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Trinuclear and tetranuclear adduct formation between sodium perchlorate and copper(II) complexes of salicylaldimine type ligands: Structural characterization and theoretical investigation

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ABSTRACT

The synthesis of two new sodium perchlorate adducts (1:2 and 1:3) with copper(II) “ligand–complexes” is reported. One adduct is trinuclear $[(CuL^1)_2NaClO_4]$ (**1**) and the other is tetranuclear $[(CuL^2)_3Na]ClO_4 \cdot EtOH$ (**2**). The ligands are the tetradentate di-Schiff base of 1,3-propanediamines and salicylaldehyde (H_2L^1) or 2-hydroxyacetophenone (H_2L^2). Both complexes have been characterized by X-ray single crystal structure analyses. In both structures, the sodium cation has a six-coordinate distorted octahedral environment being bonded to four oxygen atoms from two Schiff-base complexes in addition to a chelated perchlorate anion in **1** and to six oxygen atoms from three Schiff-base complexes in **2**. We have carried out a DFT theoretical study (RI-B97-D/def2-SVP level of theory) to compute and compare the formation energies of 1:2 and 1:3 adducts. The DFT study reveals that the latter is more stabilized than the former. The X-ray crystal structure of **1** shows that the packing of the trinuclear unit is controlled by unconventional C–H···O H-bonds and Cu^{2+}–π non-covalent interactions. These interactions explain the formation of **1** which is *a priori* disfavored with respect to **2**.

1. Introduction

Over the past several decades there has been enormous interest in the coordination chemistry of alkali-metal ions, originating mostly from a desire to develop molecular systems that can mimic naturally occurring molecules responsible for the selective transport of ions. Crown ethers, cryptands, and related ligands are the most important class of complexing agents for the alkali-metal ions and consequently structure/selectivity studies of the alkali-metal ions usually focus on such systems [1–3]. Besides these important classes of complexing agents, there are many other simpler and more affordable ligands that are also effective in this respect. The salicylaldimine or acetylacetoneimine complexes of divalent transition metals (e.g. Cu(II), Ni(II)) represent such a group of complexing agents. Due to the bridging ability of the phenoxo group (or ketone oxygen) such “ligand complexes” still show coordination ability to other metal ions and consequently, are very effective not only for the construction of hetero-metallic, multinuclear complexes with p- and d-block elements but also with alkali-metal ions [4,5]. As a result, such species can conveniently be used, in a second step of the synthesis, to facilitate the formation of homo- or hetero-metallic multi-nuclear complexes with the desirable combination of various metal ions [4,6,7]. Thus these ‘ligand complexes’ can be considered as small building blocks which in combination with another metal ion can lead through self-assembly processes, to large, well-defined structures, a procedure which is one of the most important recent developments in the field of supramolecular chemistry. The alkali metal ion adducts of such ‘ligand complexes’ in some cases are used as precursors for other molecular species relating to small molecule activation [8,9], electron storage [10–12], and magnetic materials [13–16].

Since the reports on the X-ray structures of the sodium perchlorate adducts of [Ni(acacen)] [17] and [Cu(salen)] [18] [acacen = N,N′-ethylenebis(acetylacetoneiminate) and salen = N,N′-ethylenebis(salicylideneiminate)], structures of a number of lithium, sodium, and potassium adducts of such ‘ligand complexes’ have been reported [19]. The results show that usually two ‘ligand complexes’ coordinate through the cis-oxygen atoms to the alkali metal ion along with a coordinating anion to result in trinuclear complexes. It has also been found that in very rare cases [20,21] the naked alkali

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metal ion can be encapsulated in the coordination cage provided by the six oxygen atoms of three ‘ligand complex’ units.

In this present work, we have used two ligand complexes [CuL^1] and [CuL^2], where H_2L^1 = N,N′-bis(salicylidene)-1,3-propanediamine and H_2L^2 = N,N′-bis(α-methylsalicylidene)-1,3-propanediamine (see Chart 1) for the formation of adducts with $NaClO_4$. It should be noted that these two ‘ligand complexes’ have only rarely been used for adduct formation with any alkali-metal ions [22]. The structural analyses reveal that [CuL^1] forms a 2:1 adduct, [$(CuL^1)_2NaClO_4$] (**1**) whereas [CuL^2] produces a very rare 3:1 adduct [$(CuL^2)_3Na]ClO_4$·EtOH (**2**). The differences in stoichiometry and structures of the trinuclear adducts have been rationalized by using theoretical DFT calculations. We have performed an energetic study to analyze two aspects, first the differences in the formation energies of the complexes and second the importance of the weak non-covalent forces such as C–H···O, C–H/π and cation–π interactions that influence the crystal packing. To the best of our knowledge, this is the first report in which the composition of alkali metal adducts with ‘ligand complexes’ is explained using a combined theoretical and experimental investigation.

2. Experimental section

2.1. Starting materials

The salicylaldehyde, *o*-hydroxy acetophenone and 1,3-propanediamine were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.2. Synthesis of the Schiff-base ligands H_2L^1, H_2L^2

The two di-Schiff-base ligands, H_2L^1 and H_2L^2 were prepared by standard methods. Briefly, 2 mmol of 1,3-propanediamine (0.16 mL) were mixed with 4 mmol of the required aldehyde (salicylaldehyde (0.41 mL) and 2-hydroxyacetophenone (0.48 mL) in ethanol (10 mL)]. The resulting solutions were refluxed for ca. 2 h, and allowed to cool. The yellow colored ethanolic solutions were used directly for complex formation.

2.3. Synthesis of the complex [$(CuL^1)_2NaClO_4$] (1)

To a ethanolic solution (20 mL) of $Cu(ClO_4)_2·6H_2O$ (1.852 g, 5 mmol) was added a ethanolic solution of H_2L^1 (5 mmol, 10 mL) to prepare CuL^1 complex [23]. Then CuL^1 complex (0.688 g, 2 mmol) was dissolved in ethanol (20 mL) and then 2 mL of water solution of sodium perchlorate (0.140 g, 1 mmol) was added to the solution, stirred and allowed to stand overnight when green colored X-ray quality single crystals appeared at the bottom of the vessel. The crystals were isolated, washed with ethanol and dried in vacuum desiccator containing anhydrous $CaCl_2$.

*Compound **1***: Yield: 0.651 g. (80%). *Anal.* Calc. for $C_{34}H_{32}Cl_1Cu_2N_4Na_1O_8$ (810.16): C 50.35, H 3.94, N 6.92. Found: C 50.51, H 3.87, N 6.97%. UV/Vis (MeCN): λ_{max} = 273 nm, 390 nm, 595 nm. IR: ν(C=N) = 1626 cm^{-1}, $\nu(ClO_4^-)$ = 1104–1065 cm^{-1}.

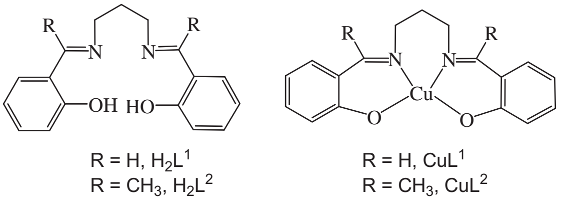


Chart 1. Ligands and ‘ligand-complexes’ used in this work.

2.4. Synthesis of the complex [$(CuL^2)_3Na]ClO_4$·EtOH (2)

To a ethanolic solution (20 mL) of $Cu(ClO_4)_2·6H_2O$ (1.852 g, 5 mmol) was added a ethanolic solution of H_2L^2 (5 mmol, 10 mL) to prepare CuL^2 complex [24]. Then CuL^2 complex (1.174 g, 3 mmol) was dissolved in ethanol (20 mL) and then 2 mL of water solution of sodium perchlorate (0.140 g, 1 mmol) was added to the solution, stirred and allowed to stand overnight when gray colored X-ray quality single crystals appeared at the bottom of the vessel. The crystals were isolated, washed with ethanol and dried in vacuum desiccator containing anhydrous $CaCl_2$.

*Complex **2***: Yield: 0.950 g. (74%). *Anal.* Calc. $C_{59}H_{66}Cl_1Cu_3N_6Na_1O_{11}$ (1284.24): C 55.13, H 5.14, N 6.54. Found: C 55.51, H 4.87, N 6.97%. UV/Vis (MeCN): λ_{max} = 270 nm, 348 nm, 532 nm. IR: ν(C=N) 1594 cm^{-1}, $\nu(ClO_4^-)$ 1089 cm^{-1}.

2.5. Crystal data collection and refinement

4745 and 16 120 independent data for **1** and **2**, respectively were collected with Mo Kα radiation at 150(2) K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analyses were carried out with the CRYSALIS program [25]. The structures were solved using direct methods with the SHELXS97 program [26]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In **2** the perchlorate anion is disordered over two sites both given 50% occupancy and two molecules of solvent ethanol were also refined with 50% occupancy. Absorption corrections were carried out using the ABSPACK program [27]. The structures were refined on F^2 using SHELXL97[26] to R_1 0.0362 and 0.0661; wR_2 0.0930 and 0.1507 for 3377 and 5923 reflections with $I > 2\sigma(I)$. Details of crystallographic data and refinements of the complexes are summarized in Table 1.

2.6. Theoretical methods

The geometries of all complexes studied in this work were fully optimized at the RI-B97-D/def2-SVP level of theory using the program TURBOMOLE version 5.7 [28]. The RI-DFT method applied to the study of weak interactions is considerably faster than the

Table 1
Crystal data and refinement details of complexes **1** and **2**.

Formula of complexes	**1**	**2**
Molecular weight	810.18	1284.27
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	22.194(3)	11.9407(7)
b (Å)	11.3602(5)	14.0388(7)
c (Å)	17.747(3)	17.9226(7)
α (°)	(90)	102.875(4)
β (°)	130.99(3)	93.077(4)
γ (°)	(90)	96.366(4)
V (Å^3)	3377.5(17)	2901.3(3)
Z, dm (gm cm^{-3})	4, 1.593	2, 1.472
μ (Mo Kα) mm^{-1}	1.410	1.470
$R_{(int)}$	0.031	0.060
No of reflections measured	4745	16120
Reflections with $I > 2\sigma(I)$	3377	5923
Number of parameters refined	227	733
R_1, wR_2 with $I > 2\sigma(I)$	0.0362, 0.0930	0.0661, 0.1507

DFT and the interaction energies and equilibrium distances are almost identical for both methods [29]. The interaction energies have been corrected for the Basis Set Superposition Error using the Boys and Bernardi counterpoise method [30].

2.7. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin–Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4500–500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. The electronic absorption spectra (1200–350 nm) in acetonitrile solution were recorded in a Hitachi U-3501 spectrophotometer. Magnetic susceptibility measurements at 300 K were carried out with a Sherwood Scientific Co., UK. magnetic susceptibility balance and diamagnetic corrections were made using Pascal's constants.

3. Results and discussion

3.1. Synthesis, IR, magnetic and UV–VIS absorption considerations

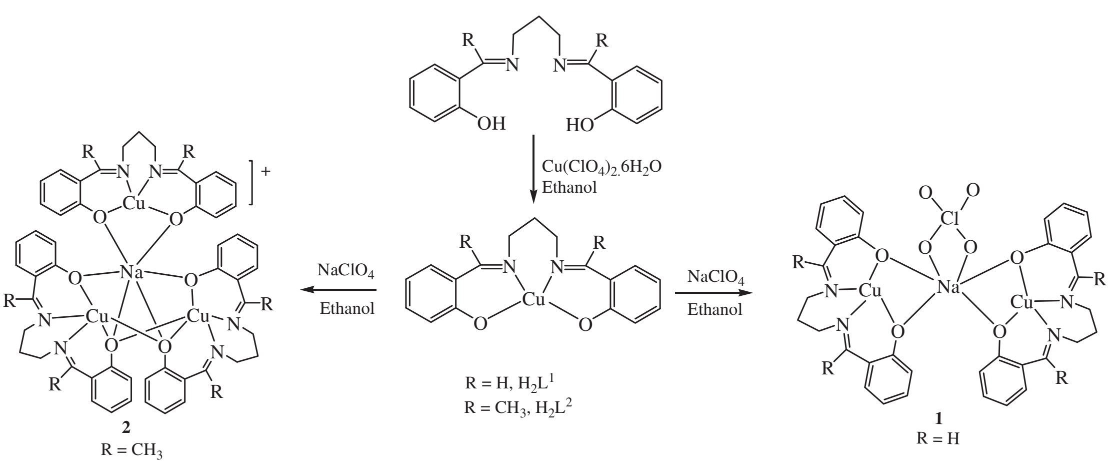
Two Schiff-base ligands (H_2L^1 and H_2L^2) and their Cu^{II} complexes, were synthesized using the reported procedure [23,24]. The Cu^{II} complexes on reaction with $NaClO_4$ in EtOH–H_2O medium (10:1, v/v) resulted in the trinuclear, $[(CuL^1)_2NaClO_4]$ (**1**) and the tetranuclear $[(CuL^2)_3Na]ClO_4{\cdot}EtOH$ (**2**) complexes by self-assembly (see Scheme 1). We have crystallized both the complexes from MeCN. The IR spectra and the elemental analyses of the crystallized products agree well with those of compounds **1** and **2** indicating that coordinating solvent such as MeCN does not displace the copper compound from sodium ion. Besides elemental analysis, both complexes were initially characterized by IR spectra. The 'ligand complexes' [CuL^1 and CuL^2] are neutral and obviously do not have any counter anion, whereas both adducts **1** and **2** contain perchlorate as counter anion. Therefore, the appearance of the characteristic intense peaks for perchlorate (ν_3) in the IR spectra of **1** and **2** around 1100 cm^{-1} (at 1104 and 1065 cm^{-1} for complex **1** and 1088 cm^{-1} for complex **2**) clearly indicates the formation of the adducts. The splitting of the band for complex **1** is indicative of a coordinated perchlorate ion as substantiated in the crystal structure. The rest of the spectral pattern and band positions of respective adducts and the 'ligand complexes' are very similar. In both adducts, a strong and sharp band due to the azomethine ν(C=N) group of the Schiff base appears at 1626 and 1593 cm^{-1} for complexes **1** and **2**, respectively. In the IR spectra of complex **2**, the broad band near 3450 cm^{-1} is probably due to the O–H stretching of the crystallized ethanol molecule. The magnetic moments of **1** and **2** at room temperature are measured at 1.68 and 1.71 BM (for each Cu ion), respectively. These values are close to the spin-only value for the discrete magnetically non coupled copper(II) system, which is 1.73 BM indicating that the Cu atoms in **1** and **2** are non coupled at room temperature.

The electronic spectra of the two complexes (measured in acetonitrile solution) display a single absorption band at 595 and 532 nm for complexes **1** and **2**, respectively. The positions of these bands are consistent with the observed square-based geometry around the copper centers. The intense band at about 365 and 358 nm for complexes **1** and **2**, respectively is due to the ligand-to-metal charge transfer absorption bands.

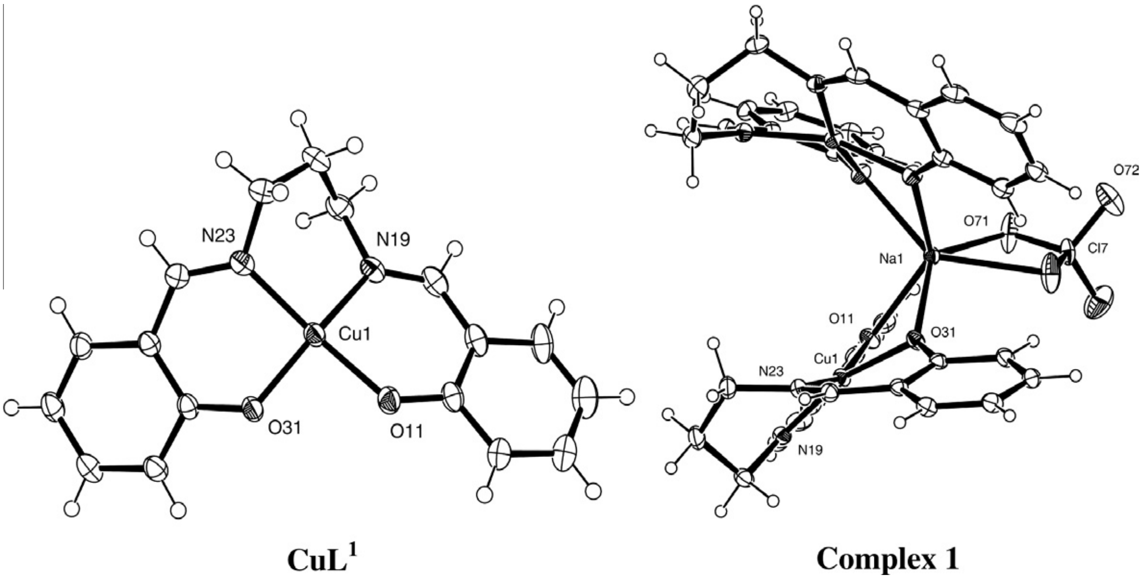
3.2. Description of the solid state structures

Both structures contain CuL moieties held together by sodium ions. The main difference between **1** and **2** is that the former contains two and the latter three CuL moieties. The coordination sphere of the copper atom in the CuL^1 moiety of **1** is shown in Fig. 1 (left) and the trinuclear adduct, which contains a crystallographic twofold axis (see Fig. 1, right). Selected bond lengths and angles are listed in Table 2. The geometry around the four-coordinate copper atoms is square planar with a tetrahedral distortion in which the r.m.s deviation of donor atoms from their plane is 0.285 Å. The metal atom is 0.036(1) Å from this plane. Regarding the Cu–O distances, they are almost 0.07 Å larger than those in the reported [31] mononuclear [CuL^1] moiety in which Cu–O distances are 1.857 Å and 1.878 Å. On the other hand, although the average Cu–N distances (1.948 Å for monomer and 1.944 Å for complex **1**) remain almost the same, the two Cu–N distances in the adduct differ considerably from each other (Table 2). The lengthening of the Cu–O bonds seems to be due to the coordination of phenoxo group to sodium ion. However, the reason for the difference in Cu–N bond lengths is not obvious but may be a consequence of the presence of the sodium ion which, as is apparent from Fig. 1, occupies a twofold axis and bridges two CuL^1 units via O(11) at 2 × 2.267(2) Å and O(31) at 2 × 2.391(2) Å. Interestingly, the sodium atom is also bonded to a bidentate perchlorate anion, also on a 2-fold axis with Na(1)–O(71) 2 × 2.512(2) Å.

The environment of the sodium ion is six-coordinate, however the geometry is very distorted from any ideal geometry, due to the small bite angle of 57.12(9)° at the chelating bidentate perchlorate. As a matter of fact there are no angles with values greater than 137.3(1)° (Table 2). The packing of the molecules is controlled by two types of intermolecular interactions, namely cation–π and



Scheme 1. Synthetic route to **1** and **2**.



CuL^1 Complex 1

Fig. 1. The structure of the copper coordination sphere in CuL^1 with ellipsoids at 50% probability. The coordination sphere of individual copper atom in CuL^2 is equivalent (left). The structure of the trinuclear complex **1** which contains a crystallographic twofold axis. Ellipsoids are drawn at the 30% probability level (right).

Table 2
Dimensions in the metal coordination spheres in complex **1**.

Distances (Å)			
Cu(1)–O(31)	1.902(2)	Cu(1)–O(11)	1.959(2)
Cu(1)–N(19)	1.908(2)	Cu(1)–N(23)	1.995 (2)
Na(1)–O(11)	2.267(2)	Na(1)–O(31)	2.391(2)
Na(1)–O(71)	2.512(2)		
Angles (°)			
O(31)–Cu(1)–N(19)	164.9(1)	O(31)–Cu(1)–N(23)	90.9 (1)
O(31)–Cu(1)–O(11)	88.9(1)	N(19)–Cu(1)–N(23)	93.0(1)
N(19)–Cu(1)–O(11)	92.1(1)	O(11)–Cu(1)–N(23)	161.07(1)
O(11)–Na(1)–O(11)′	132.8(1)	O(31)–Na(1)–O(71)′	88.8(1)
O(11)–Na(1)–O(31)′	90.1 (1)	O(11)–Na(1)–O(71)	102.2(1)
O(11)–Na(1)–O(31)	70.9(1)	O(31)–Na(1)–O(71)	137.3(1)
O(31)–Na(1)–O(31)′	132.1(1)	O(71)–Na(1)–O(71)′	57.1(1)
O(11)–Na(1)–O(71)′	119.5(1)		

(′) Represents symmetry element 2 − *x*, *y*, 0.5 − *z*.

unconventional C–H···O hydrogen bonds. Neighboring molecules are associated through cation–π interactions with centroid of the phenyl ring (C_g)···Cu(1)′ distances of 3.488 Å and two C–H···O hydrogen bonding interactions between one oxygen atom, O(72) of the perchlorate anion and iminic hydrogen atoms in adjacent molecule at symmetry element ½ + *x*, ½ − *y*, ½ + *z* with O(72)···H(18) at 2.71 Å and O(72)···H(20B) at 2.766 Å. These non-covalent interactions are responsible for the formation of an infinite one-dimensional chain as is represented in Fig. 2. This interesting architecture found in the solid state structure of **1** will be further discussed in the subsequent section.

The structure of **2** contains a discrete independent $[(CuL^2)_3Na]^+$ cation, a perchlorate ion disordered over two sites and two solvent ethanol molecules with 50% occupancy. The structure of the cation is shown in Fig. 3. The selected bond lengths and angles are summarized in Table 3. The structure of the $[(CuL^2)_3Na]^+$ cation involves three CuL^2 moieties surrounding a sodium cation. The sodium cation is six-coordinate being bonded to three pairs of oxygen atoms from each 'ligand complex'. Thus the sodium ion bridges three copper atoms each through two oxygen atoms. The structures of the CuL^2 complexes are equivalent to that of CuL^1 as shown in Fig. 1 for CuL^1 apart from the additional methyl groups. The dimensions of the three CuL^2 units are similar to those observed in **1** with similar Cu–O distances (Table 3). In complex **2** the Cu–O bond length increases slightly (ca. 0.03 Å) compared to the corresponding mononuclear complex $[CuL^2]$ [24] in which the Cu–O distances are 1.88(1) Å and 1.89(1) Å. But unlike **1** the Cu–N bond lengths in one $[CuL^2]$ unit do not differ appreciably. One of the main differences of **2** compared to **1** is that among the three

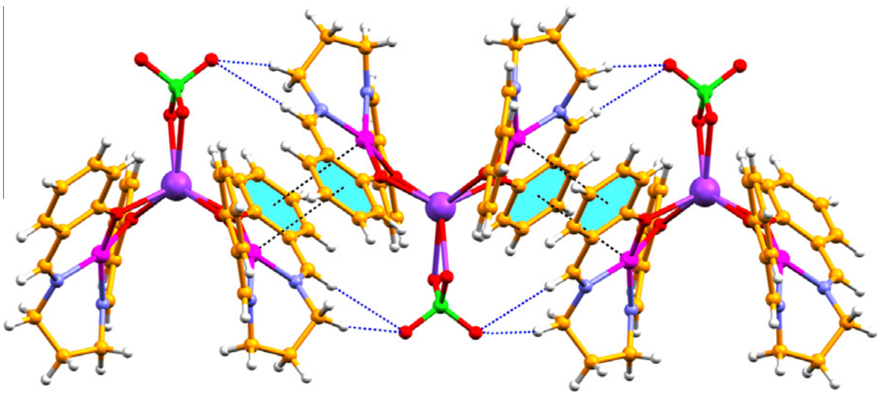


Fig. 2. Cation–π and C–H···O H-bonding interactions in **1** to form a 1D chain.

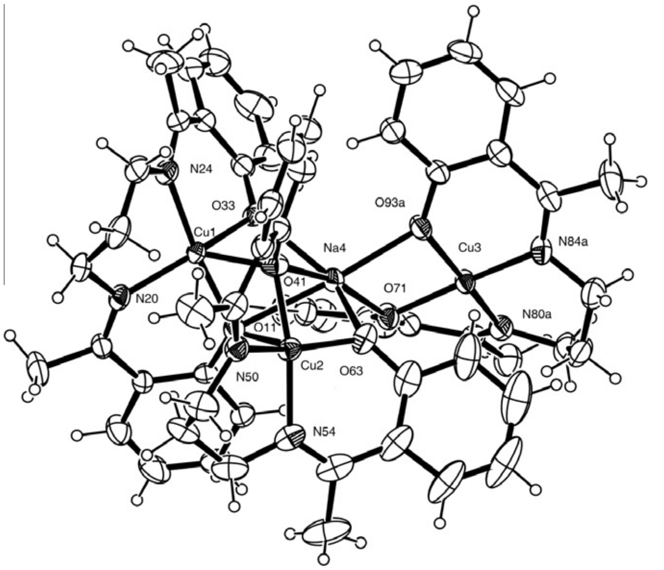


Fig. 3. The structure of the $[(CuL^2)_3Na]^+$ cation in **2** with ellipsoids at 30% probability.

Table 3
Dimensions in the metal coordination spheres in complex **2**.

Distances (Å)			
Cu(1)–O(11)	1.923(3)	Cu(3)–O(71)	1.934(3)
Cu(1)–O(33)	1.919(3)	Cu(3)–O(93)	1.898(3)
Cu(1)–O(41)	2.450(4)	Cu(3)–N(80)	1.958(4)
Cu(1)–N(20)	1.975(4)	Cu(3)–N(84)	1.989(4)
Cu(1)–N(24)	1.971(4)	Na(4)–O(63)	2.246(4)
Cu(2)–O(11)	2.599(4)	Na(4)–O(93)	2.247(3)
Cu(2)–O(41)	1.926(4)	Na(4)–O(11)	2.410(3)
Cu(2)–O(63)	1.906(3)	Na(4)–O(41)	2.819(4)
Cu(2)–N(50)	1.953(4)	Na(4)–O(33)	2.242(4)
Cu(2)–N(54)	1.963(5)	Na(4)–O(71)	2.382(4)
Angles (°)			
O(11)–Cu(1)–O(33)	87.6(1)	N(80)–Cu(3)–N(84)	97.1(1)
O(11)–Cu(1)–N(24)	172.4(2)	O(63)–Na(4)–O(93)	99.0(1)
O(33)–Cu(1)–N(24)	90.7(2)	O(63)–Na(4)–O(33)	137.2(2)
O(11)–Cu(1)–N(20)	88.6 (2)	O(93)–Na(4)–O(33)	105.1(1)
O(33)–Cu(1)–N(20)	156.8(2)	O(63)–Na(4)–O(71)	108.2(1)
N(24)–Cu(1)–N(20)	95.8 (2)	O(93)–Na(4)–O(71)	68.9(1)
O(63)–Cu(2)–O(41)	89.4(2)	O(33)–Na(4)–O(71)	113.4(2)
O(63)–Cu(2)–N(54)	92.2(2)	O(63)–Na(4)–O(11)	85.0(1)
O(41)–Cu(2)–N(54)	163.1(2)	O(93)–Na(4)–O(11)	174.7(2)
O(63)–Cu(2)–N(50)	153.0(2)	O(33)–Na(4)–O(11)	69.6(1)
O(41)–Cu(2)–N(50)	88.7(2)	O(71)–Na(4)–O(11)	113.3(1)
N(54)–Cu(2)–N(50)	97.4 (2)	O(63)–Na(4)–O(41)	63.1(1)
O(93)–Cu(3)–O(71)	86.3(1)	O(93)–Na(4)–O(41)	116.8(1)
O(93)–Cu(3)–N(80)	170.0(2)	O(33)–Na(4)–O(41)	74.5(1)
O(71)–Cu(3)–N(80)	88.7(2)	O(71)–Na(4)–O(41)	169.6(1)
O(93)–Cu(3)–N(84)	89.2(2)	O(11)–Na(4)–O(41)	61.8(1)
O(71)–Cu(3)–N(84)	170.0(2)		

CuL^2 moieties that surround the sodium ion, two units are joined together through the coordination of one phenoxo group to the axial position of the other unit at distances Cu(1)–O(41) = 2.450(4) Å and Cu(2)–O(11) = 2.599(4) Å. Thus, the phenoxo oxygen atoms O(41) and O(11) are coordinated to three metal ions (one sodium and two copper) which is very rare. The geometry of Cu(1) and Cu(2) is best described as square pyramidal with the Addison parameters[32] 0.26 for Cu(1) and 0.17 for Cu(2). The geometry around Cu(3) is square planar with a tetrahedral distortion in which the r.m.s deviation of donor atoms from their plane is 0.150 Å. The metal atom is 0.003 Å from this plane.

The environment of the six-coordinate sodium ion is more regular in geometry compared to **1**, however, there is more variation in the Na–O bond lengths. Thus, there are three short bond lengths to O(63), O(93) and O(33) with distances in the range 2.242(4)–2.247(3) Å, two longer bonds to O(71) and O(11) ranging 2.382(4)–2.410(3) Å and then a much longer bond to O(41) of 2.819(4) Å. Regarding the angles, there are two trans angles close to 180° and the third potentially trans angle O(63)–Na(4)–O(33) is far from the ideal, i.e. 137.2(2)° (Table 3). The three Na···Cu distances are slightly irregular with Na(4)···Cu(1) 3.132(2) Å, Na(4)···Cu(2) 3.178(2) Å and Na(4)···Cu(3) 3.240(2) Å. The Cu(1)···Cu(2) distance is 3.498(2) Å, significantly shorter than Cu(1)···Cu(3) at 6.273(2) Å and Cu(2)···Cu(3) at 5.884(2) Å due to the dimerization between the two units involving Cu(1) and Cu(2). However unlike compound **1**, there are no cation–π or C–H···O hydrogen bonding interactions in **2** but C–H/π interactions are found (Table 4) and are discussed below in the theoretical section.

Table 4
C–H/π distances (Å) and angles (°) for the complex **2**.

X–H···Cg(Pi-Ring)	H···Cg	∠Gamma	∠X–H···Cg	X···Cg
C(52)–H(52B)–Cg(12)	2.90	13.26	141	3.708(2)
C(541)–H(54A)–Cg(16)	2.78	9.00	153	3.665(3)
C(781)–H(78B)–Cg(14)	2.82	18.60	138	3.592(3)

'Cg' represents the centroid of phenyl ring.

3.3. CSD study

We have performed several searches in the Cambridge Structural Database in order to demonstrate that the structures reported herein are rare and scarcely found in the literature. It will be noted that in **1** the ClO_4^- ion is directly coordinated to the sodium cation thus behaving as a bidentate ligand. For instance, when the CSD is searched for the fragment highlighted in Fig. 4, 143 structures are found. No constraints were imposed in this search apart from the "no errors" option. It can be observed that the major number of hits contain X = Cu, followed by Gd and Na. Remarkably, in most of the hits (122) X is a transition metal (TM) and in only a minority is X an alkali metal (17). For sodium 12 structures are present in the database in which a majority shows a coordination index (CI) for the metal of 8 (seven structures), while in one case CI is 7 (QIYDUY) [33]. In the rest of the compounds (four structures) the sodium atom has a CI of 6. In only two structures is the sodium directly bonded to the counterion (in both structures the anion is ClO_4^-: QOHJED and QOHJAZ [4]), however in both it acts as a monodentate ligand. Therefore, chelating bidentate coordination of perchlorate to sodium in such adducts are unprecedented. On the other hand, formation of 1:3 adducts with sodium is very rare; there is only one example with [Cu(acacen)] [20]. In that adduct, three discrete [Cu(acacen)] units encapsulate the sodium ion. In compound **2** however, two $[CuL^2]$ units join together to form a dimer presumably to reduce steric hindrance. The greater bridging ability of phenoxo oxygen compared to the ketonic oxygen atom of acacen seems to facilitate dimerization via the very rare μ_3-phenoxo bridges [22]. It is also to be noted that $[CuL^2]$ has been reported as monomeric [24] but the EPR spectra show the evidence of dimerization at low temperature [34]. Complex **2** therefore reveals that dimerization can take place in the presence of Na^+ in the solid state, therefore it acts as a template for the dimerization.

3.4. Theoretical study

In Fig. 5 (top left) we show the X-ray structure of **1** $[(CuL^1)_2\text{-}NaClO_4]$ emphasizing the two intramolecular C-H···O bonds that explain the orientation of the perchlorate ligand with respect to

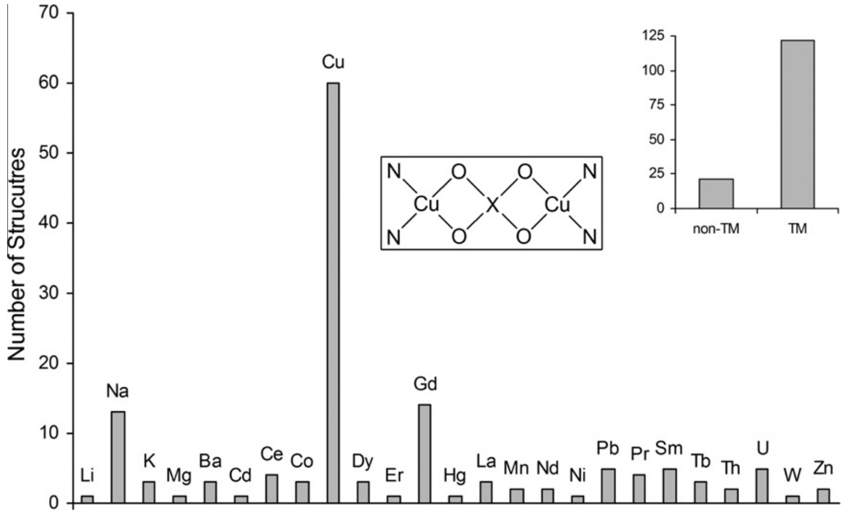


Fig. 4. Histogram showing the number of structures in the CSD for metal X in the chemical fragment highlighted. The small histogram shows the number of structures found depending on the nature of the X atom (TM = transition metal).

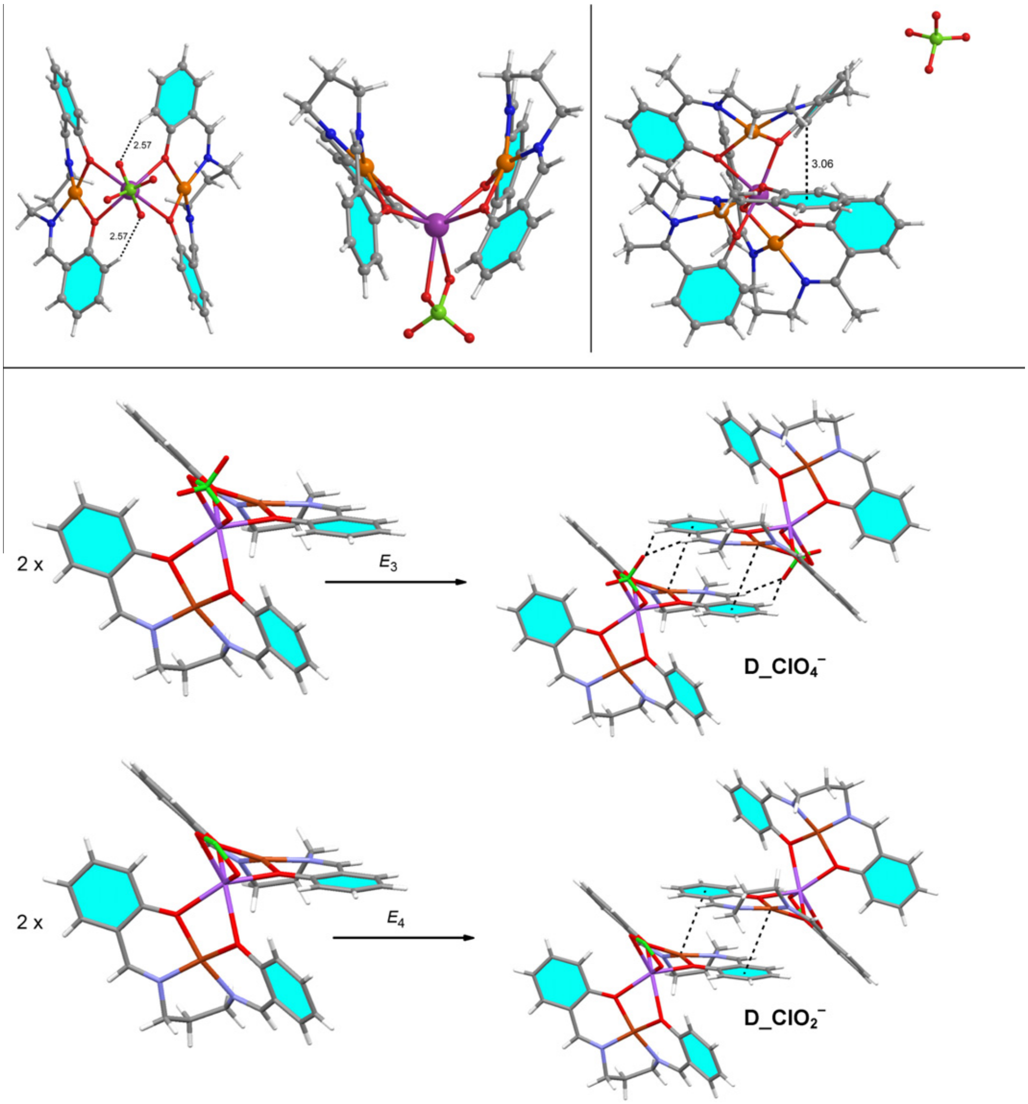
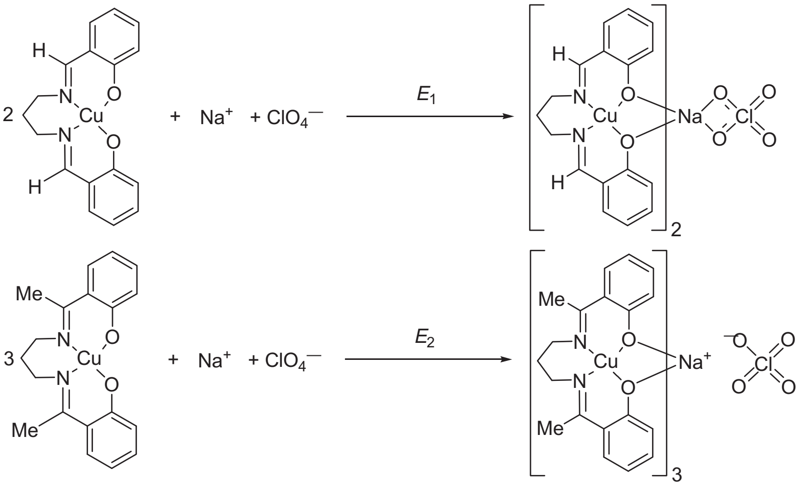


Fig. 5. Top, left: Two views of the solid state geometry of **1**. Top right: the solid state geometry of **2** where the C–H/π interaction is indicated. Distances in Å. Bottom: reactions used to compute the dimerization energy in **1** (**D_ClO$_4^-$**) and in a model of **1** (**D_ClO$_2^-$**) where the ClO$_4^-$ anion has been replaced by ClO$_2^-$.



Scheme 2. Chemical equations used to measure the formation energies of the complexes.

the other ligands. This fact is one reason that explains the aforementioned environment of the sodium ion, which presents a much distorted geometry. In Fig. 5 (top, right) the X-ray structure of **2** $[(CuL^2)_3Na]^+[ClO_4]^-$ is shown. In this case the sodium is not bonded directly to the perchlorate, instead it interacts only with the CuL^2 moieties. We have studied theoretically which arrangement is more favorable energetically. We have computed and compared the formation energies of $[(CuL^1)_2NaClO_4]$ (**1**) and $[(CuL^2)_3Na]^+$-$[ClO_4]^-$ (**2**). In Scheme 2 we show the equations used to compute the formation energies of the complexes starting from the ligands CuL^1 and CuL^2. The formation energies are $E_1 = -214.19$ kcal/mol and $E_2 = -251.37$ kcal/mol at the RI-B97-D/def2-SVP level of theory. Therefore, the formation of the complex with three ligands as in **2** is clearly favored with respect to the $[(CuL^1)_2NaClO_4]$ complex, as in **1**, where the counterion is bonded directly to the sodium cation. It should be mentioned that these binding energies are not dependent upon the presence (CuL^2) or absence (CuL^1) of the methyl group. Therefore the formation energies for a hypothetical tetranuclear arrangement with ligand CuL^1 and a hypothetical trinuclear arrangement with ligand CuL^2 do not vary. This result is in agreement with the CSD study, where in only two examples the anion is directly bonded (QOHJED and QOHJAZ) to the sodium cation. The difference in the chemical structure of the two ligands, namely the substitution in the iminic group, is crucial in the explanation of why compound **1** incorporates only two ligands in its solid state structure.

The difference between CuL^1 and CuL^2 is that the former has a hydrogen atom instead of a methyl group bonded to the carbon atom of the imine group. The examination of the solid state architecture of **1** reveals that it forms an infinite 1D chain in the crystal (see Fig. 2). This chain is stabilized by means of two hydrogen bonds from the perchlorate to C–H bonds in the ligand of an adjacent molecule (see Fig. 2). In addition, as a consequence of these hydrogen bonding interactions, a phenyl ring is positioned over a copper atom of the adjacent structure throughout the polymeric chain and thus establishing strong cation–π interactions that further stabilize the interaction. The substitution of one hydrogen atom by a methyl group (structure **1**) prevents the formation of this infinite 1D chain. Therefore the stabilization by hydrogen bonding and cation–π interactions is not possible in compound **2**. This likely explains the formation of a $[(CuL^2)_3Na]^+[ClO_4]^-$ cluster, which is energetically more favorable.

To study the importance of these interactions and how they influence the final solid state structure, we have considered a dimer of **1**, denoted as **D_ClO$_4$**$^-$ (see Fig. 5). We have computed the dimerization energy of **1** (E_3, using the reaction depicted in Fig. 5), which is −43.02 kcal/mol. This value compensates the difference in the formation energies of complexes $[(CuL^1)_2NaClO_4]$ (**1**) and $[(CuL^2)_3Na]^+[ClO_4]^-$ (**2**) that is 37.18 kcal/mol and explains the differences observed in the solid state, depending on the ligand used to synthesize the complexes.

In order to calculate the contribution of the Cu^{2+}–π interactions in the dimerization energy (E_3) we have computed the dimerization energy in a model system where the ClO_4^- anion has been replaced by ClO_2^- anion, denoted as **D_ClO$_2$**$^-$ (see Fig. 5). In this model the hydrogen bonding interaction cannot be formed and the dimerization is exclusively due to the cation–π interaction. The computed E_4 energy is -26.81 kcal/mol, therefore each cation–π interaction contributes in 13.40 kcal/mol to the stabilization of the system. Consequently, the contribution of the hydrogen bonding interaction in **1** can be roughly estimated using the following expression $(E_3–E_4)/2 = -8.11$ kcal/mol.

4. Conclusions

In summary, the preparations of two discrete clusters containing $[Na^ICu^{II}_2]$ and $[Na^ICu^{II}_3]$ structural units have been reported. They have been characterized by X-ray crystallography. Both compounds have been resulted from the self-assembly of square planar 'ligand-complex' of the type [CuL^1 or CuL^2] with the Na^I acceptor. The formation of infinite 1D-chains in **1** is achieved by a combination of non-covalent supramolecular interactions, including cation–π using the Cu^{II} cations and hydrogen bonding interactions taking advantage of the available iminic hydrogen atom (RN=CR′–H). The presence of an additional methyl group in the iminic group of **2** ($RN{=}CR'{-}CH_3$) prevents the formation of the H-bonding network as the observed in **1** and it forms a totally different cluster. These experimental results have been rationalized using DFT-D calculations that agree with the experimental results. Finally, the CSD study indicates that these clusters are not very common, giving relevance to the reported structures.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.11.005.

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