



Synthesis and crystal structure of a distorted face sharing double cubane like tetranuclear Ni^{II}-Cu₂^{II}-Ni^{II} compound derived from a reduced di-Schiff base ligand

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One new tetranuclear face sharing distorted double cubane like hetero-metallic Ni^{II}₂Cu₂^{II} compound has been synthesized using a [NiL^R] “metalloligand”, where H₂L^R = N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine. The compound has been characterized by elemental analysis, spectroscopic methods and single crystal XRD. In the compound, in addition to the μ_2 -phenoxido bridges, the two terminal Ni^{II} atoms are linked to each of the central Cu^{II} ion by means of an end-on bridging azido ($\mu_{1,1}$ -N₃) ion separately, resulting a tetranuclear cubane like structure.

Keywords: Nickel(II), Copper(II), Tetranuclear, Reduced Schiff base, End-on azide

Interest in the study of hetero-metallic coordination compounds with first row (3d) transition elements has amplified appreciably to the synthetic inorganic chemists due to their vast applications in the field of structural chemistry, medicinal chemistry, magneto-chemistry and catalysis since last few decades¹⁻⁴. In literature, there are several synthetic protocols to prepare hetero-metallic polynuclear coordination compounds. Amongst, the most constructive one is previously synthesized metal complex with active bridging atoms or groups⁵. Accordingly, neutral chelate complexes of N₂O₂ donor salen type Schiff bases have been selected as a bidentate “metalloligands” by various research groups⁶⁻⁷, to produce polynuclear hetero-metallic complexes, with fascinating structural variation. In recent times, we have found that the neutral chelates of reduced salen type di-Schiff bases have also been used as “metalloligands” in parallel to their unreduced species⁸. Interestingly, these reduced species often exhibit interesting structural variation, because of the higher flexible ligand backbone and the possibility of forming different weak interactions like H-bonds⁸⁻⁹.

The main goal of synthesizing hetero-metallic polynuclear compounds is to study their intriguing structural properties. It is worth mentioning that a large number of homo-nuclear compounds have been studied by using different 3d transition elements (like Cu(II), Ni(II), Mn(II), Fe(III), Co(II) etc.)¹⁰⁻¹¹ but the extensive work on hetero-metallic systems is still comparatively less in number. From the literature

study on hetero-metallic compounds with N₂O₂ donor di-Schiff base ligands, it has been noticed that most of these species have been prepared by using Cu(II)- or Ni(II)-metalloligands¹². More specifically, these two “metalloligands” are well established for synthesizing some dinuclear,^{12b} and mostly trinuclear M₂Cu₂¹³ or M₂Ni₂¹⁴ (M = bivalent hetero-metal) complexes. However, the numbers of tetranuclear hetero-metallic complexes, M₂Cu₂¹⁵ or M₂Ni₂¹⁶ are quite a few with both of the “metalloligands”. In a wider view, we have found that the complexes derived from Cu(II)-metalloligand are comparatively greater in number than the Ni(II) ones. When we spotlight our search only on hetero-metallic compounds with Ni(II)-metalloligands (*i.e.* Ni(II) serves as a terminal metal center in trinuclear or tetranuclear species), we find some compounds of different hetero-metallic combinations like Ni(II)-Mn(II), Ni(II)-Fe(III), Ni(II)-Co(II), Ni(II)-Zn(II), Ni(II)-Cd(II), Ni(II)-Hg(II) etc.^{7,14,16} but the compounds with the combination of Ni(II)-Cu(II) is scanty. In fact, it is seen that using the Ni(II)-metalloligands of salen type Schiff bases and copper as the central metal ion, the number of trinuclear Cu^{II}Ni^{II}₂ species is only four¹⁷ and there is no single report of tetranuclear structure (Ni^{II}-Cu₂^{II}-Ni^{II}) till the date. Although, there is a report of hetero-metallic tetranuclear compound derived from Ni(II)-metalloligand with salen type Schiff base in the literature but the hetero-metal used there, is Pb, not any transition metal¹⁸. Therefore, here we are interested to explore the field of coordination

compounds with the rare Ni(II)-Cu(II) combination (in which Ni(II) and Cu(II) would serve as terminal and central metal ions, respectively) with help of a reduced salen type Schiff base ligand.

In this study, we have focused mainly the synthesis, spectroscopic analysis and crystal structure of an unusually combined Ni(II)-Cu(II) tetranuclear compound based on Ni(II)-“metalloligand” $[\text{NiL}^{\text{R}}]$ [Where, $\text{H}_2\text{L}^{\text{R}} = N,N'$ -bis(2-hydroxybenzyl)-1,3-propanediamine]. The studied compound is the rare report of $\text{Ni}^{\text{II}}\text{-Cu}_2^{\text{II}}\text{-Ni}^{\text{II}}$ tetranuclear double cubane like structure, derived from a reduced salen type di-Schiff base ligand, in which Ni(II) and Cu(II) serve as terminal and central metal ions.

Experimental Details

Materials

Salicylaldehyde, 1,3-propanediamine and sodium borohydride have been bought from Lancaster and of reagent grade. They were used directly with no purification.

Caution! Metal perchlorate complexes with organic ligands are possibly explosive. So, material should be prepared in a small quantity and it should be treated with an intensive care.

Syntheses of the reduced salen type Schiff base ligand, N,N' -bis(2-hydroxybenzyl)-1,3-propanediamine ($\text{H}_2\text{L}^{\text{R}}$) and its corresponding reduced “metalloligand” $[\text{NiL}^{\text{R}}]$

The salen type Schiff base ligand, H_2L was prepared from salicylaldehyde and 1,3-propanediamine by a standardised procedure¹⁹: salicylaldehyde (10 mmol, 1.04 mL) was reacted with 1,3-propanediamine (5 mmol, 0.42 mL) in 30 mL methanol solution. The mixture produced was refluxed under water bath for *ca.* 1.5 h and afterwards it was kept for 20 min to cool. Then the resulting 30 mL (5 mmol) of yellow coloured ligand solution (H_2L) was cooled to 0 °C and in this solution, solid sodium borohydride (456 mg, 12 mmol) was added gradually with constant stirring with a glass rod. The consequential white solution was acidified with 8 mL concentrate hydrochloric acid solution and then evaporated to dryness on a hot water bath²⁰. The reduced di-Schiff base ligand, $\text{H}_2\text{L}^{\text{R}}$ was isolated from the solid mass with methanol, and the resulting 30 mL colourless solution was mixed with a methanol solution (10 mL) containing 5 mmol $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.820 g) and 10 mL of ammonia solution (20%) to synthesize the reduced Ni(II) based “metalloligand”²¹ as a solid green powder that was filtered, washed with

methanol and dried in a desiccator containing anhydrous CaCl_2 [Yield: 1.245 g, 69%].

Synthesis of the compound $[(\text{NiL}^{\text{R}})_2\text{Cu}_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2(\text{H}_2\text{O})_2] \cdot 2(\text{CH}_3)_2\text{CO}$ (**1**)

The precursor chelate species $[\text{NiL}^{\text{R}}]$ (0.708 g, 2 mmol) was taken in 20 mL methanol and then an aqueous solution (1 mL) of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.740 g, 2 mmol), an aqueous solution (1 mL) of sodium azide (0.328 g, 4 mmol), were mixed to this alcohol solution. The mixture was kept in a magnetic stirrer for constant stirring around four hours and filtered. The filtrate was allowed to stand overnight to obtain a dark brown microcrystalline crude product of compound **1**. The obtained crude product was dissolved in acetone solvent and filtered. Then the filtrate was allowed to stand overnight to get deep brown rhombic-shaped X-ray quality single crystals of **1**. The crystals (**1**) were washed with acetone-water mixture carefully and dried in a desiccators containing anhydrous CaCl_2 and then characterized by elemental (C, H and N) analysis, UV-visible spectroscopy, IR-spectroscopy and X-ray diffraction study.

Compound 1: Yield of the product: 0.737 g, 59%. Analytical Calculation for $\text{C}_{46}\text{H}_{68}\text{Cu}_2\text{N}_{16}\text{Ni}_2\text{O}_{10}$: C 44.21, H 5.48, N 17.93 %. Found: C 44.33, H 5.35, N 17.85%. UV/visible: $[\lambda_{\text{max}}$ in nm (ϵ_{max} in $\text{M}^{-1} \text{cm}^{-1}$)] (MeCN) = 568(508), 310(18951) and 270(30545). IR (KBr) cm^{-1} : $\nu(\text{N-H})$ 3248, $\nu(\text{N}_3^-)$ 2079, 2051.

Physical Measurements

C, H and N elemental analyses have been performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets in a range of 4000–400 cm^{-1} have been recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. UV-spectra in acetonitrile solution have been recorded in a Hitachi U-3501 spectrophotometer from 800 nm to 200 nm range.

Crystallographic data collection and refinement

A good quality single crystal of compound **1** was mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at room temperature. The single crystal was placed at 60 mm from the CCD. Frames (360) were calculated with a counting time of 10 s. The structure was solved using the Patterson method through the SHELXS 97 program. Non-hydrogen atoms were refined with independent anisotropic displacement parameters,

while subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. The hydrogen atoms bound to carbon or nitrogen atoms were placed in idealised geometric positions and given the displacements parameters equivalent to 1.2 (or 1.5 for “Me” groups) times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least-squares refinement. Absorption corrections were carried out using the SADABS program²², while all calculations were made *via* SHELXS 97²³, SHELXL 97²⁴, PLATON 99²⁵, ORTEP-32²⁶, WINGX system ver-1.64²⁷ and refined using refined using SHELXL-2014²⁸. Collection of Data, crystallographic information, and structure refinement parameters for the compound are given in Table 1.

Results and discussion

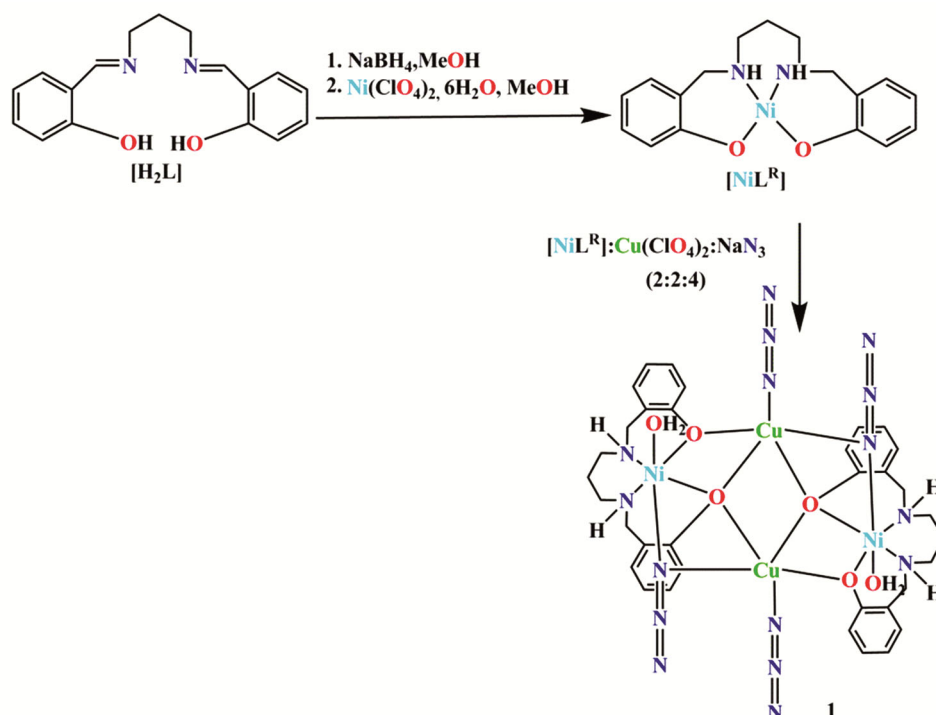
Synthesis of the compound 1

The reduced di-Schiff base ligand (H_2L^R) and its subsequent “metalloligand” $[NiL^R]$ were prepared using the well known procedure¹⁹⁻²¹. In this study, the metalloligand $[NiL^R]$ was reacted with Cu(II) perchlorate salt and sodium azide in 2:2:4 molar ratio in MeOH:H₂O 10:1 (v/v) medium, resulted in a

rare tetranuclear compound, $[(NiL^R)_2Cu_2(\mu_{1,1}-N_3)_2(N_3)_2(H_2O)_2] \cdot 2(CH_3)_2CO$ (**1**) (Scheme 1).

Table 1 — Crystal data and structure refinement parameters of compound **1**

Formula	C ₄₆ H ₆₈ Cu ₂ N ₁₆ Ni ₂ O ₁₀
M	1249.64
Crystal System	Triclinic
Space Group	$P\bar{1}$
<i>a</i> /Å	10.651(5)
<i>b</i> /Å	11.786(5)
<i>c</i> /Å	12.515(5)
α /°	98.767(5)
β /°	104.694(5)
γ /°	106.940(5)
<i>V</i> /Å ³	1409.6(11)
Z	1
<i>D_c</i> /g cm ⁻³	1.472
μ /mm ⁻¹	1.469
F (000)	650
R(int)	0.051
Total Reflections	13022
Unique reflections	4926
<i>I</i> > 2 σ (<i>I</i>)	3518
R1 ^a , wR2 ^b	0.0407, 0.1346
GOF ^c on F ²	1.03
R (all)	0.0965
Temp (K)	293
^a R1 = $\sum F_o - F_c / \sum F_o $, ^b wR2 (F _o ²) = $[\sum [w(F_o^2 - F_c^2)^2] / \sum w F_o^4]^{1/2}$ and ^c GOF = $[\sum [w(F_o^2 - F_c^2)^2] / (N_{obs} - N_{params})]^{1/2}$	



Scheme 1 — Synthesis of compound **1**

IR and UV-visible spectra

In addition to the elemental analysis, the compound was characterized by IR spectroscopy. The IR spectrum (Fig. S1, Supplementary Data) shows a quite strong and fine peak at 3248 cm^{-1} (because of N-H stretching vibration) and the non-appearance of any sharp peak at around 1620 cm^{-1} , signifying that the imine moiety of the di-Schiff base is reduced⁸⁻⁹. Besides, the appearance of strong and sharp peak at 2079 cm^{-1} along with a shoulder at 2051 cm^{-1} indicating the presence of azido ligands in compound **1**. The splitting of the band is an indicative of the existence of two different kind of coordinated azido ions (one is terminal and another is bridging) in support to its crystal structure.

The UV-visible spectrum of the compound was recorded in acetonitrile solution. As shown in Fig. S2 in Supplementary Data, the complex gives a broad absorption spectrum in the visible region at 568 nm, pointed to *d-d* transitions of Ni(II) ions for an octahedral environment, which is also seen in the “metalloligand” $[\text{NiL}^{\text{R}}]$ precursor compound. Additionally, it shows a sharp absorption band at *ca.* 310 and 270 nm (Fig. S3, Supplementary Data), accredited to ligand to metal charge transfer bands.

Description of crystal structure of compound **1**

The discrete face sharing distorted cubane like tetranuclear structure of compound **1**, along with the atomic numbering scheme is depicted in Fig. 1. The selected bond lengths and the bond angles around the metal centres are shown in Table 2. The tetranuclear

structure has a crystallographic inversion centre which is situated in the middle of the two central copper metal ions. The asymmetric unit is built with two metal centres (one is terminal Ni(II) and another is central Cu(II)), two azido ions (one is bridging and other one is terminal), one dianionic reduced di-Schiff base ligand $[(\text{L}^{\text{R}})^{2-}]$, and a water molecule (coordinated to Ni(II)). The two axial positions of terminal Ni(II) centre are bridged by a N-atom from a bridging azido ligand ($\mu_{1,1}\text{-N}_3$) at a length of $2.111(4)\text{ \AA}$ and an O-atom from a linked water molecule at a distance of $2.095(4)\text{ \AA}$. On the other hand, the basal plane of Ni(II) is formed by the two phenoxido O-atoms and two N-atoms from the deprotonated tetradentate reduced Schiff base ligand $[(\text{L}^{\text{R}})^{2-}]$. Thus Ni(II) presents a distorted octahedral geometry. The Ni(II)-O bond distances of the basal plane are almost in the similar range [$2.083(3)\text{--}2.087(3)\text{ \AA}$] and which are slightly shorter than the axial Ni(II)-O one, [$2.095(4)\text{ \AA}$]. In the same way, the basal Ni(II)-N bond lengths [$2.079(4)\text{--}2.103(4)\text{ \AA}$] are also slightly shorter with respect to the axial Ni(II)-N bond distance, [$2.111(4)\text{ \AA}$] (Table 2). The root mean squared deviation (r.m.s.) of the four donor atoms in the basal plane is $0.318(1)\text{ \AA}$, while the nickel metal ion is $0.274(1)\text{ \AA}$ shifted from the mean plane in the direction of O(1). The dihedral angle between two planes, N(18)-Ni(1)-O(10) and N(22)-Ni(1)-O(30) [$4.6(1)^\circ$] and the range of *cis* [$76.9(1)\text{--}100.3(2)^\circ$] and *trans* angles [$169.2(1)\text{--}172.2(1)^\circ$] (Table 2) of the terminal Ni(II) centre point out the presence of a

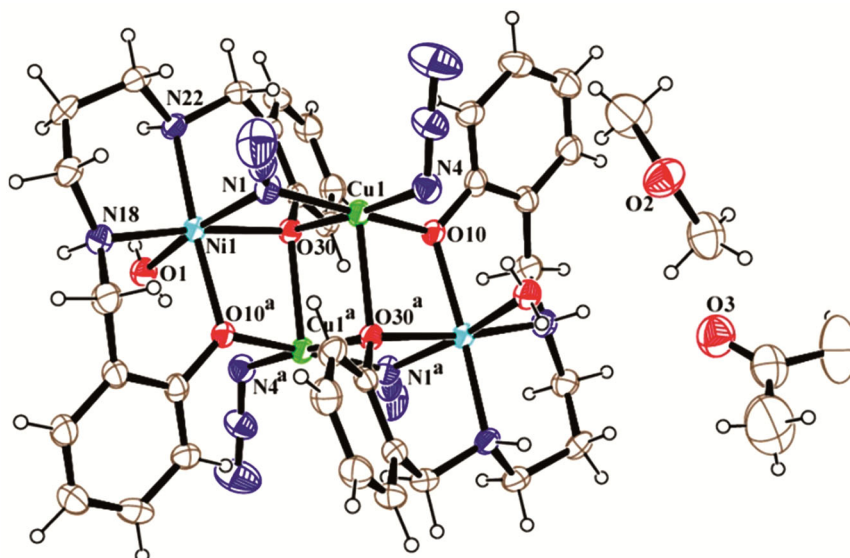


Fig. 1 — The structure of compound **1** with ellipsoids at 30% probability, Symmetry transformation ^a = 1-x, 1-y, -z

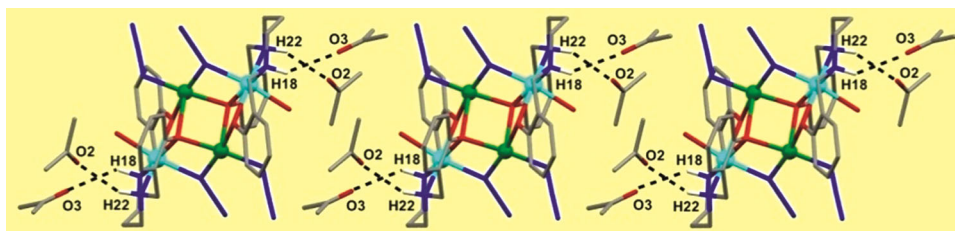


Fig. 2 — H-bonding interactions between acetone solvent molecule and the tetranuclear structure [O(3/2)···H(18/22)–N(18/22)]. Other H-atoms have been removed for clarity

Table 2 — Bond parameters (distances in Å and angles in ° unit) for compound **1**

Bond Parameters	1
Ni(1)–O(10) ^a	2.083(3)
Ni(1)–O(30)	2.087(3)
Ni(1)–N(18)	2.079(4)
Ni(1)–N(22)	2.103(4)
Ni(1)–N(1)	2.111(4)
Ni(1)–O(1)	2.095(4)
Cu(1)–O(10)	1.955(3)
Cu(1)–O(30)	2.019(3)
Cu(1)–O(30) ^a	2.327(4)
Cu(1)–N(1)	1.979(4)
Cu(1)–N(4)	1.974(4)
O(1)–Ni(1)–O(30)	92.4(1)
O(1)–Ni(1)–N(1)	169.2(1)
O(1)–Ni(1)–N(18)	89.9(2)
O(1)–Ni(1)–N(22)	92.6(2)
O(1)–Ni(1)–O(10) ^a	84.1(1)
N(1)–Ni(1)–O(30)	76.9(1)
N(1)–Ni(1)–O(10) ^a	92.1(1)
N(1)–Ni(1)–N(18)	100.3(2)
N(1)–Ni(1)–N(22)	89.9(2)
O(30)–Ni(1)–N(22)	91.7(1)
O(10) ^a –Ni(1)–N(18)	91.4(1)
O(10) ^a –Ni(1)–O(30)	81.4(1)
N(18)–Ni(1)–N(22)	95.7(2)
O(10) ^a –Ni(1)–N(22)	172.2(1)
O(30)–Ni(1)–N(18)	172.1(2)
O(30) ^a –Cu(1)–N(4)	95.5(1)
O(30) ^a –Cu(1)–O(30)	88.2(1)
O(30) ^a –Cu(1)–N(1)	105.2(1)
O(30) ^a –Cu(1)–O(10)	78.3(1)
N(1)–Cu(1)–N(4)	95.8(2)
O(30)–Cu(1)–O(10)	88.4(1)
N(1)–Cu(1)–O(30)	81.6(1)
O(10)–Cu(1)–N(4)	93.9(1)
Ni(1)–O(30)–Cu(1)	99.2(1)
Cu(1)–N(1)–Ni(1)	99.7(2)

Symmetry element^a = 1-x, 1-y, -z for complex **1**

slight distortion from the ideal octahedral geometry. The central Cu(1) presents a square pyramid geometry [CuO₃N₂] where the equatorial plane is constructed by the coordination of two μ_2 -phenoxido O-atoms from

the two separate de-protonated reduced Schiff-base ligand [(L^R)²⁻] and two N-atoms from two distinct azido ligands (one is bridging, $\mu_{1,1}$ -N₃ and other one is terminal azido ion). The axial position is coordinated by the μ_2 -phenoxido oxygen atom of a di-anionic reduced Schiff base ligand [(L^R)²⁻]. The basal Cu-O bond distances are almost in similar range [1.955(3)–2.019(3) Å] but those are considerably shorter than the axial one [2.327(4) Å] (Table 2).

The range of *cis* angles [78.3(1)–105.2(1)°] around central Cu centre is also an indicative of a distortion from the ideal square pyramidal geometry of Cu(II). The Ni(1)···Cu(1) distance is 3.208(2) Å and the two Ni-O-Cu bond angles are: 99.2(1)° and 105.2(2)°.

It is important to mention here that two similar types of H-bonding have been found in the crystal packing of compound **1**, as shown in Fig. 2. These weak H-bonding interactions are constructed between the O atoms (O3 and O2) of the acetone molecules with the hydrogen atoms (H18 and H22) of the reduced imine moiety of the complex, N(18)–H(18)···O(3) (1-x, 1-y, -z) and N(22)–H(22)···O(2) (x, y, -1+z) with dimensions H···O 2.60(6) and 2.34(4) Å, N–H···O 141(5) and 155(3)° and N···O 3.367(7) and 3.219(5) Å, respectively.

Conclusions

In this report, the use of early synthesized ligand in preparing polynuclear hetero-metallic compounds has shown one more time to be a very effective and simple synthetic tools. Here we have shown how the employment of a previously synthesized ligand compound [NiL^R] [H₂L^R = N,N'-bis(2-hydroxybenzyl)-1,3-propanediamine] towards the central copper metal ions has yielded an unusual tetranuclear Ni₂^{II}-Cu₂^{II} cluster in which the central Cu(II) is connected to the “metalloligand” through μ_2 -phenoxido bridge in addition to a $\mu_{1,1}$ -N₃ azido bridge. From CSD search on Ni^{II}-Cu^{II} hetero-metallic compounds with salen type di-Schiff bases ligands (where Ni(II) and Cu(II) serve as terminal and central

metal ions), it has been found that only a few complexes (four trinuclear) are reported till now. This study presents that compound **1** ($\text{Ni}^{\text{II}}_2\text{Cu}_2^{\text{II}}$) is the rare report of a tetranuclear distorted cubane like $\text{Ni}^{\text{II}}\text{-Cu}_2^{\text{II}}\text{-Ni}^{\text{II}}$ coordination complex based on Ni(II)-metalloligand which is derived from a reduced salen type N_2O_2 donor di-Schiff base ligand.

Supplementary Data

Supplementary information is available in the website <http://nopr.niscair.res.in/handle/123456789/58776>. CCDC 2010772 contains the supplementary crystallographic data for compound **1**. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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