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Sodium ion assisted molecular self-assembly in a class of Schiff-base copper(II) complexes

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ABSTRACT

Syntheses, characterization and crystal structures of three new sodium based heterotrinuclear ionic clusters $[(CuL1)_2Na(ClO_4\text{-}O,O')(OH_2)]\cdot C_8H_8O_2$ (**1**), $[(CuL2)_2Na(ClO_4\text{-}O,O')]$ (**2**) and $[\{Cu(L3)_2\}_2Na]^+\cdot ClO_4^-$ (**3**) derived from three different Schiff bases (L1 = 1:2 condensation of 1,2-propane diamine and o-hydroxy acetophenone, L2 = 1:2 condensation of 1,2-propane diamine and 2-hydroxy-5-methoxy acetophenone and L3 = 1:1 condensation of 2-amino pyridine and 3-ethoxy salicylaldehyde) are reported herein. The crystal structure analysis reveals that the square-planar Cu–ligand complexes act as building block for the trinuclear complex in which Na^+ ion guides the orientation of Cu(II) Schiff-base complexes into a scissor like architecture in **1** and **2**. The unique assembling feature of Na^+ ion is also evident in complex **3** where even in the presence of a widely different Schiff-base ligand, Na^+ guides two $Cu(II)(L3)_2$ complexes to assemble around it in a crown ether like environment. In complexes **1** and **2** the square planar metal coordination provide suitable sites for chelate ring π···π interaction and Cu···π interaction which ensures columnar assembly of trinuclear units at the supramolecular level. The present study reveals the unique nature of the self-assembly of square-planar Cu(II) Schiff-base complexes around Na^+.

1. Introduction

Supramolecular chemistry [1–9], the chemistry of molecular systems beyond individual molecules is highly dependent on the understanding of the molecular self-assembly. The controlled organization of simple molecular building blocks is governed by hierarchy of forces involving covalent, coordinative and various weak forces such as hydrogen bonding [10,11], π···π interaction [12–16], C–H···π interaction [17,18], metal···π interaction [19,20], etc. In the resultant self-assembled super structure there is often a compromise between various strong and weak forces. The weak forces in many cases influence the structure even in the presence of strong forces due to simultaneous cooperative effect among themselves.

In the design of metal–ligand complexes the choice of metal ions and the information encoded in the ligands are intelligently utilized. There are many factors behind the choice of the ligand such as its dimensionality, connectivities, shape, size, conformation, chirality, etc. The degree of flexibility of the ligand bearing the donor atoms is an important consideration to match the shape of the coordination sphere of the target species. In crystal engineering one often rely on certain robust self-assembly features such as hydrogen bonding synthon [21], recurrent π-stacking motifs which are generally relied in engineering of organic crystal structures. In the design of coordination complexes additional information taken into account is the stereochemical information encoded in the metal ions. In this context, with Schiff base complexes we have taken the standard synthetic approach of designing Schiff base ligands with proper sites for coordination bond as well as other weak forces such as π···π and CH···π interaction by the condensation of amines with hydroxylated aldehydes. Metal salicylaldimines with phenoxo groups in the 2 and 2′ positions are a fascinating group of ligands that can coordinate with not only p- and d-block metal elements but also alkali-metal ions. These alkali-metal complexes of metal salicylaldimines are important in small-molecule activation [22], electron storage [23,24], and the carrying of polar organometallics [25,26]. Moreover, they can coordinate with a metal ion of suitable size and form a sandwich structure of ion complexes between two sets of Schiff base oxygen atoms [27–29]. In a very interesting study Sui et al. have synthesized and reported two novel homochiral trinuclear sodium ionic

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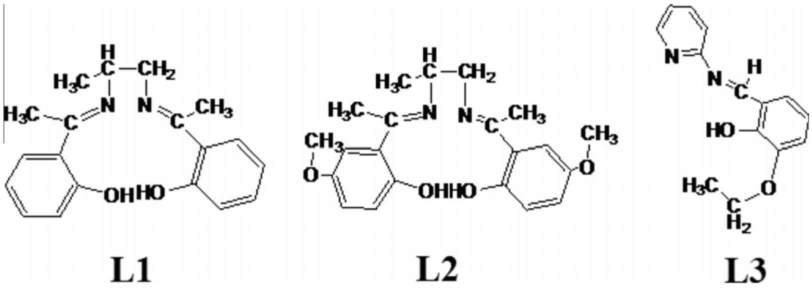

Scheme 1.

clusters with nickel salicylaldimines as host units which have extremely rare properties like ferroelectricity [28].

Here, we report three trinuclear complexes of Cu-Schiff bases and sodium namely $[(CuL1)_2Na(ClO_4\text{-}O,O')(OH_2)]\cdot C_8H_8O_2$ (**1**), $[(CuL2)_2Na(ClO_4\text{-}O,O')]$ (**2**) and $[\{Cu(L3)_2\}_2Na]^+\cdot ClO_4^-$ (**3**). Structures of ligands L1, L2 and L3 are shown in Scheme 1. L1 and L2 are deprotonated Schiff bases prepared by the 1:2 condensation of 1,2-propane diamine and o-hydroxy acetophenone for L1, and 1,2-propane diamine and 2-hydroxy-5-methoxy acetophenone for L2. Ligand L3 is similarly prepared in a 1:1 condensation of 2-amino pyridine and 3-ethoxy salicylaldehyde. The crystal structure analysis reveals that the square-planar Cu–ligand complexes act as building block for a trinuclear complex in which Na^+ ion guides the orientation of Cu(II) Schiff-base complexes into a scissor like architecture in **1** and **2**. The unique assembling feature of Na^+ ion is also evident in complex **3** where even in the presence of a widely different Schiff-base ligand, Na^+ guides two $Cu(II)(L3)_2$ complexes to assemble around it in a crown ether like environment.

2. Experimental

2.1. Materials and physical measurements

All reagents and solvents for the synthesis and analysis were commercially available and used as received without further purification. IR spectra were recorded as KBr pellets within the range 4000–400 cm^{-1} on a Perkin-Elmer Spectrum RXI FTIR Spectrometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid elemental analyzer.

2.2. Syntheses

*2.2.1. Synthesis of the complexes $[(CuL1)_2Na(ClO_4\text{-}O,O')(OH_2)]\cdot C_8H_8O_2$ (**1**) and $[(CuL2)_2Na(ClO_4\text{-}O,O')]$ (**2**)*

Caution! Perchlorates complexes of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

To a solution of *o*-hydroxy acetophenone (0.272 g, 2 mmol) in 20 mL of methanol was added 1,2-propane diamine (0.741 g, 1 mmol), and the resulting mixture was heated under reflux for 3 h. A solution of $Cu(AcO)_2\cdot H_2O$ (0.199 g, 1 mmol) and $NaClO_4$ (0.366 g, 3 mmol) in 40 mL of methanol was then added, and the mixture was refluxed for another 3 h to give a deep-red solution and black block-shaped single crystals of **1** were obtained after 3 days. Compound **2** was obtained as black block shaped crystals by a method similar to that of **1**, except that 2-hydroxy-5-methoxy acetophenone (0.332 g, 2 mmol) was used.

*Complex **1**:* Yield ca. 70%. *Anal.* Calc. for $C_{46}H_{48}N_4O_{11}Cu_2NaCl$: C, 54.2; H, 4.7; N, 5.5. Found: C, 54.8; H, 4.8; N, 6.0%. IR (KBr pellets, cm^{-1}): ν_{as}(water) 3432; ν(C=N) 1633; $\nu(ClO_4^-)$ 1144, 1111, 1088.

Table 1
Crystallographic data for **1**–**3**.

Crystal data			
Formula	$C_{38}H_{40}ClCu_2N_4NaO_9$, $C_8H_8O_2$	$C_{42}H_{48}ClCu_2N_4NaO_{12}$	$C_{56}H_{52}Cu_2N_8NaO_8$, ClO_4
Formula weight	1018.40	986.38	1214.60
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2/n$ (No. 13)	$P2/c$ (No. 13)
a, b, c (Å)	14.2170(6), 22.9540(6), 16.046(1)	12.1043(6), 11.5222(6), 16.0902(10)	8.4593(3), 15.7526(4), 20.8509(5)
α, β, γ (°)	90, 118.456(6), 90	90, 106.725(6), 90	90, 103.002(3), 90
V ($Å^3$)	4603.8(5)	2149.1(2)	2707.27(14)
Z	4	2	2
D_{calc} ($g\ cm^{-3}$)	1.469	1.524	1.490
μ(Mo Kα) (mm^{-1})	1.056	2.463	2.100
$F(000)$	2104	1020	1252
Crystal size (mm)	0.12 × 0.18 × 0.27	0.12 × 0.19 × 0.25	0.14 × 0.19 × 0.28
Data collection			
T (K)	293	293	293
Radiation (Å)	(Mo Kα) 0.71073	(Cu Kα) 1.54184	(Cu Kα) 1.54184
θ (°)	1.6–25.1	3.8–67.2	3.5–70.7
Dataset	−16:16; −22:27; −19:16	−14:14; −13:9; −19:17	−7:10; −18:19; −25:25
Total, unique data, R_{int}	16746, 8244, 0.030	7777, 3860, 0.035	10047, 5211, 0.056
Observed data [$I > 2.0\sigma(I)$]	5894	2828	3303
Refinement			
N_{ref}, N_{par}	8244, 593	3860, 285	4947, 364
R, wR_2, S	0.0970, 0.3146, 1.20	0.0743, 0.2158, 1.04	0.0511, 0.1450, 1.03
w	$1/[\backslash s^2(F_o^2)+(0.2000P)^2]$ where $P=(F_o^2+2F_c^2)/3$	$1/[\backslash s^2(F_o^2)+(0.0984P)^2+2.3473P]$ where $P=(F_o^2+2F_c^2)/3$	$1/[\backslash s^2(F_o^2)+(0.0493P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Maximum and average shift/error	0.00, 0.00	0.00, 0.00	0.00, 0.00
Minimum and maximum residual density (e $Å^{-3}$)	−1.54, 1.74	−0.64, 0.42	−0.26, 0.28

Table 2
Selected bond distances (Å) and bond angles (°) in **1–3**.

Complex **1**		Complex **2**		Complex **3**	
Bond distances (Å)					
Cu1–O1	1.893(5)	Cu1–O1	1.889(4)	Cu1–O1	1.900(2)
Cu1–O2	1.883(5)	Cu1–O2	1.883(4)	Cu1–O2	1.906(3)
Cu1–N1	1.931(6)	Cu1–N1	1.933(5)	Cu1–N1	1.965(3)
Cu1–N2	1.935(6)	Cu1–N2	1.939(5)	Cu1–N3	1.968(3)
Cu2–O3	1.885(4)	Na1–O1	2.341(4)	Na1–O2_b	2.311(2)
Cu2–O4	1.885(5)	Na1–O2	2.416(3)	Na1–O4_b	2.666(4)
Cu2–N3	1.941(5)	Na1–O1_a	2.341(4)	Na1–O4	2.666(4)
Cu2–N4	1.941(5)	Na1–O2_a	2.416(3)	Na1–O1	2.421(3)
Na1–O1	2.385(5)	Na1–O100	2.563(9)	Na1–O2	2.311(2)
Na1–O2	2.389(5)	Na1–O100_a	2.563(9)	Na1–O1_b	2.421(3)
Na1–O3	2.379(5)				
Na1–O4	2.390(6)				
Na1–O9	2.423(9)				
Na1–O10	2.513(9)				
Na1–O1W	2.600(2)				
Bond angles (°)					
O1–Cu1–O2	85.6(2)	O1–Cu1–O2	87.6(2)	O1–Cu1–O2	87.4(1)
O1–Cu1–N1	174.6(2)	O1–Cu1–N1	93.0(2)	O1–Cu1–N1	93.7(1)
O1–Cu1–N2	93.8(2)	O1–Cu1–N2	176.1(2)	O1–Cu1–N3	151.8(1)
O2–Cu1–N1	93.1(2)	O2–Cu1–N1	176.6(2)	O2–Cu1–N1	149.5(1)
O2–Cu1–N2	177.0(2)	O2–Cu1–N2	92.5(2)	O2–Cu1–N3	91.6(1)
N1–Cu1–N2	87.7(2)	N1–Cu1–N2	87.2(2)	N1–Cu1–N3	101.2(1)
O3–Cu2–O4	87.5(2)	O1–Na1–O2	66.6(1)	O1–Na1–O4	129.3(8)
O3–Cu2–N3	93.3(2)	O1–Na1–O100	111.1(2)	O1–Na1–O2	67.4(1)
O3–Cu2–N4	176.0(2)	O1–Na1–O1_a	90.3(2)	O2–Na1–O4_b	106.4(1)
O4–Cu2–N3	173.3(2)	O1–Na1–O2_a	100.3(1)	O1_b–Na1–O4	121.4(9)
O4–Cu2–N4	92.7(2)	O1–Na1–O100_a	158.3(2)	O2_b–Na1–O4	106.4(1)
N3–Cu2–N4	87.1(2)	O2–Na1–O100	92.0(2)	O4–Na1–O4_b	77.9(1)
Cu1–O1–Na1	96.1(2)	O1_a–Na1–O2	100.3(1)	O1_b–Na1–O2_b	67.4(1)
Cu1–O2–Na1	96.2(2)	O2–Na1–O2_a	162.1(2)	O1_b–Na1–O4_b	129.3(8)
Cu2–O3–Na1	100.2(2)	O2–Na1–O100_a	104.4(2)	O2_b–Na1–O4_b	62.0(1)
Cu2–O4–Na1	99.8(2)	O1_a–Na1–O100	158.3(2)	O1–Na1–O4_b	121.4(9)
O1–Na1–O1W	91.0(3)	O2_a–Na1–O100	104.4(2)	O2–Na1–O4	62.0(1)
O1–Na1–O2	65.0(2)	O100–Na1–O100_a	48.1(3)	O1_b–Na1–O2	124.2(1)
O1–Na1–O3	148.8(2)	O1_a–Na1–O2_a	66.6(1)	O2–Na1–O2_b	166.2(2)
O1–Na1–O4	94.4(2)	O1_a–Na1–O100_a	111.1(2)	O1–Na1–O1_b	84.1(1)
O1–Na1–O9	108.0(2)	O2_a–Na1–O100_a	92.0(2)	O1–Na1–O2_b	124.2(1)
O1–Na1–O10	103.6(2)	Cu1–O1–Na1	100.2(2)	Cu1–O1–Na1	99.2(1)
O2–Na1–O3	91.0(2)	a = 3/2 − *x*, *y*, 1/2 − *z*		b = 1 − *x*, *y*, 1/2 − *z*	
O2–Na1–O4	93.7(2)				
O2–Na1–O9	131.3(3)				
O2–Na1–O10	168.5(2)				
O3–Na1–O4	66.3(2)				
O3–Na1–O9	102.8(2)				
O3–Na1–O10	99.1(2)				
O4–Na1–O9	134.7(3)				
O4–Na1–O10	85.5(2)				
O9–Na1–O10	51.6(3)				
O1W–Na1–O2	91.0(5)				
O1W–Na1–O3	110.0(4)				
O1W–Na1–O4	174.0(4)				
O1W–Na1–O9	40.3(6)				
O1W–Na1–O10	90.5(6)				

*Complex **2**:* Yield ca. 60%. *Anal.* Calc. for $C_{42}H_{48}N_4O_{12}Cu_2NaCl$: C, 51.1; H, 4.86; N, 5.7. Found: C, 51.4; H, 4.9; N, 5.9%. IR (KBr pellets, cm^{-1}): ν(C=N) 1591; $\nu(ClO_4^-)$ 1110, 1072, 1043, 1025.

2.2.2. Synthesis of the complex $[\{Cu(L3)_2\}_2Na]^+\cdot ClO_4^-$ (3)

To a solution of 3-ethoxy salicylaldehyde (0.332 g, 2 mmol) in 20 mL of methanol was added 2-amino pyridine (0.188 g, 2 mmol), and the resulting mixture was heated under reflux for 3 h. A solution of $Cu(AcO)_2\cdot H_2O$ (0.199 g, 1 mmol) and $NaClO_4$ (0.366 g, 3 mmol) in 40 mL of methanol was then added, and the mixture was refluxed for another 3 h to give a deep-red solution and black block-shaped single crystals of **3** were obtained after 2 days.

*Complex **3**:* Yield ca. 60%. *Anal.* Calc. for $C_{56}H_{52}N_8O_{12}Cu_2NaCl$: C, 55.3; H, 4.3; N, 9.2. Found: C, 56.1; H, 4.9; N, 8.9%. IR (KBr pellets, cm^{-1}): ν(C=N) 1606; $\nu(ClO_4^-)$ 1091.

2.3. Crystal structure determinations of 1–3

Crystal data for all the three compounds are given in Table 1. The bond distances and bond angles for all the three compounds are given in Table 2. 8244, 3860 and 5211-independent data for **1**, **2** and **3**, respectively, were collected on a Bruker Smart Apex II CCD Area Detector equipped with a graphite monochromator Mo Kα radiation ($\lambda = 0.71073$ Å). Data collections were carried out using Bruker Apex2 software for all the compounds [30]. Multiscan absorption corrections were carried out using SADABS [31] in all the cases. The structure of the complex was solved by direct methods with SHELXL [32] for compounds **1**, **2** and **3**, respectively. The structure refinements were also performed by full-matrix least squares based on F^2 with SHELXL [32] in all the cases. All non-hydrogen atoms were refined anisotropically. The C-bound H atoms were constrained to ideal geometry and were included in the refinement in the riding model approximation. Data for molecular geometry, intermolecular interactions and pictures were produced using PLATON-2003 [33] and ORTEP3.2 [34] programs.

3. Results and discussion

3.1. Synthesis of the complexes

All three Schiff base ligands and their complexes were synthesized in a very facile and essentially identical way. The respective diamines and the carbonyl compounds were mixed in stoichiometric ratios 1:2 for L1 and L2 and 1:1 for L3, respectively, in methanol and refluxed. The methanolic solution of copper acetate monohydrate and sodium perchlorate was added to the methanolic solution of the Schiff base ligand prepared and refluxed for 3 h and the desired complexes were separated after a few days.

The characteristics of the ligands as well as the substrates are crucial in molecular recognition, because the selective bonding between the ligand and the substrate originates from this information. This information is literally stored in the ligand and is read out by the substrate. This characteristic information helps to define the stability and selectivity of the complexes. Ion–molecule complexes are usually stronger than the molecule–molecule complexes, because of the strong interaction between ions and the molecule.

3.2. IR spectroscopy

The first two complexes show two broad and hump bands at 3432 cm^{-1} for complex **1** respectively. These bands can be attributed to the ν_{H_2O} frequency. The third complex does not show this type of band at this region as water molecule is not present in this complex. The band corresponding to the azomethine (C=N) group is distinct in all the three complexes; it occurs at 1633, 1591, and 1606 cm^{-1} for complexes **1**, **2**, and **3**, respectively. Concerning the ClO_4^- anions, the ν_3 mode occurs at 1144, 1111, 1088 cm^{-1} for complex **1** and 1110, 1072, 1043, 1025 cm^{-1} for complex **2**, respectively. These bands are extremely broadened and divided into many parts suggesting that these anions are coordinated to the central sodium atoms as substantiated by the crystal structures. There is no splitting of the band at 1091 cm^{-1} for complex **3** is indicative for the presence of non coordinated perchlorate ion.

3.3. Description of the structures

3.3.1. Complex *1*

X-ray crystallographic analysis reveals a trinuclear complex in the asymmetric unit containing two Cu(II) centers and a Na^+ center (Fig. 1). There is also a *o*-hydroxy acetophenone molecule in the asymmetric unit. Two Cu(II) centers have square planar coordination geometry with the hepta-coordinated sodium in between. The tetra dentate Schiff base ligand L1 binds to Cu(II) centers producing square planar Cu(II)L1 complexes. The interesting aspect of the complexation phenomena is that these Cu(II)L1 units act as building block for a higher level complexation in which two such Cu(II)L1 units are organized around a Na^+ ion giving a open scissor like topology of the trinuclear complex (Fig. 1). In the Cu(II)L1 units, the ligand L1 encircles the Cu(II) center by binding it with two adjacent N atoms of the amine group in one side and by two hydroxyl oxygen atoms on the other side. The two long edges of the square plane of the Cu(II) coordination environment is thus asymmetric with three methyl groups arranged on one of the sides making it sterically congested. On the other side of the square plane two hydroxyl oxygen atoms are arranged and these two oxygen atoms simultaneously act as the binding sites to the Na^+ ion. Na^+ ion thus plays the role of a mediator to organize two Cu(II)L1 units around it. Due to the stereo electronic disposition of the Na^+ ion, two Cu(II)L1 units are slightly rotated with respect to each other in the outer coordination sphere of the Na^+ ion. This gives rise to the open scissor topology of the whole trinuclear system. All the terminal methyl groups of the two Cu(II)L1 units also facilitate the open scissor topology due to relative rotation of the two Cu(II)L1 units with respect to each other to reduce steric congestion. Due to one sided arrangement of the two Cu(II)L1 units around the Na^+ ion in which Na^+ ion spends four of its coordination, the other side of the coordination sphere of the Na^+ ion is relatively unhindered. A perchlorate anion and a water molecule balance the charge and saturate Na^+ coordination by double coordination through O9 and O10 of perchlorate anion from this unhindered side. It is interesting to observe that though Cu(II)L1 neutral complexes could be self-assembled into a hypothetical crystal structure in the absence of Na^+ ion, the presence of Na^+ ion has made the present complex to accept perchlorate ions for charge balancing.

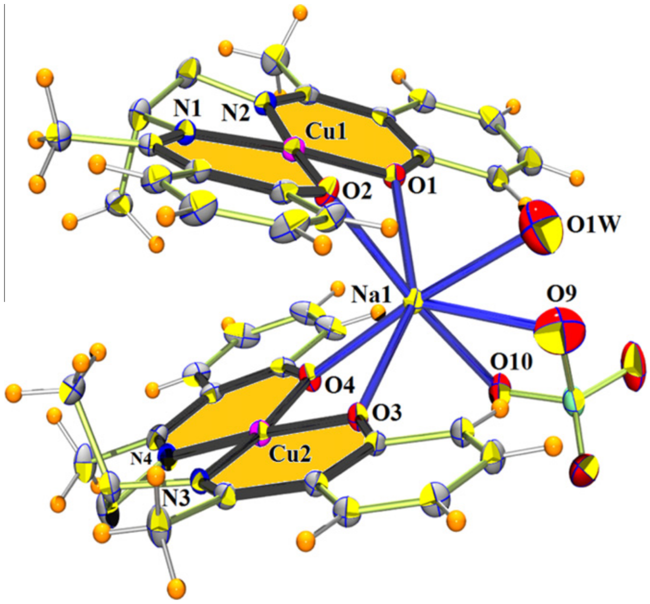

Fig. 1. ORTEP diagram of complex **1** (30% ellipsoidal probability) with atom numbering scheme. There also exists one acetophenone molecule in the asymmetric unit (not shown here for clarity).

In the Cu(II)L1 units the maximum and minimum Cu–N bond distances are 1.931(6) and 1.941(5) Å, respectively, and the Cu–O bond distances are in the range 1.883(5)–1.893(5) Å (Table 2). The Na–O (hydroxyl) bond distances fall in the range 2.379(5)–2.390(6) Å [28,29]. Two Na–O (perchlorate) distances are 2.423(9) and 2.513(9) Å, respectively. The Na–O1W distance is 2.600(2) Å.

The supramolecular assembly of the trinuclear complexes is built up by weak π-interaction involving not only the ligand phenyl rings but also, more interestingly, the Cu(II)L1 chelate rings (shaded orange[1] in Fig. 1). The π···π and C–H···π interaction involving the ligand phenyl ring and the metal-chelate ring is responsible for columnar assembly (Fig. 2) of the successive trinuclear units along the crystallographic *c*-axis. The square planar nature of the Cu(II) coordination environment facilitates the π···π interaction (for details, see Table 3) between the metal-chelate rings of adjacent trinuclear units which are centrosymmetrically

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[1] For interpretation of the references to color in Figs. 1 and 4, the reader is referred to the web version of this article.

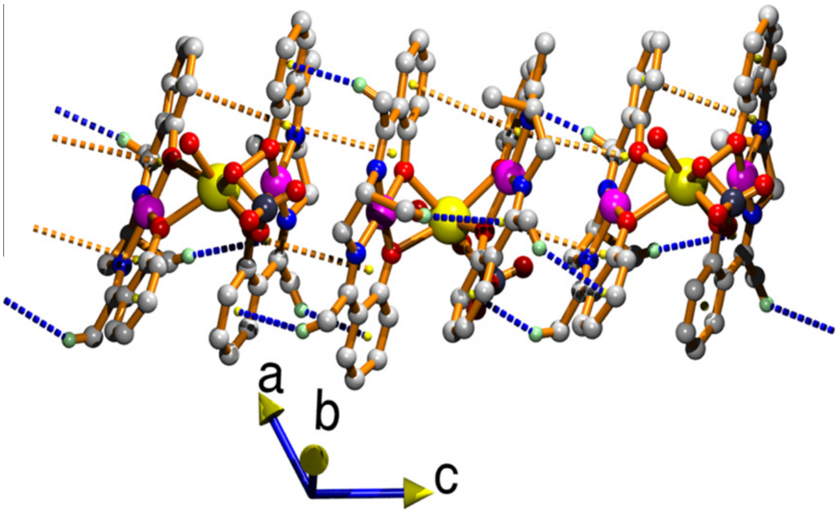

Fig. 2. One dimensional supramolecular assembly of molecular complexes along the crystallographic c-axis. CH···π interaction is denoted by blue dotted lines and the π···π interaction by orange dotted lines. (Color online.)

Table 3
Geometrical parameters (Å, °) for the face to face π-stacking interactions involving metal-chelate rings and phenyl rings in compounds **1–3**.

Complexes	Ring(i) → ring(j)	Dihedral angle (i,j) (°)	Slip angle (i,j) (°)	Distance between ring-centroid(i) and ring-centroid(j) (Å)	Perpendicular distance of ring(i) centroid and ring(j) plane (Å)
1	R(3) → R(6)^{i}	1.58	19.12	3.671(3)	3.497
	R(4) → R(5)^{i}	5.12	19.60	3.743(3)	3.601
	R(5) → R(8)^{ii}	26.40	5.34	3.954(4)	3.658
	(i) = $X, 3/2 - Y, -1/2 + Z$; (ii) X, Y, Z				
	R(3) → Cu1–O1–C1–C6–C7–N2; R(4) → Cu1–O2–C19–C14–C12–N1; R(5) → Cu2–O3–C20–C25–C26–N3; R(6) → Cu2–O4–C38–C33–C31–N4; R(8) → C14–C15–C16–C17–C18–C19				
2	R(2) → R(5)^{i}	7.79	17.56	3.795(3)	3.430
	R(3) → R(3)^{i}	0.00	19.44	3.721(3)	3.508
	(i) = $1 - X, -Y, -Z$				
	R(2) → Cu1–O1–C6–C5–C8–N1; R(3) → Cu1–O2–C16–C15–C13–N2; R(5) → C15–C16–C17–C18–C19–C20				
3	R(3) → R(4)^{i}	25.38	17.19	3.758(4)	3.425
	R(5) → R(5)^{ii}	5.96	26.68	3.813(3)	3.406
	(i) = X, Y, Z; (ii) = $1 - X, Y, 1/2 - Z$				
	R(3) → N2–C1–C2–C3–C4–C5; R(4) → N4–C17–C22–C21–C20–C19; R(5) → C8–C9–C10–C11–C12–C13				

Table 4
Geometrical parameters (Å, °) for the C–H···π interactions involving metal-chelate rings and phenyl rings in compounds **1** and **2**.

Complexes	X–H → ring(j)	X–H···R(i) angle (°)	Distance between hydrogen atom and ring-centroid(j) (Å)	X···centroid ring(j) distance (Å)
1	C8–H8C → R(10)^{i}	146	2.75	3.590(11)
	C13–H13C → R(9)^{i}	135	2.74	3.483(12)
	C27–H27A → R(8)^{ii}	131	3.00	3.704(10)
	C32–H31C → R(7)^{ii}	137	2.75	3.512(13)
	(i) = $X, 3/2 - Y, -1/2 + Z$; (ii) = $X, 3/2 - Y, 1/2 + Z$			
	R(7) → C1–C2–C3–C4–C5–C6; R(8) → C14–C15–C16–C17–C18–C19; R(9) → C20–C21–C22–C23–C24–C25; R(10) → C33–C34–C35–C36–C37–C38			
2	C11–H11B → R(4)^{i}	141	2.95	3.749(10)
	(i) = $3/2 - X, Y, 1/2 - Z$			
	R(4) → C1–C2–C3–C4–C5–C6			

arranged. The methyl group of the acetophenone part of the ligand is involved in C–H···π interaction (Table 4) which acts in unison with the chelate ring π···π interaction. The π···π interaction involving metal chelate rings have been explored only in recent years [16] and detailed nature of this type of interaction is yet to be ascertained. The present complex is an example which shows that square planar metal coordination may provide suitable sites for chelate ring π···π interaction.

An interesting side of the crystal structure is the presence of orthohydroxy acetophenone molecules. These molecules form hydrogen bonded dimers with $R_2^2(10)$ hydrogen bonded motif in Etter's graph [35] notation (Fig. 3). These dimers are intercalated between supramolecular columns of trinuclear units formed through π-interaction. The acetophenone dimers are sandwiched among the $-CH_3$ groups from both sides and interact by CH–π interaction with the methyl group attached to the 1,2-propane diamine part of the ligand L1. The three dimensional packing arrangement of the complexes inside the crystal is depicted in Fig. S1 (see Supplementary material).

3.3.2. Complex 2

X-ray crystallographic analysis reveals a similar trinuclear complex with two Cu(II) centers and a Na$^+$ center in complex **2** as that was found in **1** (Fig. 4). Unlike **1**, here the Na$^+$ ion (Na1) occupies the center of inversion and two Cu(II)L2 building blocks that are organized into a similar scissor like topology are symmetric counter parts of each other. Two Cu(II) centers have square planar coordination geometry with the tetradentate Schiff base ligand L2 encircling Cu(II) ions by two of the amine nitrogen atoms (N1, N2) and two hydroxyl oxygen atoms (O1, O2) producing six membered chelate rings (shaded orange in Fig. 4). Instead of hepta coordinated sodium that was observed in **1**, in **2** the Na^+ ion is hexa-coordinated. Due to much more torsion (than that was found in **1**) between the scissor arms consisting of Cu(II)L2 complexes, no

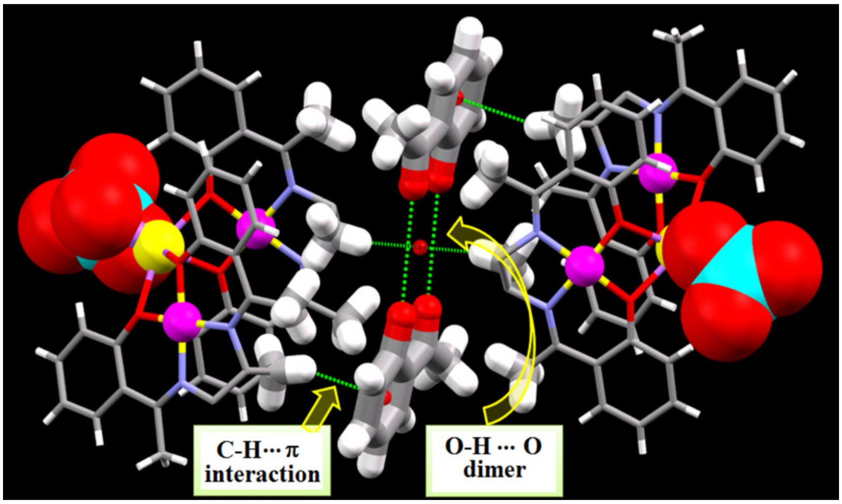

Fig. 3. The hydrogen bonded acetophenone dimers are sandwiched between successive supramolecular columns of trinuclear units and are surrounded by the terminal methyl groups of ligand L1.

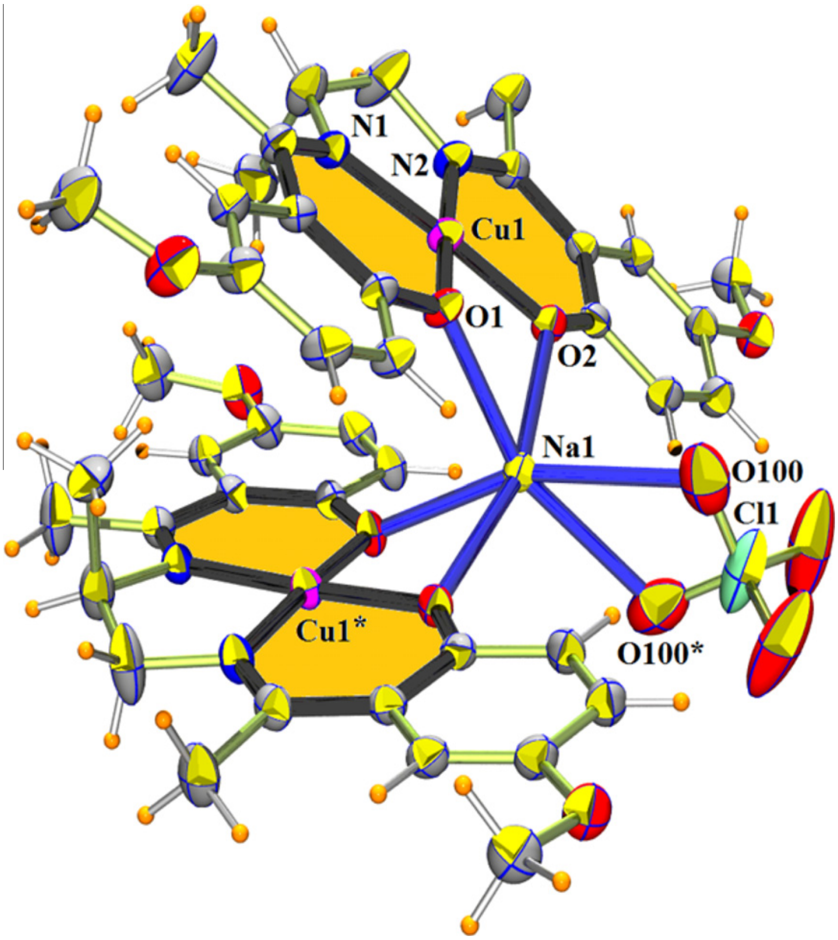

Fig. 4. ORTEP diagram of complex **2** (20% ellipsoidal probability) with atom numbering scheme. Planarity of the chelate rings (shaded) facilitates π-stacking interaction in the supramolecular assembly.

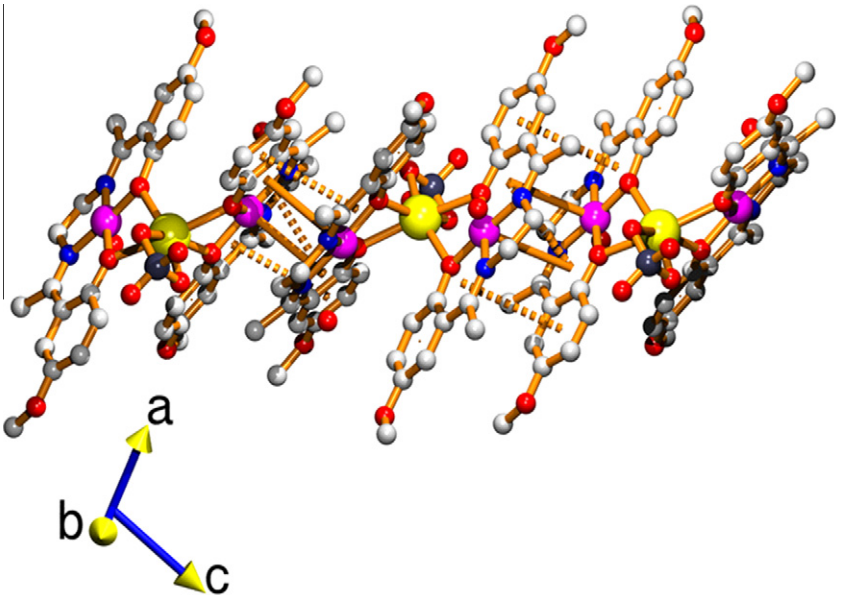

Fig. 5. One dimensional supramolecular assembly of molecular complexes in the crystal of complex **2**. Cu$\cdots\pi$ interaction involving the metal chelate ring is the unique supramolecular feature of the complex. $\pi\cdots\pi$ interaction involving phenyl ring and metal chelate ring acts in unison with the Cu$\cdots\pi$ (chelate ring) interaction.

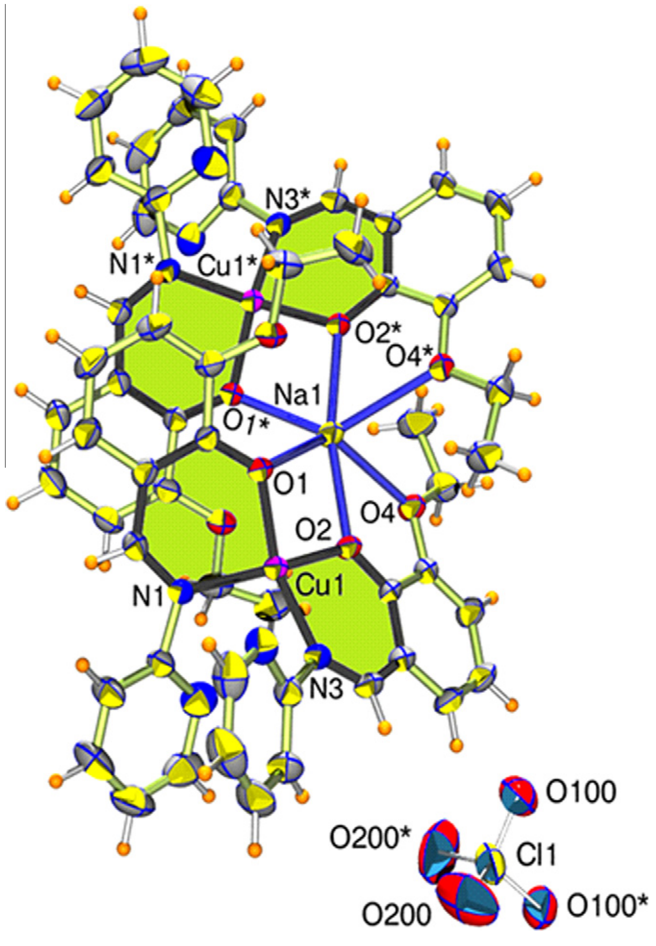

Fig. 6. The ORTEP diagram (30% ellipsoidal probability) of complex **3** in which role of Na$^+$ ion self-organizes Cu(II)(L3)$_2$ in a crown ether like topology.

water molecule is present in the coordination sphere of Na$^+$. Here, only the perchlorate ion could coordinate to Na$^+$ ion by two of its oxygen atoms (O100 and O100*, $* = 3/2 - x, y, 1/2 - z$).

The Cu–N bond distances in Cu(II)L2 units are 1.933(5) and 1.939(5) Å respectively whereas the Cu–O bond distances are 1.889(4) and 1.883(4) Å (Table 2). The Na–O (hydroxyl) bond distances fall in the range 2.341(4)–2.416(3) Å [28,29]. Two Na–O (perchlorate) distances are 2.563(9) Å each.

The supramolecular assembly of the trinuclear complexes in **2** is also governed by similar kind of π interaction in which the Cu(II)L2 chelate ring plays important role. Unlike in **1**, here Cu(II)$\cdots\pi$ interaction between adjacent units is the dominant force in organizing successive trinuclear units into a one dimensional columnar assembly (Fig. 5). Cu1 interacts with the 6-membered chelate ring [Cu1–O2–C16–C15–C13–N2] with ring centroid$\cdots$Cu^a [a = $1 - x, -y, -z$] distance 3.721(3) Å and a slip angle of 19.44°. Along with the Cu(II)$\cdots\pi$ forces the $\pi\cdots\pi$ interaction (Tables 3 and 4) between the phenyl rings and metal-chelate rings helps this assembly. It is to be noted that in **2**, no CH$\cdots\pi$ interaction involving metal-chelate ring comes into play which is present in **1**. Due to greater torsion between the two scissor arms this interaction is prohibited in **2**. The three dimensional packing patterns of the columnar units is depicted in Fig. S2 (see Supplementary material).

3.3.3. Complex *3*

The X-ray crystallographic study reveals a trinuclear super complex where Na$^+$ ion plays analogous organizing role as that was found in **1** and **2**. Here two Cu(II)(L3)$_2$ complexes are united into a esthetically attractive butterfly like architecture with Na$^+$ coordinated in a crown-ether like topology (Fig. 6). The ligand L3 is the result of condensation of 2-aminopyridine and 3-ethoxy salicylaldehyde, having a different nature than ligand L1 and L2. Here two ligands bind the Cu(II) ion by the amino nitrogen and the hydroxyl oxygen giving rise to a distorted square planar complex Cu(II)(L3)$_2$. Two chelate ring planes in the complex Cu(II)(L3)$_2$ are rotated with respect to each other due to the intra-molecular $\pi\cdots\pi$ interaction between the dangling pyridine rings of the two ligands that bind to Cu(II) ion. In the complex assembled by the Na$^+$ ion, each of the Cu(II)(L3)$_2$ complexes donate three coordination to the Na$^+$ ion making it octa coordinated. Besides the two hydroxyl oxygens of two L3 that bind to Cu(II) the ethoxy oxygen atom also coordinates the Na$^+$ ion. Crown ether like topology of the Na$^+$ ion is due to intra-molecular $\pi\cdots\pi$ interaction between the phenyl groups of the two Cu(II)(L3)$_2$ complexes that are organized by Na$^+$ ion keeping itself at the core of the complex. It is interesting to note that the perchlorate ion in this case cannot coordinate to the Na$^+$ ion; instead it remains as counterion outside the coordination sphere. Another interesting feature of complex **3** is that, in the supramolecular assembly of the trinuclear complexes the weak forces involving the Cu–ligand chelate rings is absent. Here a different supramolecular organization is mainly governed by dispersion forces (Fig. S3, Supplementary material) having a layered architecture with grooves accommodating perchlorate counter ions. This is expected as in this case the two chelate rings around Cu(II) ion are heavily twisted with respect to each other, having a non-planar geometry of the coordination plane.

4. Conclusion

The present study reveals that sodium ion assisted self-assembly of square planar Cu(II)-Schiff base complexes may be a unique feature that can be utilized in the design of polynuclear coordination complexes. Also this class of complexes can be intelligently engineered through ligand modification so that they can reveal many finer details of weak intermolecular forces especially the π-interaction involving the metal-chelate rings. Complexes **1** and **2** are two such examples that reveal how a slight modification in the ligand structure can influence the coordinative behavior of the copper–ligand complexes towards Na$^+$ metal ion as well as the weak forces that operate among them. An increase in ligand bulkiness due to the presence of ethoxy group at the terminal position of the ligand may cause exclusion of water from the sodium coordination sphere. More planarity of Cu–ligand chelate ring favors Cu$\cdots\pi$ (metal-chelate)-interaction in **2** which does not exist in **1**. The ligand in the complex **3** which is widely different from that used in **1** and **2** was designed to test the unique self-assembly feature of Na$^+$ ion. The uniqueness of this Na$^+$ assisted self-assembly is evident from **3**, where to maintain this assembly the planarity of the Cu(II)(L3)$_2$ complex is compromised. In **3**, the perchlorate ion could not enter the Na$^+$ coordination sphere due to the assembly of Cu(II)(L3)$_2$ complexes around the Na$^+$ ion giving rise to a metalla crown effect. In summary present study reveals the unique nature of the self-assembly of square-planar Cu(II)-Schiff base complexes around Na$^+$ and hints that other alkali metals and transition metal-Schiff base complexes may be designed utilizing this path. Work in this direction is in progress in our laboratory.

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Appendix A. Supplementary data

CCDC 826103, 826104, and 826105 contains the supplementary crystallographic data for **1**, **2**, and **3**, respectively. These 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2012.01.004.

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