

## Syntheses, characterization, and X-ray crystal structure of heteronuclear dicyanamide-bridged Cu/Na Assembled with Salen-type Schiff Base and Dicyanamide

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**Abstract:** Reaction of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  with 2-(2-(2-hydroxy-3-methoxybenzylideneamino)phenylimino)methyl-6-methoxyphenol ( $\text{H}_2\text{L}$ ) gives the metalloligand  $[\text{Cu}(\text{L})] \cdot (\text{H}_2\text{O})$  (**1**). Reaction of metalloligand (**1**) with three fold of sodium dicyanamide  $\text{Na}[\text{N}(\text{CN})_2]$  gives the new tetranuclear compound  $[\{\text{Cu}(\mu\text{-L})\text{Na}(\text{EtOH})\}(\mu\text{-1,5-N}(\text{CN})_2)\{\text{Cu}(\mu\text{-L})\text{Na}(\text{N}(\text{CN})_2)\}]$  (**2**). Suitable crystals of (**2**) were grown by slow evaporation of ethanol solution for one week. The metalloligand (**1**) and the tetranuclear (**2**) complexes are characterized by IR and physical measurement. The Schiff base  $\text{H}_2\text{L}$  behave an  $\text{N}_2\text{O}_2\text{O}'_2$  coordination hexadentate ligand which can encapsulate two metal ions. The structure of (**2**) was elucidated by X-ray diffraction analysis. The asymmetric unit of the compound contains two dideprotonated ligand molecules, two tetracoordinated copper ions, two hexacoordinated sodium ions, one monodentate dicyanamide unit, one coordinated ethanol molecule and one dicyanamide ion which acts as a bridge between the two entities:  $[\{\text{Cu}(\mu\text{-L})\text{Na}(\text{EtOH})\}]$  and  $[\{\text{Cu}(\mu\text{-L})\text{Na}(\text{N}(\text{CN})_2)\}]$ . In the structure the tetracoordinated  $\text{Cu}^{\text{II}}$  ion is situated in the  $\text{N}_2\text{O}_2$  inner. The environment around the copper (II) is best described as a planar square geometry. The two six-coordinated  $\text{Na}^{\text{I}}$  ion are situated in  $\text{NO}_5$  and  $\text{N}_2\text{O}_4$ , respectively. The geometries around the  $\text{Na}^{\text{I}}$  ions are described as pentagonal pyramidal. The interplanar angles between the two phenyl rings with a methoxy substituent is  $4.208(4)^\circ$ . The Cu-Na distances are  $3.3777(16) \text{ \AA}$  and  $3.4001(15) \text{ \AA}$ . Intermolecular hydrogen bonds arranged the tetranuclear units into layers parallel to a axis.

**Keywords:** Iron, Metalloligand, o-Vanillin, Sodium Dicyanamide.

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### I. Introduction

Specialists in coordination chemistry have shown interest in the synthesis of complexes derived from a Schiff base ligand because of the wide applicability of these complexes in fields such as catalysis, design of ferro- or ferrimagnetic materials, medical diagnostics, biomimetic reactions, and heterogeneous catalysts [1-9]. Several authors have successfully reported a large number of transition metal complexes derived from Schiff bases [7, 10-16]. Depending on the number of coordination sites of the Schiff base used, a variety of metal complexes among which the coordination number of the metal ion is incomplete were obtained. In such cases, the metal ion can be saturated by providing anionic co-ligands such as  $\text{NOC}^-$ ,  $\text{NSC}^-$ ,  $\text{N}_3^-$ ,  $(\text{CN})_2\text{N}^-$ ,  $\text{CH}_3\text{CO}_2^-$  which can generate mononuclear or polynuclear complexes [3, 17-21] in which the ligands can act as a bridging agent. Dicyanamide  $(\text{CN})_2\text{NH}$  is a good candidate because of its multiple possibilities of coordination. It can act as  $\mu_2^{-1,1}$ ,  $\mu_2^{-1,3}$ ,  $\mu_3^{-1,5}$ ,  $\mu_3^{-1,3,5}$ ,  $\mu_3^{-1,1,5}$ ,  $\mu_4^{-1,1,3,5}$ , and  $\mu_5^{-1,1,3,5,5}$  ligand [22-28]. It can also act as a terminal ligand [25,29]. In this context we report the synthesis of a new Cu (II) / Na (I) complex with a Schiff base having a small internal site  $\text{N}_2\text{O}_2$  and a larger external  $\text{O}_2\text{O}'_2$  site. As expected, the  $\text{N}_2\text{O}_2$  site hosts the Cu (II) ion while the external site hosts the sodium ion, thus forming a dinuclear unit. The dicyanamide anion acts as a terminal ligand on the one hand and as a  $\mu\text{-1,5}$ -bridging agent to produce a tetranuclear complex. This complex is characterized by different spectroscopic methods and its structure is elucidated by X-ray diffraction.

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## II. Experimental

### 2.1. Starting materials and instrumentations

o-Vanillin and 1,3-diaminobenzene, copper chloride dihydrate, and sodium dicyanamide were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. The ligand (H<sub>2</sub>L) was synthesized following the reported procedure [30]. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000–400 cm<sup>-1</sup> region. The molar conductance of 1 × 10<sup>-3</sup> M in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: Hg[Co(SCN)<sub>4</sub>]).

### 2.2. Preparation of the metallo-ligand {6,6'-Di-methoxy-2,2'-[1,2-phenylenebis(nitrilomethylidyne)]diphenolato-κ<sup>4</sup>O,N,N'O'}copper(II) monohydrate (1).

The compound **1** is obtained following the reported procedure with slight modification [30]. In a round bottomed flask, the ligand (H<sub>2</sub>L) (10 mmol, 0.374 g) was dissolved in 5 mL of acetonitrile. A solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (10 mmol, 0.1704 g) in 5 mL of ethanol was added. After two hours under reflux, the brown precipitate was recovered by filtration, washed with ether (2 × 10 mL) and dried in air. The compound was formulated as [Cu(L)]·(H<sub>2</sub>O). Yield: 83%. Elemental Anal. Found (Calcd.) (%): C, 57.95 (57.92); H, 4.42 (4.40); N, 6.14 (6.10). IR (ν, cm<sup>-1</sup>): [ν(O-H) 3371, ν(OH<sub>2</sub>) 851]; 1627 ν(C=N), 1597; ν(C-OPh), 1236; ν(C-OMe), 1201. Λ (S.cm<sup>2</sup>.mol<sup>-1</sup>): 3. μ<sub>eff</sub> (MB): 1.70.

### 2.3. Preparation of the the complex [{6, 6'-di-methoxy-2,2'-[1,2-phenylenebis(nitrilomethylidyne)]diphenolato-κ<sup>8</sup>1:2O<sup>6</sup>, O<sup>1</sup>,O<sup>1</sup>, O<sup>6'</sup>:-O<sup>1</sup>, N, N', O<sup>1</sup>}(ethanol-κO)copper(II)natrium(I)] (μ<sub>2</sub>-1,5-dicyanamido-κ<sup>2</sup>N<sup>1</sup>:N<sup>5</sup>)[{6, 6'-di-methoxy-2,2'-[1,2-phenylenebis(nitrilomethylidyne)]diphenolato-κ<sup>8</sup>1:2O<sup>6</sup>, O<sup>1</sup>,O<sup>1</sup>, O<sup>6'</sup>:-O<sup>1</sup>, N, N', O<sup>1</sup>}(dicyanamido-κN<sup>1</sup>)copper(II)natrium(I)] (2).

To a solution of [Cu(L)]·H<sub>2</sub>O (**1**) (1 mmol, 0.4556 g) in 5 mL of DMF was added a solution of Na[N(CN)<sub>2</sub>] (3 mmol, 0.261 g) in 5 mL of ethanol. The mixture was refluxed for two hours. On cooling greenish precipitate, which appears, was recovered by filtration. The filtrate was left for slow evaporation. On standing for two weeks, green crystals of (**2**) suitable for X-ray diffraction were isolated. Yield: 55%. Elemental Anal. Found (Calcd.) (%): C, 54.59 (54.57); H, 3.85 (3.81); N, 12.73 (12.69). IR (ν, cm<sup>-1</sup>): ν(C=N) = 1599; ν(C-OPh) = 1241; ν(C-OMe) 1197; ν(C≡N): 2250, 2201 and 2142. Conductance Λ (S.cm<sup>2</sup>.mol<sup>-1</sup>) = 5. μ<sub>eff</sub> (MB): 3.40.

### 2.4. X-ray crystallography

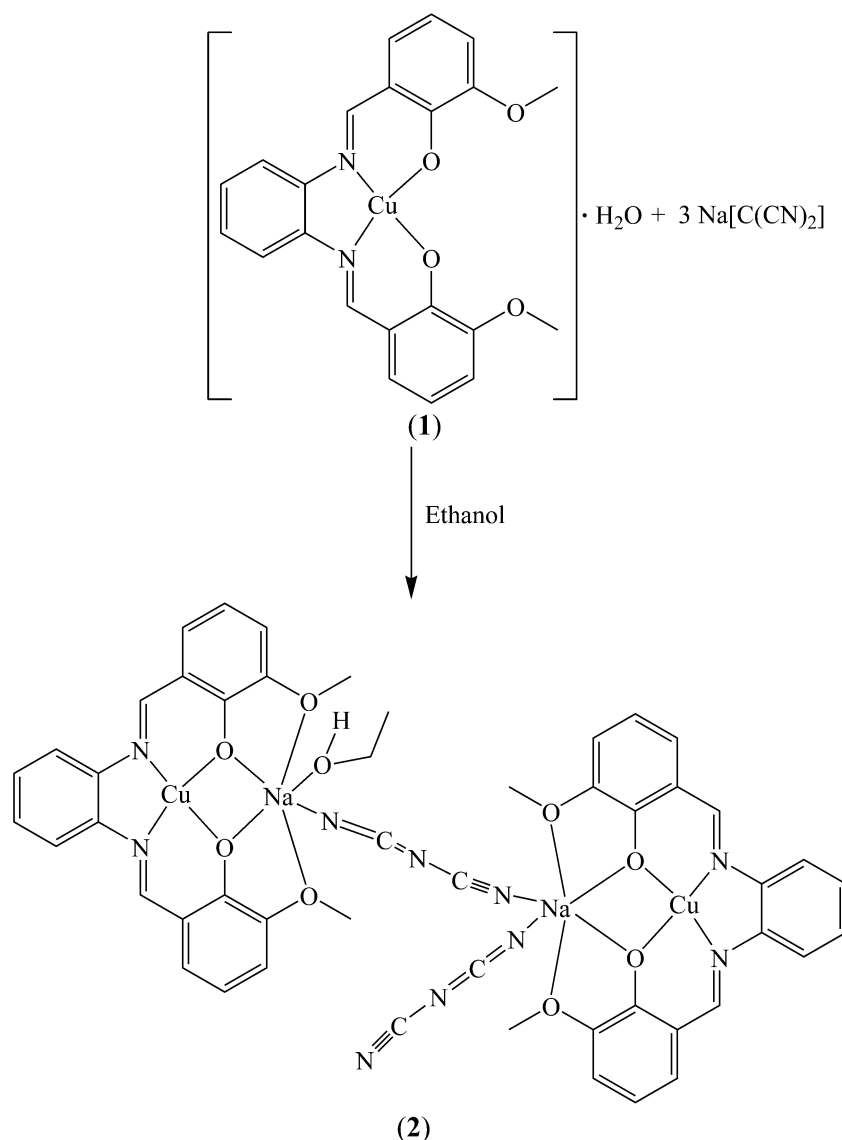
Crystals suitable for single-crystal X-ray diffraction, of the reported compounds, were grown by slow evaporation of EtOH solution of the complexes. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [31]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F<sup>2</sup> by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [32]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH<sub>3</sub> groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [33].

## III. Results and discussion

### 3.1. General study

H<sub>2</sub>L react with CuCl<sub>2</sub>·2H<sub>2</sub>O to afford a mononuclear hydrated copper(II) complex [(CuL)·(H<sub>2</sub>O)] as shown in scheme 1. The FT-IR spectrum of complex (**1**), the broad band at 3371 cm<sup>-1</sup> combined with the band at 851 cm<sup>-1</sup> indicated the presence of lattice water molecule. In fact, the first band is due to the ν<sub>O-H</sub> stretching vibration, while the second one is due to the δ<sub>O-H</sub> deformation. A medium intensity band at 1627 cm<sup>-1</sup> is indicative of the presence of a C=N function which is coordinated through the azomethine atom to the metal ion. A DMF solution of complex [(CuL)·(H<sub>2</sub>O)] is treated with Na[N(CN)<sub>2</sub>] and the tetranuclear compound [{Cu(μ-L)Na(EtOH)}][μ<sub>2</sub>-1,5-(N(CN)<sub>2</sub>)]<sub>2</sub> [(Cu(μ-L)Na(N(CN)<sub>2</sub>))] (**2**) was obtained on standing for two week as green crystals (Scheme 1). The IR spectrum of compound (**2**) exhibits a sharp medium intensity band at 2201 cm<sup>-1</sup>, 2142 cm<sup>-1</sup> and 2250 cm<sup>-1</sup> which are characteristic of a coordinated dicyanamide group [34]. Additional bands at 3382 cm<sup>-1</sup> and 1604 cm<sup>-1</sup> are observed and are attributed, respectively, to the coordinated molecule solvent of

ethanol and the coordinated C=N group. The molar conductivity which is  $3 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for (1) and  $6 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  for (2) shows that the complexes are neutral electrolyte in DMF solution [35]. The bands signature of aromatic ring vibration are observed in the region of  $1400\text{--}1500 \text{ cm}^{-1}$  [36].



**Scheme 1.** Synthesis procedure of the metallo-ligand (1) and the complex (2).

Magnetic moment at room temperature are  $1.70 \mu_{\text{B}}$  for (1) and  $3.40 \mu_{\text{B}}$  for (2). The magnetic moment value of (1) is close proximity of the spin only value of  $1.73 \mu_{\text{B}}$  expected for one  $d^9$  copper(II) ion [37]. The magnetic moment for complex (2) is close proximity to the value of  $3.46 \mu_{\text{B}}$  expected for the simultaneous presence of two independent copper(II) ions [38]. These absence of exchange interactions between the two  $d^9$  copper(II) present in complex (2) is compatible with the long Cu–Cu distance of  $14.338 \text{ \AA}$  observed in the structure.

**Table-1.** Crystal data and details of the structure determination of the complex 1.

Chemical formula	$\text{C}_{50}\text{H}_{42}\text{Cu}_2\text{N}_{10}\text{Na}_2\text{O}_9$
Mr	1099.99
Crystal shape/color	Prismatic/Green
Crystal system, space group	Triclinic, P1
Crystal size (mm)	$0.1 \times 0.09 \times 0.07$
$a$ (Å)	11.4090 (4)

<i>b</i> (Å)	12.5916 (5)
<i>c</i> (Å)	17.7482 (6)
$\alpha$ (°)	104.328 (3)
$\beta$ (°)	103.276 (3)
$\gamma$ (°)	91.285 (3)
<i>V</i> (Å <sup>3</sup> )	2395.82 (16)
<i>Z</i>	2
<i>D</i> <sub>cal</sub> (g cm <sup>-3</sup> )	1.525
Mo K $\alpha$ (Å)	0.71073
<i>T</i> (K)	293
$\mu$ (mm <sup>-1</sup> )	0.98
Index ranges	-13 ≤ <i>h</i> ≤ 13; -15 ≤ <i>k</i> ≤ 15; -21 ≤ <i>l</i> ≤ 21
<i>F</i> (000)	1128
$\theta$ range (°)	1.675-25.242
No. of measured reflections	62589
No. of independent	8779
No. of observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	7029
<i>R</i> <sub>int</sub>	0.086
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.053
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.203
Goodness-of-fit (Gof)	1.08
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.68, -1.41

### 3.2. Structure of the complex (2)

Complex (2) formulated as  $[\{\text{Cu}(\mu\text{-L})\text{Na}(\text{EtOH})\}][\mu\text{-1,5-(N(CN)}_2)]\{\{\text{Cu}(\mu\text{-L})\text{Na}(\text{N(CN)}_2)\}\}$  crystallizes in the triclinic system with a space group *P*1. The crystal data collection and refinement are reported in Table 1. The ORTEP diagram of the structure of the heteronuclear complex is illustrated in Figure 1. Selected bonds lengths and angles are listed in Table 2. The structure of the neutral tetranuclear complex consists of two heterodinuclear units  $[\text{Cu}(\mu\text{-L})\text{Na}(\text{EtOH})]$  and  $[\text{Cu}(\mu\text{-L})\text{Na}(\text{N(CN)}_2)]$  bridged by the ambidentate dicyanamide  $[\text{N(CN)}_2]^-$  anion. Each of the two bridged entities contains one tetracoordinated copper(II) ion and one hexacoordinated sodium(I) ion. In the first unit the  $\text{Na}^{\text{I}}$  cation is coordinated by an ethanol molecule while in the second unit, the  $\text{Na}^{\text{I}}$  cation is coordinated by a terminal dicyanamide  $[\text{N(CN)}_2]^-$  anion. Both copper(II) ions are situated in a very slightly distorted  $\text{N}_2\text{O}_2$  square planar geometry with tetragonality index  $\tau_4$  of 0.005177 (Cu1) and 0.00007 (Cu2) ( $\tau_4 = (360 - \beta - \alpha)/141$ ;  $\alpha$  and  $\beta$  are the two largest angles around the central atom:  $\tau_4 = 0$  designates a perfect square planar geometry and  $\tau_4 = 1$  gives a perfect tetrahedron) [39]. The square base of each copper ion is defined by two phenolate oxygen atoms and two imino nitrogen atoms from the ligand. Both of the angles around the Cu1 ion (N1–Cu1–N2 and O1–Cu1–O3) and both angles around the Cu2 ion (N9–Cu2–N10 and O6–Cu2–O7) are smaller than the ideal value of 90° [overall range 84.57(12)–85.51(11)] while the *cisoid* N–Cu–O angles [overall range 94.62(11)–95.35(11)] are greater than the ideal value of 90°. The *transoid* O–Cu–N angles also deviate slightly from the ideal angle value of 180° [overall range 177.20(11)–179.67(12)]. The Cu1 and Cu2 copper ions are respectively displaced by 0.0117 Å and -0.0027 Å from the square base. The average Cu–O and Cu–N are 1.891 Å and 1.940 Å, respectively and are comparable to the values reported for the similar complex  $[\{\text{Cu}(\text{L})\text{Na}(\text{ClO}_4)\}_2(\mu\text{-H}_2\text{L})]$  ( $\text{H}_2\text{L}$  is 2-(2-(2-hydroxy-3-methoxybenzylideneamino)-1,2-diphenylethylimino)methyl)-6-methoxyphenol) [40]. Among the two dicyanamide groups present in the crystal, one is  $\mu\text{-1,5}$ -bridging and one is unidentate terminal. The Na1 of the first unit and the Na2 of the second unit are linked by one dicyanamide group in  $\mu\text{-1,5}$ - mode through the nitrile nitrogen atoms. The Na2 ion is also linked to the unidentate dicyanamide group through one nitrile nitrogen atom, while the second nitrile nitrogen atom remains uncoordinated. The bond angles N/O–Na–N/O are 60.45(9)–172.21(11)° (Na1) and 61.27(9)–

169.76(11)° (Na2). The environment around the two Na<sup>I</sup> are best described as a pentagonal pyramidal. Each of the two basal planes around the Na<sup>I</sup> ions are occupied by two phenolate oxygen anions, two methoxy oxygen atoms and one nitrile nitrogen atom from the bridged dicyanamide group. The apical positions are occupied by a nitrile nitrogen atom from the unidentate dicyanamide group for Na1 ion and an ethoxy oxygen atom for Na2 ion. In each unit the two different geometries of the copper ion and the sodium ion share a common edge defining by the bridged phenolate cation. The bridge angles in the two units Cu1–O2–Na1, Cu1–O3–Na1, Cu2–O6–Na2 and Cu2–O7–Na2 are 104.18(11)°, 105.02(11)°, 104.65(11)° and 104.34(11)° respectively. The Cu1O2Na1O3 (rms 0.0294) and Cu2O6Na2O7 (rms 0.0252) cores are almost planar. The dihedral angle between O2Cu1O3 and O2Na1O3 planes is 3.58° while the planes O6Cu2O7 and O6Na2O7 form a dihedral angle of 4.13°. The Cu1···Na1 and the Cu2···Na2 distances are respectively 3.378(2) Å and 3.400(1) Å. The Na–O<sub>methoxy</sub> [2.603(3)–2.650(3) Å] bond distances are longer than the bridging Na–O<sub>phenoxo</sub> [2.368(3)–2.403(3) Å] bond distances. The distances are comparable to the values observed for a similar complex [Cu(vanpn)Na(N<sub>3</sub>)(CH<sub>3</sub>OH)] (H<sub>2</sub>vanpn is *N,N'*-propylene-bis(3-methoxysalicylideneimine) [41]. The tetranuclear units are connected by weak intermolecular hydrogen bonds of type C–H···N (C8–H···N3<sup>i</sup>, –x+2, –y+2, –z+2) and C–H···O (C37–H···O9<sup>ii</sup>, (ii) –x, –y, –z+1) (Table 3). The combined hydrogen bonds arranged the tetranuclear units into layers parallel to *a* axis (Figure 2).

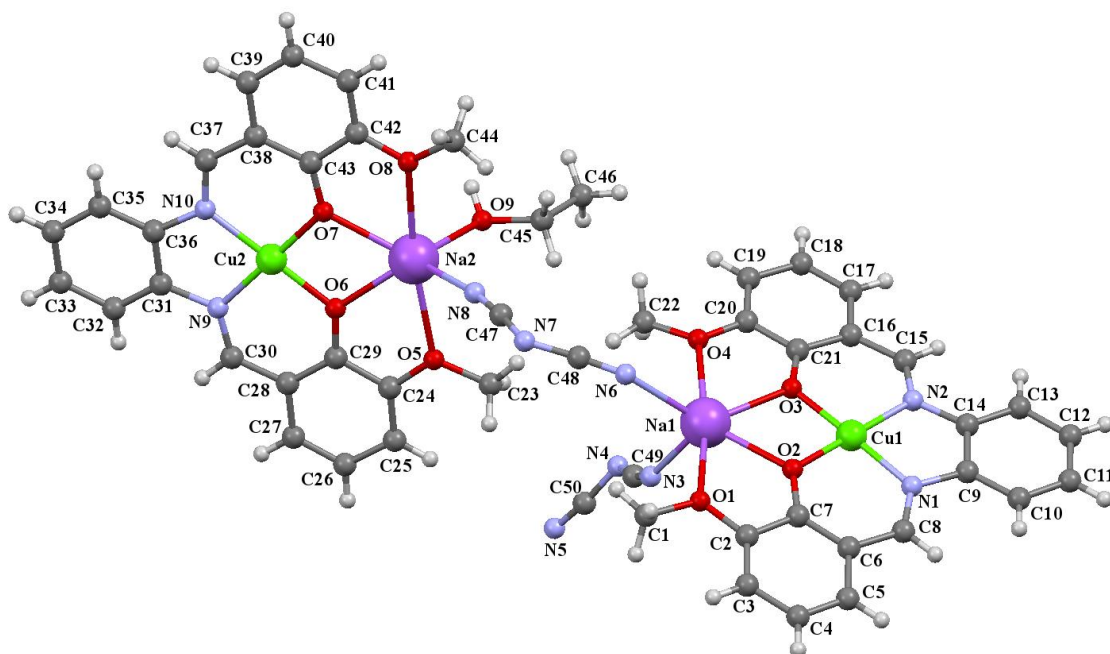
**Table-2.** Selected bond distances [Å] and angles [°] for the complex.

Cu1–O2	1.889 (2)	Na1–O2	2.403 (3)
Cu1–O3	1.897 (2)	Na1–N6	2.415 (4)
Cu1–N1	1.940 (3)	Na1–N3	2.416 (5)
Cu1–N2	1.940 (3)	Na1–O4	2.603 (3)
Cu1–Na1	3.4001 (15)	Na1–O1	2.613 (3)
Cu2–O6	1.883 (3)	Na2–O7	2.368 (3)
Cu2–O7	1.893 (2)	Na2–O6	2.368 (3)
Cu2–N9	1.940 (3)	Na2–N8	2.406 (5)
Cu2–N10	1.941 (3)	Na2–O9	2.443 (4)
Cu2–Na2	3.3777 (16)	Na2–O5	2.605 (3)
Na1–O3	2.373 (3)	Na2–O8	2.650 (3)
O2–Cu1–O3	85.51 (11)	O7–Na2–O6	65.45 (9)
N1–Cu1–N2	84.57 (12)	O6–Na2–O5	61.88 (10)
O6–Cu2–O7	85.40 (11)	O7–Na2–O8	61.27 (9)
N9–Cu2–N10	84.79 (13)	Cu1–O3–Na1	105.02 (11)
O3–Na1–O2	65.11 (9)	Cu2–O7–Na2	104.34 (11)
O3–Na1–O4	61.42 (9)	Cu2–O6–Na2	104.65 (11)
O2–Na1–O1	60.45 (9)	Cu1–O2–Na1	104.2(1)

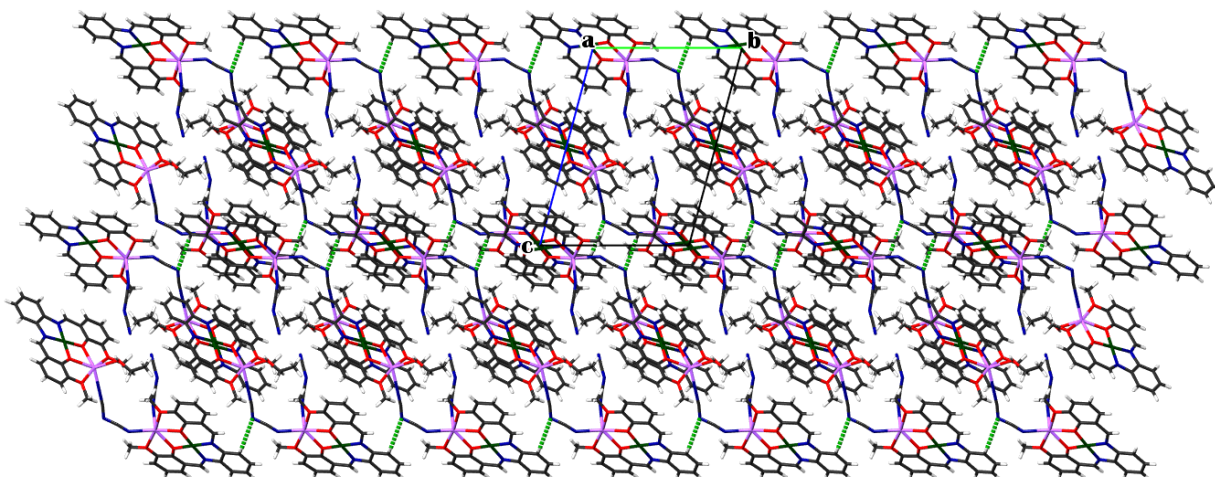
**Table-3.** Hydrogen-bond geometry (Å, °) in the complex (2).

D–H···A	D–H	H···A	D···A	D–H···A
C8–H8···N3 <sup>i</sup>	0.93	2.52	3.412 (5)	160.8
C37–H37···O9 <sup>ii</sup>	0.93	2.64	3.511 (5)	155.7

Symmetry codes: (i) –x+2, –y+2, –z+2; (ii) –x, –y, –z+1.



**Figure 1:** The crystal structure of the complex (2). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small sphere.



**Figure 2:** Layers of the complex (2) viewed along the *a* axis.

#### IV. Conclusion

The reported work is concerned the synthesis of a copper(II) metallo-ligand and its use to prepare a new tetranuclear compound. The reaction of the bicompartamental Cu(II) metallo-ligand and Na(I) dicyanamide salt afford interesting heteronuclear compound  $[\{Cu(\mu-L)Na(EtOH)\}(\mu-1,5-N(CN)_2)\{Cu(\mu-L)Na(N(CN)_2)\}]$ . In the yielded crystal the copper (II) ion occupied the inner  $N_2O_2$  site, while the Na(I) ion is situated in the outer  $O_2O'_2$  site. Both copper(II) ions are tetraordinated, while both Na(I) are hexacoordinated. The different dinuclear units  $[Cu(\mu-L)Na(EtOH)]$  and  $[(Cu(\mu-L)Na(N(CN)_2))]$  are bridged by the ambidentate dicyanamide anion acting as  $\mu-1,5$ -bridging ligand through the terminal nitrogen atoms. One dicyanamide anion acts as terminal ligand. In the structure, each of the two Cu(II) are situated in a square planar environment, while each of the two Na(I) occupy a pyramidal pentagonal environment. In each unit, the square planar geometry around Cu(II) and the pyramidal pentagonal environment around Na(I) share one vertex.

## V. Supporting information

CCDC-2080369 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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Pokpa HABA, et. al. "Syntheses, characterization, and X-ray crystal structure of heteronuclear dicyanamide-bridged Cu/Na Assembled with Salen-type Schiff Base and Dicyanamide." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 14(4), (2021): pp 57-64.