**):

The bunch of crystals of **regenerated 2** was dried at room temperature and then the powdered sample was loaded in thermogravimetric crucible for TGA/Mass analysis.

The typical TGA curve has been divided into four groups (Figure 6). The first weight loss of 3.02% corresponds to the loss of eleven lattice water molecules per formula unit in the temperature range of 50–100°C (calculated mass loss for eleven water molecules is 3.06%). The mass loss in **regenerated 2** (3.02% for eleven lattice water molecules) in this stage is approximately comparable to the mass loss obtained in parent compound **2** where the same was 2.63% for nine lattice water molecules). The second weight loss of 3.90% corresponds to the loss of fourteen water molecules in the temperature range of 100–190°C (calculated mass loss for fourteen water molecules is 3.90%). The major mass losses of 32.90% and 7.52%, observed in the temperature range of 190–1100°C, are due to the decomposition of the cluster structure. The evolution of water molecules and carbon dioxide gas molecules are confirmed by the TGA/Mass curves that are shown in blue and purple color respectively as shown in Figure 6.

3.4 X-ray crystallographic studies

3.4a $[Fe_3(\mu_3-O)(ClCH_2COO)_6(H_2O)_3]_4$

$[SiW_{12}O_{40}] \cdot 18H_2O \cdot 2ClCH_2COOH$ (**1**): Compound **1** crystallizes in monoclinic system with space group $C2/c$ and single crystal X-ray data, obtained at 298 K, are summarized in Table 1. In compound **1**, the asymmetric unit contains half part of Keggin anion (in which Si atom has half occupancy), two basic trinuclear iron-oxo macrocations, one lattice $ClCH_2COOH$ and nine non-coordinated (lattice) water molecules.

Figure 14. (a) C-H...O hydrogen bonding interactions in [Cr₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 14H₂O · 2ClCH₂COOH (**2**) along with relevant symmetry code. (b) O-H...O Hydrogen bonding interactions in compound **2**; (c) O-H...O hydrogen bonding interactions with relevant symmetry codes in compound **2**. Color code: W, yellow; Si, cyan; O, red; Cr, violet; Cl, light green; C, gray; H, purple; [Cr₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]¹⁺ cluster, violet polyhedra; C-H...O hydrogen bonding interactions, brown dotted lines; O-H...O hydrogen bonding interactions, green dotted lines.

Accordingly, compound **1** can be formulated as [Fe₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]₄[SiW₁₂O₄₀] · 18H₂O · 2ClCH₂COOH (**1**). The thermal ellipsoidal plot of the asymmetric unit of compound **1** is presented in Figure 7(a) (the solvent water molecules and lattice chloroacetic acid are not shown). The molecular structure of compound **1** is shown in Figure 7(b). The structure of Keggin anion can be described as four W₃O₁₃ groups surrounding the central hetero atom Si. Each W₃O₁₃ group is formed by three WO₆ octahedra sharing edges and having a common oxygen atom which is also shared by the central hetero atom. On the whole, the oxygen bonding modes in Keggin (POM) anion can be grouped into four different categories: (i) W-O_t (O_t is terminal oxygen) 1.694(7)

–1.716(7) Å; (ii) W – O(μ₂), 1.894(7) – 1.950(7) Å; (iii) W – O(μ₄), 2.333(6) – 2.360(6) Å; (iv) Si – O(μ₄), 1.625(6) – 1.627(6) Å.

The structure of [Fe₃(μ₃-O)(ClCH₂COO)₆(H₂O)₃]¹⁺ macrocation can be described as follows: Each ClCH₂COOH bridges two adjacent iron metal centers in bidentate fashion through carboxylate functionality and every two adjacent iron metal centers are bridged by two such bidentate ligands. Further, the terminal position of each metal center is occupied by a monodentate water molecule. All three iron metal ions (Fe³⁺) are bridged by a triply bridging oxygen atom. The geometry around each iron metal center is octahedral and the overall charge of each macrocation is +1. In the molecular struc-

Table 10. Geometrical parameters of the C–H···O hydrogen bonds (Å, °) involved in supramolecular network of compound $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2**). D=donor; A=acceptor.

D–H···A	d(D···H)	d(H···A)	d(D···A)	∠(DHA)
C6–H6B...O30#1	0.97	2.60	3.383(11)	137.9
C12–H12A...O9#2	0.97	2.90	3.472(9)	118.8
C12–H12A...O10#2	0.97	2.57	3.475(10)	155.9
C18–H18B...O17#3	0.97	2.62	3.494(12)	150.7
C18–H18A...O35	0.97	2.96	3.587(11)	123.3
C22–H22B...O4	0.97	2.41	3.382(9)	177.2
C22–H22A...O24	0.97	2.70	3.547(10)	145.7
C24–H24A...O8	0.97	2.95	3.527(10)	118.9
C24–H24A...O10	0.97	2.69	3.594(10)	154.4
C24–H24A...O18#4	0.97	2.59	3.374(10)	138.6
C24–H24A...O20#4	0.97	2.74	3.444(10)	130.3

Symmetry transformations used to generate equivalent atoms: #1 -x, 1-y, -z; #2 0.5-x, 0.5+y, 0.5-z; #3 -0.5+x, 0.5+y, z; #4 1-x, y, 0.5-z; #5 0.5-x, -0.5+y, 0.5-z; #6 0.5-x, 0.5-y, 1-z; #7 0.5+x, -0.5+y, z; #8 x, y, -1+z; #9 1+x, y, z; #10 -1+x, y, z; #11 x, y, 1+z.

Table 11. Geometrical parameters of the O–H···O hydrogen bonds (Å) involved in supramolecular network of compound $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2**).

O(7)–O(38)	2.912(7)	O(9)–O(48)	2.726(7)
O(13)–O(41)#5	2.992(7)	O(13)–O(43)#5	3.003(8)
O(15)–O(55)#6	3.069(10)	O(17)–O(33)#7	2.899(7)
O(17)–O(34)#7	2.890(7)	O(18)–O(32)#7	2.909(7)
O(22)–O(46)	2.900(8)	O(22)–O(58)	2.712(9)
O(27)–O(55)#8	2.715(11)	O(32)–O(54)#8	2.740(2)
O(32)–O(18)#3	2.909(7)	O(33)–O(17)#3	2.899(7)
O(34)–O(17)#3	2.890(7)	O(38)–O(56)	2.638(12)
O(41)–O(13)#2	2.992(7)	O(43)–O(13)#2	3.003(8)
O(43)–O(57)	2.677(13)	O(48)–O(58)	2.749(9)
O(53)–O(54)#9	2.680(5)	O(54)–O(53)#10	2.680(5)
O(54)–O(32)#11	2.740(2)	O(55)–O(27)#11	2.715(11)

Symmetric codes are already specified in the footnote of Table 10.

ture of compound **1**, four macrocations neutralize the charge of a Keggin anion $[\text{SiW}_{12}\text{O}_{40}]^{4-}$. Compound **1** contains two lattice ClCH_2COOH and eighteen lattice water molecules per formula unit. Out of these lattice water molecules, two types of water clusters, namely water trimer (water molecules O53, O56 and O58, O···O separation distance is in the range of 2.820(3) – 2.910(3) Å) and water dimer (water molecules O57 and O60, O···O separation distance is 3.030(5) Å) are observed in the crystal lattice of compound **1** (located in hydrophilic channels) as shown in Figure 8(a). Lattice ClCH_2COOH is considerably disordered and hence refined isotropically only. The overall structure is stabilized by the electrostatic interactions between $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]^{1+}$ macrocation and

$[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster anion. Further, the supramolecular C–H···O and O–H···O hydrogen bonding interactions offer extra stability in obtaining this ion pair system. The possible C–H···O and O–H···O hydrogen bonding interactions are shown in Figure 9. The relevant hydrogen bonding parameters (for C–H···O interactions, D···A distance is considered up to 3.6 Å, whereas for O–H···O interactions, the same is considered up to 3.1 Å) are presented in Tables 2 and 3.

3.5 Water exclusion (dehydration) and inclusion (regeneration) experiments in compound 1

Compound **1** originally contains eighteen lattice water molecules. When the crystals of compound **1** are heated

Figure 15. (a) C–H...O hydrogen bonding interactions in $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}]\cdot 8\text{H}_2\text{O}\cdot 2\text{ClCH}_2\text{COOH}$ (2') along with relevant symmetry code. (b) O–H...O Hydrogen bonding interactions in compound 2'. (c) O–H...O Hydrogen bonding interactions with relevant symmetry codes in compound 2'. Color code: W, yellow; O, red; Cr, violet; Cl, light green; C, gray; H, purple; $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]^{1+}$ cluster, violet polyhedra; $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ cluster, golden yellow polyhedra; C–H...O hydrogen bonding interactions, brown dotted lines; O–H...O hydrogen bonding interactions green dotted lines.

at 85°C and 135°C for the period of 3.5 hours, they lose considerable number of lattice water molecules and generate the dehydrated analogues $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}]\cdot 10\text{H}_2\text{O}\cdot 2\text{ClCH}_2\text{COOH}$ (1') and $[\text{Fe}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}]\cdot 8\text{H}_2\text{O}\cdot 2\text{ClCH}_2\text{COOH}$ (1''), respectively.

The dehydrated compounds 1' and 1'' are structurally characterized. The relevant crystal data and refinement parameters are given in the Table 1. Crystal structure of compounds 1' and 1'' contains ten and eight lattice water molecules per formula unit, respectively. The regular arrangement of lattice water molecules in hydrophilic channels (that include water dimer) of the crystal structure of compound 1' is depicted in Fig-

ure 8(b). The less number of hydrogen bonded lattice water molecules compared to those in the parent compound 1 is expected in a dehydrated crystal. We have chosen 135°C as maximum temperature for reversible water exclusion experiment because if we heat the crystals beyond this temperature range, the pertinent crystals do not diffract in the X-ray diffractometer. The metal coordinated water molecules are supposed to leave at high temperature resulting in the formation of polycrystalline material. The release of lattice water molecules from 1 to 1'' leads to the shrinkage of the unit cell volume gradually as: 1 ($V=17106(8) \text{ \AA}^3$) > 1' ($V=15084(7) \text{ \AA}^3$) > 1'' ($V=14941(11) \text{ \AA}^3$). The shrinkage of unit cell, occurred in the crystallographic *c* axis (see Table 1

Table 12. Geometrical parameters of the C–H···O hydrogen bonds (Å, °) involved in supramolecular network of compound $[\text{Cr}_3(\mu_3\text{-O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4[\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}$ (**2'**). D=donor; A=acceptor.

D–H···A	d(D···H)	d(H···A)	d(D···A)	∠(DHA)
C2–H2A....O8#1	0.97	2.58	3.386(14)	140.8
C2–H2A....O10#1	0.97	2.77	3.440(15)	127.0
C2–H2A....O18#2	0.97	3.04	3.592(15)	117.4
C2–H2B....O51#3	0.97	2.56	3.352(14)	138.3
C4–H4B....O16#2	0.97	2.47	3.444(15)	179.2
C4–H4B...O18#2	0.97	2.98	3.597(16)	122.6
C8–H8B....O7#4	0.97	2.56	3.429(17)	149.2
C10–H10A....O9#5	0.97	2.57	3.222(15)	124.7
C12–H12B....O6	0.97	2.75	3.391(14)	123.8
C12–H12B....O19	0.97	2.30	3.116(16)	140.8
C14–H14A....O13#6	0.97	2.52	3.392(17)	149.9
C18–H18A...O16	0.97	2.85	3.541(16)	129.1
C20–H20A....O40#7	0.97	2.57	3.500(2)	162.5
C22–H22A....O20#8	0.97	2.61	3.520(14)	157.1
C22–H22B...O27#9	0.97	2.75	3.337(14)	119.5
C24–H24B...O3#10	0.97	2.43	3.383(14)	168.6
C24–H24B...O42#7	0.97	2.81	3.443(16)	123.2
C24–H24A...O45#7	0.97	2.56	3.518(16)	171.5

Symmetry transformations used to generate equivalent atoms: #1 - 0.5+x, -0.5+y, z; #2 0.5-x, -0.5+y, 0.5-z; #3 x, -1+y, z; #4 1-x, y, 0.5-z; #5 0.5-x, 0.5-y, -z; #6 0.5-x, 1.5-y, -z; #7 -x, 1-y, -z; #8 0.5-x, 0.5+y, 0.5-z; #9 x, 1+y, z; #10 -0.5+x, 0.5+y, z; #11 0.5+x, -0.5+y, z; #12 x, y, -1+z; #13 x, y, 1+z; #14 -1+x, y, z; #15 1+x, y, z.

Table 13. Geometrical parameters of the O–H···O hydrogen bonds (Å) involved in supramolecular network of compound **dehydrated 2-85°**.

O(7)–O(51)#11	2.919(11)	O(7)–O(52)#11	3.006(11)
O(8)–O(38)#11	2.765(10)	O(9)–O(54)#5	3.073(13)
O(17)–O(22)#8	2.905(11)	O(19)–O(27)#8	2.736(10)
O(22)–O(17)#2	2.905(11)	O(22)–O(54)	2.717(12)
O(27)–O(19)#2	2.736(10)	O(27)–O(55)#2	2.793(13)
O(29)–O(48)#2	2.913(12)	O(32)–O(2)	2.856(11)
O(32)–O(43)#5	3.049(13)	O(32)–O(53)#12	2.540(2)
O(34)–O(2)	3.036(11)	O(38)–O(8)#10	2.765(10)
O(38)–O(54)#7	2.750(12)	O(48)–O(29)#8	2.913(12)
O(48)–O(55)	2.795(13)	O(51)–O(7)#10	2.919(11)
O(52)–O(7)#10	3.006(11)	O(53)–O(32)#13	2.540(2)
O(54)–O(56)#14	2.735(18)	O(55)–O(27)#8	2.793(13)
O(56)–O(54)#15	2.735(18)		

Symmetric codes are already specified in the footnote of Table 12.

for unit cell data), confirms that the water molecules accommodated in the crystallographic *c* axis are readily released from the crystal lattice.

The packing diagrams of compounds **1** and **1'** viewed down the crystallographic *b* axis are presented in Figure 10. For an assessment of the unit cell volume shrinkage, the corresponding internuclear distances

between two Keggin anion clusters (for compounds **1** and **1'**) along the *c* axis are measured and represented in Table 4. The C–H···O and O–H···O hydrogen bonding interactions, observed in the crystal structure of compound **1'**, are shown in Figure 11 and the relevant parameters are given in Tables 5 and 6, respectively.

Likewise, in compound **1'**, C–H...O and O–H...O hydrogen bonding interactions are shown in Figure 12 and appropriate parameters are presented in Tables 7 and 8, respectively. Crystals of compounds **1'** (heated compound) on exposure to water vapor at ambient condition for two weeks, get moistened without their dissolution and reverts back to the parent compound, **regenerated 1**. The color of the heated crystals (light red) became dark red after exposing to the water vapor. A single crystal with suitable size from this water regenerated bunch of the crystals has been mounted on the single crystal X-ray diffractometer for data collection. Re-entering of the water molecules in the crystal lattice leads to expansion of the unit cell volume as: **1'** ($V = 15084.00 \text{ \AA}^3$) < **regenerated 1** ($V = 17039 \text{ \AA}^3$). The obtained cell data for compound **regenerated 1** exactly match to that of parent compound **1**; however, we have not succeeded to solve the crystal structure of **regenerated 1** because of the poor quality of reflection data.

Dark green colored crystals of compound **2** were grown from an acidic aqueous medium containing $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, ClCH_2COOH and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Compound **2** crystallizes in monoclinic system with space group $C2/c$ and single crystal X-ray data obtained at 298 K are summarized in Table 9. The pertinent asymmetric unit contains half part of Keggin anion (in which Si atom is in half occupancy), two basic trinuclear chromium-oxo macrocations, one lattice ClCH_2COOH and seven non-coordinated water molecules. Thermal ellipsoidal plot of compound $\text{Cr}_3(\mu_3 - \text{O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4 [\text{SiW}_{12}\text{O}_{40}] \cdot 14\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}(\mathbf{2})$ with atom labeling scheme is presented in Figure 13.

Compound **2** is isostructural to compound **1** and hence coordination bonding environments around metal centers are similar. In the crystal structure, two non-coordinated ClCH_2COOH were located in the lattice and those were refined isotropically due to considerable disorder. Crystal structure of compound **2** contains fourteen lattice water molecules. A water dimer, exclusively formed by lattice water molecules, O53 and O54, is crystallographically characterized. The O–H...O hydrogen bonding distance is $2.68(5) \text{ \AA}$. Overall, C–H...O and O–H...O hydrogen bonding interactions are shown in Figure 14. The relevant hydrogen bonding parameters are presented in Tables 10 and 11, respectively.

3.7 Water exclusion (dehydration) and inclusion (regeneration) experiments in compound 2

The similar heating experiments were repeated for compound **2** as performed with compound **1**. Heating the bunch of crystals of compound **2** at 85°C and 135°C for the period of 3.5 hours loses considerable number of lattice water molecules and generate corresponding dehydrated analogues $[\text{Cr}_3(\mu_3 - \text{O})(\text{ClCH}_2\text{COO})_6(\text{H}_2\text{O})_3]_4 [\text{SiW}_{12}\text{O}_{40}] \cdot 8\text{H}_2\text{O} \cdot 2\text{ClCH}_2\text{COOH}(\mathbf{2}')$.

The dehydrated compounds **dehydrated 2-85° (2')** and **dehydrated 2-135° (2')** were structurally characterized and crystal data and refinement parameters are presented in the Table 9. The C–H...O and O–H...O hydrogen bonding interactions observed in the crystal structure of compound **2'** is shown in Figure 15 and the relevant hydrogen bonding parameters are given in Tables 12 and 13, respectively. The release of lattice water molecules (water exclusion) from **2** to **2'** leads to the shrinkage of the unit cell volume as follows: **2** ($V=16907(16) \text{ \AA}^3$) > **2'** ($V=14936(5) \text{ \AA}^3$).

When dehydrated compound **2'** is exposed to water vapor for the period of one week, it regenerates the parent compound **2** (**regenerated 2**). The unit cell parameter of water regenerated compound (**regenerated 2**) is as follows: $a = 30.319 \text{ \AA}$, $b = 17.655 \text{ \AA}$, $c = 32.771 \text{ \AA}$ and $\beta = 102.588^\circ$, $V = 17120.53 \text{ \AA}^3$. The obtained unit cell volume exactly matches to the parent compound **2**, which clearly indicates the expansion of unit cell as, **dehydrated 2'** ($V=14936(5) \text{ \AA}^3$) < **regenerated 2** ($V = 17120.53 \text{ \AA}^3$). Although we could obtain the unit cell parameters of the water regenerated compound by X-ray diffractometry, the corresponding structure could not be solved because of the poor quality of reflection data.

4. Conclusions

In summary, we have synthesized compounds **1** and **2** and we have generated their dehydrated forms. We have characterized them unambiguously by single crystal X-ray structure determination. The rehydrated compounds have been characterized by determination of their unit cell parameters. The solid state properties of compound **1** and **1'** are described in the view of exclusion (shrinkage of unit cell volume) and inclusion (expansion of unit cell volume) of water molecules in the crystal lattice. This phenomenon can be described as breathing of the crystals. We report here the first example of 'ionic crystal' in which macrocation/polyoxometalate ratio is 4:1, without the presence of alkali metal ions.

To the best of our knowledge, 4:1 is the highest trinuclear macrocation/polyoxoanion ratio observed in the crystal structure. The supramolecular O–H $\cdots$ O and C–H $\cdots$ O hydrogen bonding interactions of all the compounds are discussed elaborately. The adsorption and desorption properties of trinuclear macrocation and polyoxometalate based ion pair complexes systems will be an interesting study. The macrocations with similar coordination functionalities will be prepared and corresponding adsorption properties of ionic crystal and their related studies will be performed in near future.

Supplementary Information (SI)

CCDC 1541077, CCDC 1541078, CCDC 1541084, CCDC 1541100 and CCDC 1541105 contain the supplementary crystallographic data for compounds **1**, **1'**, **1''**, **2** and **2'**, respectively. Relevant crystal data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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