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A novel Na^{I}/Cu^{II} complex Synthesis, Spectral and Structural Characterisation

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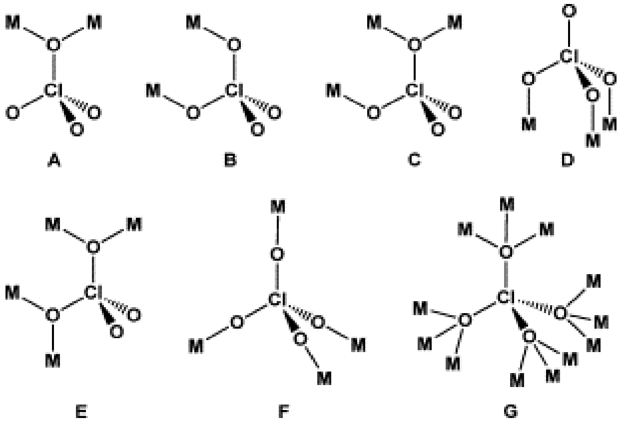
ABSTRACT

A novel cluster $[Cu_2(L)(\mu_{1,1,2}\text{-}ClO_4)Na(ClO_4)(H_2O)].0.25H_2O$*, where (*$H_3L$ *= 2-(2'-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine) has been synthesised and characterized by elemental analyses, IR, UV–Vis spectroscopy and single crystal X-ray diffraction studies. The result shows that a perchlorate ligand in the* μ_3*-1,1,2 binding mode is seen as the sole support for the assembly of* $[Na^{I}Cu^{II}{}_2L]$ *unit. The copper atoms of dinuclear unit is in a distorted square-pyramidal environment and are held together by phenolate oxygens, imidazolidinyl nitrogens in the equatorial plane and perchlorate bridge at axial with Cu----Cu separation of av. 3.21 Å, phenolic oxygen atoms of ligand, perchlorate and water molecule are connected to second metal ion sodium. Investigation on the ESR of complexes in frozen DMF solution at 77 K revealed the existence of the imidazolate-bridged dicopper structure in solution. XRD structure shows that extensive hydrogen bonding, C-H···π interactions lead to the formation of 3D framework.*

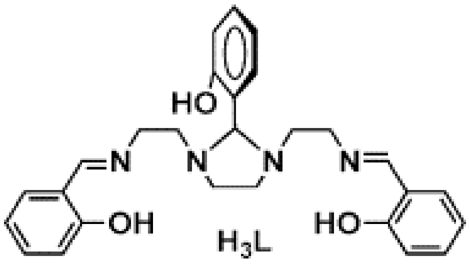
Keywords: N_4O_3 ligand, Cluster, perchlorate ion, μ_3-1,1,2 binding mode, XRD.

INTRODUCTION

Preorganised dinucleating ligands are important for the designed syntheses of homo/hetero metallic copper complexes because the tetrahedrally-disposed four oxygen atoms of a perchlorate ion can adopt various bridging modes. Seven different bridging modes (**Scheme-1**) for perchlorate ion have been identified till date, and those can be described as (A-G) in scheme-1 μ-1,1(**A**) [1,2], μ-1,2 (**B**) [3,4], μ_3-1,1,2 (**C**) [5],μ_3-1,2,3 (**D**) [6],μ_4-1,1,2,2 (**E**) [7,8], μ_4-1,2,3,4 (**F**) [9], and μ_{12}-1,1,1,2,2,2,3,3,3,4,4,4 (**G**) [10], which include both supported and unsupported bridging modes. In some of the reported examples, the scaffolding sustaining the metallic cluster is carried out by other multi nucleating ligands, whereas perchlorate is playing a rather innocent role, almost reduced to saturating free coordination sites [4, 7, 8**]**. In other cases, by contrast, this group seems to act as a template around which the aggregation of metals occurs [10] and, much more rarely, it is the only species keeping the individual metals together [9]. Sometimes, the ligand ClO_4 is found to play other roles, such as modulating the magnetic interaction between the paramagnetic centres [11]. For some time, others have been investigating the coordination behaviour of the dinucleating ligandH_3L (**Scheme 2**:H_3L= 2-(2'-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine) or its derivatives for the assembly of dicopper complexes. The Ligand (H_3L) has N4O3 donor centres and it has potential to coordinate two 3d metal ions, which on further reaction with other metal salt produces homo/hetero metallic systems. As the O3 compartment of ligand can coordinate with various types of metal ions, tri/poly nuclear systems of metal ion combinations 3d–s/p with secondary bridging ligands has been reported. To explore the hetero metallic 3d-s/d^{10} complexes derived from N4O3 ligand, we have reacted dinuclear complex synthesised from H_3L ligand with $Na^{I}ClO_4$ and isolated a heterometallic complex $[Cu_2(L)(\mu_{1,1,2}\text{-}ClO_4)Na(ClO_4)(H_2O)]_2.0.25H_2O$ (**1**). Herein, we report the synthesis, characterization and crystal structure of heterometallic complex. A bridge of special interest is the $\mu_{1,1,2}$-ClO_4^- group, known to generally mediate ferromagnetic interactions.[9,10].



Scheme-1: Variours modes of bridging for perchlorate listed in the literature.



Scheme -2: Structure of ligand H_3L**.**

MATERIALS AND METHODS

Materials: The chemicals salicylaldehyde, triethylenetetraamine, Cupric acetate monohydrate, Sodium perchlorate monohydrate (Aldrich) Ethanol, Methanol, Acetonitrile (Merck, India) were used as received. The commercial solvents were distilled and then used for the preparation of ligand and complex.

Synthesis: The reaction in a CH_3CN/MeOH mixture of $Cu(OCOCH_3)_2.H_2O$ with H_3L[12] and $NaClO_4$ in the 2:1:4 molar ratio leads to a green product that precipitates directly from the reaction mixture. The elemental analysis and solution electrical conductivity data in dimethylformamide are consistent with the formula $[Cu_2(L)(\mu_{1,1,2}\text{-}ClO_4)Na(ClO_4)(H_2O)].0.25H_2O$ (**1**), and the yield was thus calculated as 85%. Anal. Cal. for C27 H27.5 Cl2 N4 Cu2 Na O10.5 (%): C: 40.69; H: 3.48; Cl: 8.90; Cu: 15.95; N: 7.03; Na: 2.88; O: 21.08 Found (%): C, 40.91; H, 3.60; Cl: 8.68; N, 7.13; Na: 2.80; O: 21.15.

Physical Measurements: Elemental analyses for C, H, N and S were carried out on Flash 2000 Organic Elemental analyzer. UV-vis spectra was measured on a Shimadzu UV-2450 PC spectrophotometer at 200 K. Infrared (IR) spectra were recorded on a Nicolet iS10 instrument using KBr pellets. The single crystal X-ray structure was performed on an Oxford Diffraction Xcalibur Diffractometer equipped with graphite monochromatic Mo-Kα radiation (λ = 0.71073Å) at 300˚K. X-Ray crystallography A suitable single crystal of title compound (C27 H27.5 Cl2 N4 Cu2 Na O10.5) was selected and mounted on a Xcalibur, Eos Diffractometer. Using Olex2.1.2 [13], the structure was solved with the ShelXS [14] structure solution program by Direct Methods. Refinements were performed using the ShelXL [15] refinement package using Least Squares minimization. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were placed in calculated positions with a C–H bond distance of 0.93Å. Table 1 lists crystallographic details. For further details on the crystal structure investigations and refinements, see the ‘‘Supplementary material’’.

RESULTS AND DISCUSSION

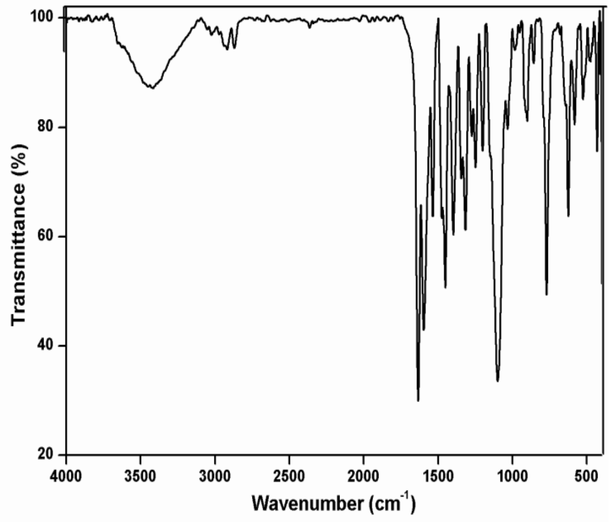
Spectroscopic Characterization: IR spectrum was recorded in the range of 4000-400 cm^{-1}. The *v*(O-H) stretching band associated with lattice water molecule is observed as very strong and broad bands in 3566 – 3383 cm^{-1} region typically with maxima at 3419 cm^{-1}. In IR, azomethine (-HC = N-) characteristic band in free ligand [H_3L] was observed at 1635 cm^{-1}. Coordination of the nitrogen with the metal centre was expected to reduce the electron density in the azomethine moiety and thus lower the $\nu_{C=N}$ [16]. Decrease in stretching frequency for $\nu_{C=N}$ in complex **1** clearly indicate the ligation of azomethine nitrogen to metal centre. Complex **1** showed IR bands near 1150 and1090 cm^{-1} together with a band at 622 cm^{-1} (Figure 1). The splitting of these two bands suggested the presence of coordinated perchlorate ion to the metal centre [17]. Predominant vibrations associated with O-H are 2800 cm^{-1} {ν(O-H)}, 1417 cm^{-1} {δ(OH)} and 927 cm^{-1} {γ(O-H)} [18-20].

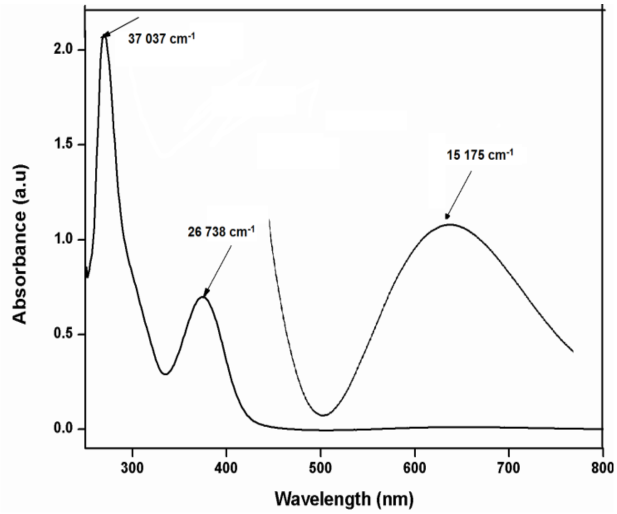
Table-1: Crystal data and structure refinement for complex (**1**)

Empirical formula	$C_{108}H_{110}N_{16}O_{42}Na_4Cl_6Cu_8$	Θ-range for data collection	5.118 to 25°
Formula weight	3117.09	Index ranges	$-14 \leq h \leq 14$
Temperature	200 K		$-14 \leq k \leq 13$
Wavelength	0.71073Å		$-26 \leq l \leq 25$
Crystal system	Monoclinic	Reflections collected	15044
Space group	$P2_1/c$	Independent reflections	5520 [$R_{(int)}$ = 0.0508]
a/b/c(Å)	11.7804(3);11.7910(3);22.6857(6)	Refinement method	Full-matrix least-squares on F^2
α/β/ γ(°)	90;94.764(2);90	Data / restraints / parameters	5520 / 0 /453
Volume	3140.22(14) $Å^3$	Goodness-of-fit on F^2	1.038
Z	1	Final R-indices [I>2σ(I)]	R_1 = 0.0470, wR_2 = 0.1192
Density (calculated)	1.648 $\mu g/m^3$	R-indices (all data)	R_1 = 0.0656, wR_2 = 0.1284
F(000)	1584		
Crystal size	0.35 x 0.15 x 0.05 mm^3		

However, none of these bands were observed, indicating the deprotonation of –OH group and coordination with the Cu(II). The interpretations of IR spectra are well supported by XRD structure. The UV visible spectrum of the complex **1** (figure-2) was recorded in a methanolic solution in the range of 200 to 800nm. The UV-VIS spectra shows peak at 270nm which may be assigned to ligand cantered *n*-π*, peak observed at 373nm assigned to charge transfer from perchlorate ion to copper and peak at 618nm assigned to d-d transition.

Description of the crystal Structure: The structure of **1** (Figure-3) was determined from crystals obtained by slow evaporation of a MeCN/MeOH (1:1) solution (see the Supporting Information for the crystallographic data for **1**). It revealed a very interesting multi component complex arising from the assembly of two cation $[NaCu_2L]^+$ fragments through the intermediacy of an intercalated ClO_4^- anion, located at a crystallographic center of symmetry.





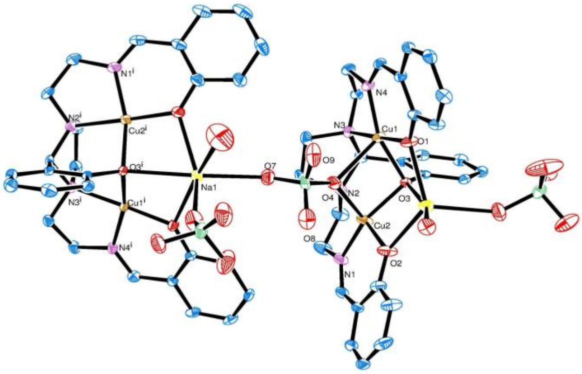
In each half of the ligand, the phenolate group, the imine atom and one N-donor of the imidazolidine fragment occupy three basal positions of CuII in form of a six- adjacent to a five-membered chelate ring. The central phenoxide of L^{3-} bridges both metals, occupying their fourth basal site. The coordination geometry at each copper centers in the Cu2N4O3 are distorted square pyramidal with τ=0.33, 0.40 [$\tau = |\beta - \alpha|/60^{\circ}$, where β and α are the two largest angles around the central atom; τ = 0 and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively][21]. The four equatorial sites of the each five coordinated copper centers are occupied by two imine and imidazoline nitrogen atoms and by two phenoxo oxygens (μ_2-phenoxo and μ_3-phenoxo) of L^{3-} respectively. The fifth coordination is completed by an O-atom from perchlorate, bridging the adjacent copper atom in a symmetric (apical – apical) fashion with long Cu – O contact [2.378(2) Å] forming the apex. The polyhedra around copper thus share the L^{3-} ligand's central phenolate oxygen (common basal vertex) and one of its oxygen from perchlorate (common apical vertex). As a result, the (idealized) basal planes are not co-planar but form an angle of 135.9°. The $ClO^{4\,-}$ ligand plays the same role on a neighboring $[NaCu_2L]^+$ fragment through another of its O-atoms, thereby bridging two dinuclear entities and adopting theμ-1,1,2 coordination mode (Figure-3), for the first time unsupported. Electro neutrality is ensured by a coordination of ClO^{4-} anion to sodium ion. Other related [Cu2L′(X)] moieties (L′ is a ligand equal or related to L; X^- is AcO^-, NO_3^-, Cl^-, OMe^-, N_3^- etc.) have been reported in the literature [22-25] as independent species, suggesting that the dinuclear components assembled to form **1** may be stable as discrete molecules. The important bond lengths and bond angles of complex (**1**) are given in tables 2 and 3.

Table-2: Selected bond lengths (Å) for complex **1**

Atom	Atom	Length/Å
Cu1	N4	1.921(3)
Cu1	O1	1.895(2)
Cu1	O4	2.312(3)
Cu1	O3	1.998(2)
Cu1	N3	2.066(4)
Cu2	O2	1.908(3)
Cu2	O4	2.378(2)
Cu2	O3	1.992(2)
Cu2	N1	1.927(3)
Cu2	N2	2.068(4)
Na1	O1	2.333(3)
Na1	O2	2.367(4)
Na1	O3	2.462(3)
Na1	O5'	2.430(3)
Na1	O6	2.660(2)
Na1	O7	2.345(4)

Table-3: Selected Bond angles (°) for complex **1**

Atom1	Atom2	Atom3	Angle/°
N4	Cu1	O1	94.9(1)
N4	Cu1	O4	122.4(1)
N4	Cu1	O3	158.1(1)
N4	Cu1	N3	84.2(1)
O1	Cu1	O4	91.2(1)
O1	Cu1	O3	88.1(1)
O1	Cu1	N3	178.1(1)
O4	Cu1	O3	79.2(1)
O4	Cu1	N3	90.7(1)
O3	Cu1	N3	92.1(1)
O2	Cu2	O4	89.4(1)
O2	Cu2	O3	90.1(1)
O2	Cu2	N1	94.4(1)
O2	Cu2	N2	178.3(1)
O4	Cu2	O3	77.7(1)
O4	Cu2	N1	126.0(1)
O4	Cu2	N2	91.1(1)
O3	Cu2	N1	155.9(1)
O3	Cu2	N2	91.6(1)



Scheme 3: Line diagram showing the numbering scheme (30% displacement ellipsoids). Hydrogen atoms are not shown for clarity.

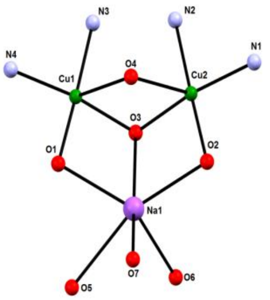


Figure-3: ORTEP structure of the title compound viewed with atom NaI//CuII heterometallic cluster structure of **1**.

TheCu_2O_2 square base is non planar but folded by 29.3°. The two copper centers are 3.2159(7) Å apart and both are 3.290(2) Å away from Na which sits above the Cu2O2 ring. The sodium atom can be considered as having a distorted octahedral environment with one pair of phenoxo oxygen atoms [μ-O(1),O(2) 2.333(3) Å, 2.367(4) Å] occupying the two coordination sites and another two coordination sites are occupied by two oxygen atoms of end-to-end bridging perchlorate ligand O(7) [2.345(4) Å], perchlorate anion oxygen atom O(6) [2.430(3) Å]. The final two long contacts are between Na and the oxygen atom of water molecule O(5) [2.660(2) Å], Na and the μ3-phenoxo O(3) [2.462(3) Å] atom which already bridge two copper atoms. The $\mu_{1,1,2}$ bridge of perchlorate bents at O(7) [140.5(2)°] and thereby links the sodium centers of the adjacent molecule to generate a 1D chain (Figure-4). The adjacent heterometallic cluster molecules are oriented in an inverted fashion to each other along the chain. These chains are staggered relative to one another. The crystal packing is stabilized by an intermolecular C − H···O hydrogen bonding and C − H···π interactions (Figure-5). The ligand carbon atoms are acting as H-donors to form strong intermolecular hydrogen bonding [C(24)-H(24) ···O(10), C(7)-H(7)···O(11) and C(21)-H(21)···O(12)] with the oxygen atoms [O(10), O(11) and O(12)] of perchlorate coordinated to sodium.

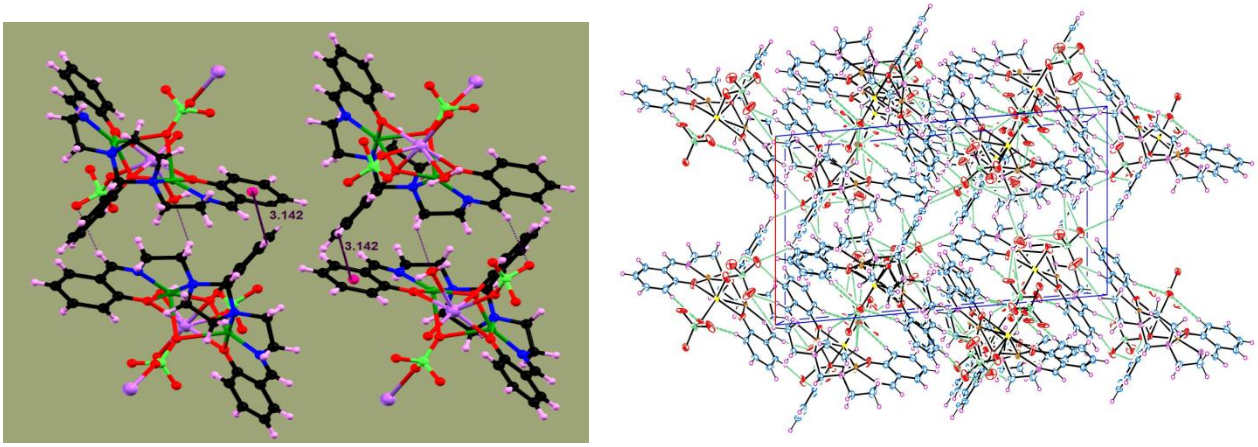


Figure-4: Crystal Packing diagram along a axis including 1D supramolecuar network connected by hydrogen bonding interactions (dashed lines).

Intermolecular H-bondings formed by perchlorate molecules with hydrogen atoms of water coordinated to sodium play an important role in bridging the two cages [O(6)-H(6B)···O(12) and O(6)-H(6A)···O(9)]. Table-4 list the main hydrogen bond distances and angles. The C-H···π interactions are in the distance of 3.142 Å. Charge neutrality of the complex is obtained by considering Schiff base two copper atoms in 2+ oxidation states, one sodium in 1+ which neutralizes the five negative charges of the three deprotonated oxygen atoms of L^{3-}and two perchlorate ions. The other much longer Cu-N bond lengths for thetwo five coordinated copper centers involved in the cage formation [Cu(2)-N(1)=1.927(3), Cu(1)-N(4)=1.921(3), Cu(1)-N(3)=2.066(4) and Cu(2)-N(2)=2.068(4) Å] are also in good agreement with the earlier reported Cu-N distances observed for the square pyramidal copper(II) ions coordinated to [L]$^{3-}$.

Table-4: Selected geometrical parameters of hydrogen bonds (Å and ˚)

Donor-----H...Acceptor	d(D---H)Å	d(H....A)Å	d(D....A)Å	< (DHA)/°
C(7) ---H(7) ---O(11)	0.95	2.51	3.427(6)	161
C(10) ---H(10A) --O(11)	0.99	2.51	3.462(6)	160
C(21) ----H(21) ---O(12)	1.00	2.55	3.409(5)	144
C(24) ----H(24) ---O(10)	0.95	2.56	3.389(5)	146

APPLICATIONS

This Cu(II)/NaI heterometallic complex is expected to be a potential anti-microbial agent and homogeneous catalyst in the oxidation of catechol to benzo quinone. These studies are underway.

CONCLUSIONS

A novel CuII/NaI complex with ligand *2*-(2'-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine was successfully synthesized and characterised. The copper atoms present in the complex has distorted square pyramidal structure and the sodium has distorted octahedral structure which are almost perpendicular to each other. The supramolecular framework is largely a consequence of a wide range of non-covalent interactions, consisting of hydrogen bonding, C-H···π interactions.

Supplementary material : CCDC 953975 contains the supplementary crystallographic data of this complex and it can be obtained free of charge from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Telephone: 044-(0)1223-762-910, Fax: 044-(0)1223-336-033;or e-mail: deposit@ccdc.cam.ac.uk.

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