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Use of Cu(II)-di-Schiff bases as metalloligands in the formation of complexes with Cu(II), Ni(II) and Zn(II) perchlorate

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ABSTRACT

One linear homo-metallic trinuclear [{CuL¹(CH₃OH)}₂Cu(ClO₄)₂] (**1**); five trinuclear hetero-metallic; bent [(CuL¹)₂Ni(H₂O)₂](ClO₄)₂·H₂O (**2**), linear [(CuL¹)₂Zn(ClO₄)₂] (**3**), bent [{CuL²(ClO₄)}{CuL²(CH₃OH)} Ni(CH₃OH)₂](ClO₄)₂·(CH₃OH)·0.25(H₂O) (**4**), triangular [(CuL²){CuL²(CH₃CN)}Ni(CH₃CN)₂](ClO₄)₂ (**5**), triangular [(CuL²)₂Ni(H₂O)₂](ClO₄)₂·3H₂O (**6**) and one rare tetranuclear star-shaped [{CuL²(H₂O)}₂(CuL²)-Zn](ClO₄)₂·H₂O (**7**) complexes have been synthesized by reacting the "metalloligand", [CuL¹] or [CuL²] with corresponding metal perchlorate where the di-Schiff base ligands H₂L¹ = *N*,*N'*-bis(salicylidene)-1,3-propanediamine and H₂L² = (*N*,*N'*-bis(α -methylsalicylidene)-1,3-propanediamine. The structures of all the seven complexes have been determined by X-ray crystallography. Structural analysis shows that complexes **1–6** are discrete trinuclear species where phenoxido groups of two terminal "metalloligands" coordinate to a central Cu(II) in **1** or Ni(II) in **2**, **4–6** or Zn(II) in **3**. In **1** and **3** two *trans* axial positions of the central Cu(II) are weakly coordinated by the oxygen atoms of perchlorate anions and the molecules are linear. However, in **2**, **4–6** two solvent molecules coordinate to the *cis* positions of the central Ni(II) to complete its distorted octahedral geometry that makes the molecules bent or triangular. On the other hand, complex **7** is a star-shaped tetranuclear species. In which three metalloligands bind a central Zn(II) ion through double phenoxido bridge.

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1. Introduction

In the past several decades, the design and synthesis of polynuclear transition metal complexes have been drawing the attention of coordination chemists not only because of their variety of architectures and topologies as observed in the metal-organic frameworks but also in many possible applications e.g. in catalysis [1,2], magnetism [3–6], electron transport processes [7] and sensing [8]. There are various strategies to synthesize polynuclear complexes; one of them is to use the neutral complex of divalent transition metal ion with salen type N₂O₂ donor tetradentate di-Schiff base ligands (salen = *N*,*N*'-ethylenebis(salicylideneimine)). The oxygen atoms of the coordinated Schiff base are capable of bridging another metal ion to form multinuclear complexes in which these chelates act as "metalloligands" [9]. Among the divalent first transition elements, Cu(II) forms the most stable complexes with these Schiff bases [10-13] and therefore, these neutral Cu-chelates have been used frequently to form complex with another metal ions. In most of these complexes, the oxygen atoms of two "metalloligands" coordinate to a second ion to result in trinuclear complexes [14-28]. These trinuclear complexes can be homonuclear *i.e.* the second metal ion is also a Cu(II) or heteronuclear *i.e.* it is other than Cu(II) ion. The molecular shapes of the trinuclear complexes show an interesting trend; the homonuclear Cu(II) complexes are usually linear [25-28] with some exceptions [23,24]. However, in the hetero trinuclear complexes when the bridging anionic co-ligands (nitrate, acetate, perchlorate etc.) act as an additional bridge between two adjacent metal centers, the shape of the molecule is linear whereas the monodentate anionic co-ligands (thiocyanate, dicyanamide, cyanate etc.) results in a bent structure. On the other hand, when the counter anions are non-coordinating or weakly coordinating such as perchlorate, three "metalloligands" can coordinate to a central metal ion to result in rather unusual star-shaped tetranuclear complexes [17,20,21]. However, trinuclear complexes with such anions are limited and hence no generalization on the shape of the trinuclear molecules could be done.

As a part of our ongoing study in the development of homo- and hetero-polynuclear complexes using Cu(II) chelate with salen type Schiff bases and various anionic co-ligands, we would like to investigate the preferred nuclearity and molecular shape of the resulted complexes with non-coordinating perchlorate salts. Herein, we report the synthesis and crystal structures of seven complexes, two linear trinuclear [{CuL¹(CH₃OH)}₂Cu(ClO₄)₂] (**1**) and [(CuL¹)₂Zn(ClO₄)₂] (**3**); two bent trinuclear [(CuL¹)₂Ni(H₂O)₂]







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 $(ClO_4)_2 \cdot H_2O (2) \text{ and } [\{CuL^2(ClO_4)\}\{CuL^2(CH_3OH)\}Ni(CH_3OH)_2] \\ (ClO_4) \cdot (CH_3OH) \cdot 0.25(H_2O) (4); \text{ two triangular } [(CuL^2)\{CuL^2 (CH_3CN)\}Ni(CH_3CN)_2](ClO_4)_2 (5), [(CuL^2)_2Ni(H_2O)_2](ClO_4)_2 \cdot 3H_2O \\ (6) \text{ and a rare star-shaped tetranuclear } [\{CuL^2(H_2O)\}_2(CuL^2)Zn] \\ (ClO_4)_2 \cdot H_2O (7) \text{ where } H_2L^1 = N,N'-bis(salicylidene)-1,3-propanediamine and } H_2L^2 = (N,N'-bis(\alpha-methylsalicylidene)-1,3-propanediamine. It is to be noted that a compound having similar composition to that of 1 has been reported earlier [29]. In that compound the coordinated methanol molecules were not present. Moreover, the coordination mode of the perchlorate ions was different.$

2. Experimental

2.1. Starting materials

The salicylaldehyde, 2-hydroxyacetophenone 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 and H_2L^2 and their metalloligands $[CuL^1]$ and $[CuL^2]$

The two di-Schiff-base ligands, H_2L^1 and H_2L^2 were prepared by standard methods [10,11]. Briefly, 5 mmol of 1,3-propanediamine (0.42 mL) were mixed with 10 mmol of the required aldehyde (salicylaldehyde (1.04 mL) or 2-hydroxyacetophenone (1.21 mL)) in methanol (20 mL). The resulting solutions were refluxed for *ca*. 2 h, and allowed to cool. The yellow colored methanolic solutions were used directly for complex formation. To a methanolic solution (20 mL) of Cu(ClO₄)₂.6H₂O (1.852 g, 5 mmol), was added a methanolic solution of H_2L^1 or H_2L^2 (5 mmol, 10 mL) to prepare the respective precursors "metalloligands" [CuL¹] [10] and [CuL²] [11] as reported earlier (Scheme 1).

2.3. Synthesis of $[{CuL^{1}(CH_{3}OH)}_{2}Cu(ClO_{4})_{2}]$ (1), $[(CuL^{1})_{2}Ni(H_{2}O)_{2}]$ ($ClO_{4})_{2}$ · $H_{2}O$ (2) and $[(CuL^{1})_{2}Zn(ClO_{4})_{2}]$ (3)

The "metalloligands" [CuL¹] (0.688 g, 2 mmol) was dissolved in methanol (30 mL) and then 5 mL aqueous solution of Cu(ClO₄)₂· $6H_2O$ (0.370 g, 1 mmol) was added to the solution, stirred for 30 min and then allowed to stand overnight when brown X-ray quality single crystals of complex **1** appeared at the bottom of the vessel. The crystals were isolated, washed with ether and dried in vacuum desiccator containing anhydrous CaCl₂. Complexes **2** and **3** were obtained by following a similar procedure to that of **1**, but Ni(ClO₄)₂· $6H_2O$ (0.365 g, 1 mmol) or Zn(ClO₄)₂· $6H_2O$ (0.375 g, 1 mmol) were used respectively, for complexes **2** and **3** instead of Cu(ClO₄)₂· $6H_2O$. The crystals which separated on keeping the solution were green in color.

Complex 1: Yield: 0.778 g. (77%). Anal. Calc. for $C_{36}H_{40}Cl_2Cu_3N_{4-}$ O₁₄ (1014.27): C, 42.63; H, 3.98; N, 5.52. Found: C, 42.81; H, 3.87;



Scheme 1. Ligands and 'metalloligands' used in this work.

N, 5.47%. UV–Vis (CH₃CN): $\lambda_{max}(nm)$ (ε , M⁻¹ cm⁻¹) = 600 (365), 356 (7700), 268 (21150), 230 (42200). IR: ν (C=N) = 1623 cm⁻¹, ν (ClO₄⁻) = 1107 cm⁻¹.

Complex **2**: Yield: 0.580 g. (58%). *Anal.* Calc. for $C_{34}H_{38}NiCu_2N_4$. O₁₅Cl₂ (999.37): C, 40.86; H, 3.83; N, 5.61. Found: C, 40.61; H, 3.87; N, 5.87%. UV–Vis (CH₃CN): $\lambda_{max}(nm)$ (ε , M⁻¹ cm⁻¹) = 1020 (30), 618 (327), 347 (11925), 269 (36525), 232 (67125). IR: ν (C=N) 1619 cm⁻¹, ν (ClO₄⁻) 1090 cm⁻¹.

Complex **3**: Yield: 0.638 g. (67%). *Anal.* Calc. for $C_{34}H_{32}ZnCu_2N_{4-}O_{12}Cl_2$ (952.03): C, 42.89; H, 3.39; N 5.89. Found: C, 42.61; H, 3.47; N, 5.87%. UV–Vis (CH₃CN): $\lambda_{max}(nm)$ (ε , M⁻¹ cm⁻¹) = 616 (319), 336 (10770), 269 (33419), 235 (58020). IR: ν (C=N) 1619 cm⁻¹, ν (ClO₄⁻) 1097 cm⁻¹.

2.4. Synthesis of

 $[\{CuL^{2}(ClO_{4})\}\{CuL^{2}(CH_{3}OH)\}Ni(CH_{3}OH)_{2}](ClO_{4})\cdot(CH_{3}OH)\cdot0.25H_{2}O(\mathbf{4}), \\ [(CuL^{2})\{CuL^{2}(CH_{3}CN)\}Ni(CH_{3}CN)_{2}](ClO_{4})_{2}(\mathbf{5}), \\ [(CuL^{2})_{2}Ni(H_{2}O)_{2}](ClO_{4})_{2}\cdot3H_{2}O(\mathbf{6}) \text{ and } [\{CuL^{2}(H_{2}O)\}_{2}(CuL^{2})Zn](ClO_{4})_{2}\cdotH_{2}O(\mathbf{7})$

The "metalloligands" $[CuL^2]$ (1.174 g, 3 mmol) was dissolved in methanol (30 mL) and then 5 mL aqueous solution of $Zn(ClO_4)_{2-}$ ·6H₂O (0.375 g, 1 mmol) was added to the solution, stirred for 30 min and then allowed to stand overnight when green X-ray quality single crystals of complex **7** appeared at the bottom of the vessel. The crystals were isolated, washed with ether and dried in vacuum desiccator containing anhydrous CaCl₂. Complexes **4–6** were obtained by following a similar procedure to that of **7**, using "metalloligands" [CuL²] (0.782 g, 2 mmol) and Ni(ClO₄)₂·6H₂O (0.365 g, 1 mmol) in various of solvents, methanol, acetonitrile and acetone for complexes **4–6**, respectively. The crystals which separated on keeping the solution were green in color.

Compound **4**: Yield: 0.836 g. (74%). *Anal.* Calc. for $C_{42}H_{56.5}Cl_2$. Cu₂NiN₄O_{16.25} (1134.11): C, 44.88; H, 5.02; N, 4.94. Found C, 45.11; H, 4.87; N, 5.17%. UV–Vis (CH₃CN): $\lambda_{max}(nm)$ (ε , M⁻¹ - cm⁻¹) = 1004 (145), 608 (338), 333 (11685), 263 (27822) and 235 (51521). IR: ν (C=N) = 1594 cm⁻¹, ν (ClO₄⁻) = 1096 cm⁻¹.

Complex **5**: Yield: 0.710 g. (63%). *Anal.* Calc. for C₄₄H₄₉NiCu₂N₇-O₁₂Cl₂ (1124.59): C, 46.99; H, 4.39; N, 8.72. Found: C, 46.61; H, 4.61; N, 8.87%. UV–Vis (CH₃CN): λ_{max} (nm) (ε , M⁻¹ cm⁻¹) = 1004 (150), 608 (350), 333 (13530), 263 (31676) and 233 (58407). IR: ν (C=N) 1596 cm⁻¹, ν (ClO₄⁻) 1097 cm⁻¹.

Compound **6**: Yield: 0.588 g. (54%). *Anal.* Calc. for $C_{38}H_{50}Cl_2Cu_2$. NiN₄O₁₇ (1091.51): C, 41.81; H, 4.62; N, 5.13. Found: C, 41.63; H, 4.87; N, 5.09%. UV–Vis (CH₃CN): λ_{max} (nm) (ε , M⁻¹ cm⁻¹) = 1004 (112), 608 (261), 333 (12500), 264 (30790) and 235 (55277). IR: ν (C=N) = 1593 cm⁻¹, ν (ClO₄⁻) = 1086 cm⁻¹.

Compound **7**: Yield: 0.965 g. (67%). *Anal.* Calc. for $C_{57}H_{66}Cl_2Cu_3$. $N_6O_{17}Zn$ (1434.05): C, 47.74; H, 4.64; N, 5.86. Found: C, 47.81; H, 4.87; N, 5.67%. UV–Vis (CH₃CN): $\lambda_{max}(nm)$ (ε , M^{-1} cm⁻¹) = 608 (220), 330 (13920), 267 (35280) and 228 (67880). IR: v(C=N) = 1597 cm⁻¹, $v(ClO_4^-) = 1089$ cm⁻¹.

2.5. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm⁻¹) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra (1200–200 nm) were recorded in a Hitachi U-3501 spectrophotometer in acetonitrile solution.

2.6. Crystal data collection and refinement

Suitable single crystals of all the complexes were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo K α (λ = 0.71073 Å) radiation.

The crystals were positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 10s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 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 program [30]. All calculations were carried out using SHELXS 97 [31], SHELXL 97 [32], PLATON 99 [33], ORTEP-32 [34] and WINGX system Ver-1.64 [35]. Data collection and structure refinement parameters and crystallographic data for the seven complexes are given in Table 1.

3. Results and discussion

3.1. Synthesis, IR and UV-Vis absorption considerations

The di-Schiff base ligands H_2L^1 and H_2L^2 and its Cu^{II} complexes $[CuL^{1}]$ and $[CuL^{2}]$ were synthesized using the reported procedures [10,11]. [CuL¹] on reaction with Cu(ClO₄)₂·6H₂O, Ni(ClO₄)₂·6H₂O and Zn(ClO₄)₂·6H₂O separately in a 2:1 M ratios in CH₃OH-H₂O (6/1, v/v) medium resulted in the trinuclear complexes [{CuL¹(CH₃₋ OH) $_2$ Cu(ClO₄) $_2$] (**1**), [(CuL¹) $_2$ Ni(H₂O) $_2$](ClO₄) $_2$ ·H₂O (**2**) and [(CuL¹) $_2$ - $Zn(ClO_4)_2$ (3) by self-assembly (see Scheme 2). All three trinuclear complexes are formed by the coordination of two phenoxido oxygen atoms from each of the two terminal [CuL¹] units to the central Cu(II) (for 1), Ni(II) (for 2) and Zn(II) (for 3) but their geometries are very different: complexes 1 and 3 are linear whereas complex 2 is bent. On the other hand, $[CuL^2]$ on reaction with Ni(ClO₄)₂·6H₂O, Zn(ClO₄)₂·6H₂O and Cu(ClO₄)₂·6H₂O separately in 2:1 M ratios in CH_3OH-H_2O medium resulted in the bent trinuclear [{ $CuL^2(ClO_4)$ } ${CuL^{2}(CH_{3}OH)}Ni(CH_{3}OH)_{2}(ClO_{4})\cdot(CH_{3}OH)\cdot0.25(H_{2}O)$ (4), starshaped tetranuclear $[{CuL^2(H_2O)}_2(CuL^2)Zn](ClO_4)_2 \cdot H_2O$ (7) and linear $[(CuL^2)Cu(ClO_4)_2]$ [36] species. In order to isolate a trinuclear species with central zinc ion and terminal metalloligand [CuL²], we decreased the proportion of [CuL²] in the reaction mixture but even when the molar ratio of zinc salt:[CuL²] was 1:1, the separated so-

Table 1

Crystal data and refinement details of the complexes 1-7.

lid was found to be complex 7. On the other hand, with an aim to obtain a star-shaped tetranuclear complex with Ni(II) as central metal ion, we increased the proportion of $[CuL^2]$ up to the molar ratios of nickel salt: [CuL²] = 1:4 using methanol as solvent but the resulted species was the trinuclear complex 4. As there are two cis coordinated solvent molecule in the central Ni(II) ion of 4, we presumed that they probably prevented the chelation of another molecule of metalloligand. We therefore, used two other solvent mixtures (acetonitrile and acetone) in order to get tetranuclear Cu^{II}₃Ni^{II} complex but in both the cases only the triangular complexes $[(CuL^2){CuL^2(CH_3CN)}Ni(CH_3CN)_2](ClO_4)_2$ (5), $[(CuL^2)_2Ni(H_2O)_2](ClO_4)_2 \cdot 3H_2O$ (6) were formed. Similarly, we also tried to prepare a tetranuclear species with [CuL²] precursor and Cu(II) as central metal ion on changing the molar ratios of Cusalt:[CuL²] as well as the solvent systems but in all cases only the linear trinuclear complex which was reported earlier [36] was isolated.

Besides elemental analysis, all the complexes were initially characterized by IR spectra. The "metalloligands" were neutral and obviously they have not any counter anions, whereas all the complexes, **1–7** contain perchlorate anions which are easily detected by the appearance of the characteristic intense peak in the IR spectra in the range of 1086–1107 cm⁻¹. The rest of the spectral patterns and band positions of all the complexes are very similar to the corresponding "metalloligands". The azomethine v(C=N) group of the Schiff base appears at 1623, 1619, 1622, 1594, 1596, 1593 and 1597 cm⁻¹ for complexes **1–7**, respectively. In the IR spectra of the complexes **1, 2, 5, 6** and **7**, there is a broad band near 3434, 3440, 3443, 3449 and 3450 cm⁻¹ due to the O–H stretching of the crystallized water/methanol molecule.

The electronic spectra of all the complexes have been measured in acetonitrile solution. The spectra of complex **1** display a broad absorption band near 600 nm. The position of this band is consistent with the observed square-based geometry around the copper center. However, the band is broader compared to [CuL¹] probably due to the presence of different types of environments in the central and terminal Cu(II). On the other hand in complex **2**, a broad band is observed at 618 nm for both Cu(II) and Ni(II) (${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$). Another weaker broad band at 1020 nm is assignable to the transition ${}^{3}T_{2g}$. $\leftarrow {}^{3}A_{2g}$ for Ni(II). This value is in agreement with the literature value for octahedral Ni(II) compounds [37]. The d–d transition band of complex **3** was observed at 616 nm for Cu(II). The intense bands

Complex	1	2	3	4	5	6	7
Formula	C36H40Cl2Cu3N4O	14C34H38Cu2NiN4O15C	$I_2C_{34}H_{32}Cu_2ZnN_4O_{12}Cl_2$	2C42Cu2NiCl2N4H56.5O76.2	25C44H49Cu2NiN7O12C	l ₂ C ₃₈ H ₅₀ Cu ₂ Cl ₂ NiN ₄ O ₁	7C57H66Cu3O17ZnCl2N6
Formula Weight	1014.27	999.37	952.03	1131.08	1124.59	1091.51	1434.05
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	C2/c	PĪ
a (Å)	10.586(5)	11.342(5)	9.028(5)	10.990(5)	20.59(2)	19.244(5)	12.292(5)
b (Å)	13.306(5)	22.117(5)	11.767(5)	34.611(5)	11.989(13)	13.025(5)	15.262(5)
c (Å)	14.847(5)	15.545(5)	17.300(5)	13.578(5)	22.569(16)	15.516(5)	18.500(5)
α (°)	90	90	90	90	90	90	69.906(5)
β (°)	107.841(5)	94.678(5)	104.234(5)	100.959(5)	121.25(6)	93.299(5)	78.534(5)
γ (°)	90	90	90	90	90	90	69.480(5)
V (Å ³)	1990.7(14)	3887(2)	1781(1)	5071(3)	4763(8)	3883(2)	3040(2)
Ζ	2	4	2	4	4	4	2
D_{calc} (g cm ⁻³)	1.692	1.708	1.775	1.482	1.568	1.850	1.566
μ (mm $^{-1}$)	1.692	1.777	2.072	1.373	1.457	1.790	1.584
R _{int}	0.0667	0.0593	0.0805	0.0799	0.1872	0.0419	0.0291
Unique data	5336	7700	3175	9163	8070	3463	12391
Data with $I > 2(I)$	3385	4787	1875	4917	2949	1865	4827
R_1	0.0437	0.0518	0.0807	0.0737	0.1013	0.1203	0.0650
wR_2	0.1156	0.1534	0.1959	0.1920	0.2348	0.3242	0.1920
Goodness-of-fit	1.027	1.037	1.047	1.028	0.952	1.207	1.056
(GOF) on F^2							



Scheme 2. Synthetic route to the complexes 1-7.

at about 356, 268, 230; 347, 269, 232 and 336, 269, 235 nm for complexes **1–3** respectively, correspond to the ligand-to-metal charge transfer, π – π * transition of aromatic rings and n– π * transition, respectively [38,39]. The absorption bands of the complexes **4–6** are more or less similar to each other. The d–d transition bands appear at 608 nm (for both Cu(II) and Ni(II)) and 1004 nm for Ni(II)). The ligand-to-metal charge transfer, π – π * transition of aromatic rings and n– π * transition bands are found near at 333, 263 and 235 nm, respectively. In complex **7**, spin-allowed d–d transition bands for Cu(II) is observed at 608 nm. The ligand-to-metal charge transfer, π – π * transition bands and n– π * transition bands and n– π * transition bands and n– π * transition bands at a 330, 267 and 228 nm, respectively.

3.2. Description of the structures

3.2.1. Complex **1**: $[{CuL^{1}(CH_{3}OH)}_{2}Cu(ClO_{4})_{2}]$

The discrete trinuclear unit of complex **1** is shown in Fig. 1 and the bond parameters are given in Table 2 and Table 3. The complex contains two [CuL¹] units, one Cu(II) atom, two methanol molecules and two perchlorate anions. The structure contains a crystallographic inversion centre at central Cu(2) atom which is six-coordinate being bonded to six oxygen atoms: four from two "metalloligands" and two from perchlorate anions. The four phenoxido oxygen atoms O(1), O(1)^a, O(2) and O(2)^a (symmetry operation ^a = 2 - *x*, -*y*, 2 - *z*) define the basal plane and oxygen atoms of perchlorate ions [O(11) and O(11)^a] coordinate weakly to the elongated side to complete the distorted octahedral geometry around Cu(2). Bond lengths are 1.933(2) Å to O(1), 1.942(2) Å to O(2) and 2.748(5) Å to O(11).

The coordination sphere of terminal Cu(1) atom is penta-coordinated with square-pyramidal geometry. The equatorial plane is formed by the two imine N atoms N(1) and N(2), with the distances 1.955(3) and 1.966(3) Å and the two phenoxido O atoms, O(1) and O(2) of the Schiff base with the distances 1.958(2) and 1.947(2) Å, respectively. An oxygen atom O(5) from a methanol coordinates to the axial position at 2.329(3) Å (Fig. 1). The r.m.s deviation of the four equatorial donor atoms is 0.022 Å with the metal atom 0.089(1) Å from the plane towards O(5) atom. The Addison parameter ($\tau = |b - a|/60^\circ$ where *b* and *a* are the two largest angles around the central atom; $\tau = 0$ and 1 for perfect square pyramidal and trigonal bipyramidal geometries, respectively) of Cu(1) is 0.019, indicating its square pyramidal geometry [40].

The packing of the molecules is controlled by two types of Hbonding interactions, namely $O-H\cdots O$ and $C-H\cdots O$. Hydrogen atom H(18) of methanol shows hydrogen bonding interaction with O(13) to form a 2D network in crystallographic '*bc*' plane (Fig. 2 and Table 4). This 2D sheets are further connected by $C-H\cdots O$ interaction along crystallographic '*a*' axis to form a 3D supramolecular structure (Fig. 2 and Table 4).

In this context, it is to be mentioned that a similar compound $[(CuL^1)_2Cu](ClO_4)_2$ with slightly different composition has been synthesized by reacting copper acetate, di-Schiff base ligand (H₂L) and sodium perchlorate in 8:5:5 M ratios in methanol–water (4:1, v/v) medium. In that compound, the coordinated methanol molecules were not present and the perchlorate ions bridge each terminal copper ion to the central one. The axial bond distances of perchlorate oxygen atoms to the central Cu(II) in that compound is shorter (2.488 Å) and the av. bond distance of four basally



Fig. 1. The structure of **1** with ellipsoids at 30% probability. The dotted bonds show the weak $Cu(2) \cdots O(11)$ axial interactions.

coordinated phenoxido atoms is longer (1.957 Å) compare to those in 1 (1.938 Å).

3.2.2. Complex **2**: $[(CuL^1)_2Ni(H_2O)_2](ClO_4)_2 \cdot H_2O$

The asymmetric unit of the complex **2** contains two [CuL¹] units, one Ni(II) atom, three water molecules and two perchlorate anions. The ORTEP view is shown in Fig. 3 and the bond distances and angles are given in Table 2 and Table 3, respectively. Both Cu(II) ions present a tetra-coordinated square planar geometry where four donor atoms (two imine N atoms and two phenoxido O atoms) are from di Schiff ligand. The bond distances around both copper atoms are in the range of 1.934(3)-1.972(4) Å. The τ_4 value [41] measures the distortion between a perfect tetrahedron ($\tau_4 = 1$) and a perfect square planar geometry ($\tau_4 = 0$) with the formula:

Table 2						
Dimensions in the metal	coordination	sphere of	both the	complexes,	angles	(°).

Atoms	Distances
Complex 1	
Cu(1)-O(5)	2.329(3)
Cu(1)–O(1)	1.958(2)
Cu(1)–O(2)	1.947(2)
Cu(1)–N(1)	1.955(3)
Cu(1)–N(2)	1.966(3)
Cu(2)-O(1)	2.748(5)
Cu(2)-O(1)	1.933(2)
Cu(2)–O(2)	1.942(2)
Complex 2	
Cu(1)–O(1)	1.939(3)
Cu(1)–O(2)	1.947(3)
Cu(1)-N(1)	1.972(4)
Cu(1)-N(2)	1.953(5)
Cu(2)-O(3)	1.940(3)
Cu(2)-O(4)	1.934(3)
Cu(2)-N(3)	1.945(5)
Cu(2)-N(4)	1.957(4)
Ni(1)-O(1)	2.066(4)
Ni(1)-O(2)	2.074(3)
Ni(1)-O(3)	2.065(3)
Ni(1)–O(4)	2.088(3)
Ni(1)–O(5)	2.050(5)
Ni(1)-O(6)	2.039(5)

Table 3

Dimensions in the metal coordination sphere of both the complexes, angles (deg).

Complex 1		Complex 2	
Atoms	Angles	Atoms	Angles
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Angles 93.03(12) 87.55(15) 77.65(9) 96.40(16) 92.60(13) 91.36(10) 167.38(12) 168.53(10) 91.32(11) 99.23(12) 77.64(13) 77.64(13) 77.64(13) 102.36(13) 102.36(13) 102.71(15) 78.37(9) 180.00 101.63(9) 180.00	Atoms $O(4)-Ni(1)-O(5)$ $O(4)-Ni(1)-O(6)$ $O(5)-Ni(1)-O(6)$ $O(5)-Ni(1)-O(6)$ $O(1)-Cu(1)-O(2)$ $O(1)-Cu(1)-N(1)$ $O(1)-Cu(1)-N(1)$ $O(2)-Cu(1)-N(1)$ $O(2)-Cu(1)-N(2)$ $N(1)-Cu(1)-N(2)$ $N(1)-Cu(1)-N(2)$ $O(3)-Cu(2)-N(4)$ $O(3)-Cu(2)-N(4)$ $O(4)-Cu(2)-N(3)$ $O(4)-Cu(2)-N(4)$ $O(4)-Cu(2)-N(4)$ $O(1)-Ni(1)-O(2)$ $O(1)-Ni(1)-O(3)$ $O(1)-Ni(1)-O(4)$ $O(1)-Ni(1)-O(5)$ $O(1)-Ni(1)-O(5)$ $O(2)-Ni(1)-O(4)$ $O(2)-Ni(1)-O(4)$	Angles 171.33(16) 89.43(15) 94.61(18) 78.00(14) 91.93(17) 169.96(17) 168.00(17) 91.97(16) 97.97(19) 79.07(13) 92.37(16) 170.91(17) 171.31(16) 91.84(16) 96.71(18) 72.43(13) 90.55(16) 170.49(16) 164.49(13) 96.71(16)
		O(2)-Ni(1)-O(5) O(2)-Ni(1)-O(6) O(3)-Ni(1)-O(4) O(2) Ni(1) O(5)	90.74(16) 99.48(16) 72.83(13)
		O(3)-Ni(1)-O(5) O(3)-Ni(1)-O(6)	99.36(16) 91.46(16)

Symmetry element ^a = 2 - x, -y, 2 - z for complex **1**.

 $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$, α and β (in °) being the two largest angles around the central metal in the complex. The values are 0.156 and 0.126 for Cu(1) and Cu(2), respectively, confirming a slightly distorted square planer geometry for both metal centers.

The environment of the nickel ion is distorted octahedral both in the bond lengths and bond angles (Table 2 and Table 3). The hexa-coordinated Ni(II) ion has four donor phenoxido oxygen atoms from two terminal [CuL¹] moieties and two *cis*-coordinated water molecules. The bond distances are in the range of 2.039(5)– 2.088(3) Å. Regarding the angles, three *trans* angles are 164.49(13), 170.49(16) and 171.33(16) and the *cis* angles vary in the range of 72.43(13)–99.48(16).

The packing of the complex **2** is controlled by two types of weak supramolecular interactions; namely, cation– π and hydrogen bonding. These cation– π interactions again are of two types: intra-molecular and inter-molecular. For the intermolecular interaction, the centroid of the phenyl ring (Cg) is located at a distance of Cg…Cu(1) = 3.498 Å while for intra-molcular Cg…Cu(2) distance is at 3.910 Å (Fig. 4). The Cg…Cu(1) interaction builds a 1D chain that propagates diagonally to the crystallographic *ac* plane. The intra-molecular cation– π interaction holds the two [CuL¹] moieties closer and thus stabilized the bent structure. On the other hand, each trinuclear unit forms H-bond with its neighboring trinuclear units with the help of coordinated water molecules and perchlorate anions to form a 1D chain along crystallographic *a* axis (Fig. 5 and Table 4). These two types of chains form a 2D sheet along the crystallographic *ac* plane.

3.2.3. Complex **3**: $[(CuL^1)_2Zn(ClO_4)_2]$

The discrete trinuclear unit of complex **3** is shown in Fig. 6 and the bond parameters are given in Table 5. The complex contains two $[CuL^1]$ units, one Zn(II) atom and two bridging perchlorate anions. The structure contains a crystallographic inversion centre at central Zn(1) atom. The central Zn(1) is six-coordinate being



Fig. 2. Supramolecular H-bonding interaction of complex 1, 2D (left, view along crystallographic a axis) and 3D (right, view along crystallographic b axis) networks.

 Table 4

 Hydrogen bond dimensions of both the complexes 1 and 2.

	D−H···A	D-H (Å)	H···A (Å)	$D{\cdots}A\;(\mathring{A})$	∠D-H···A (°)	Symmetry
1	05-H18···013	0.61(7)	2.35(7)	2.902(7)	153(9)	x, 1/2 - y, 1/2 + z
1	C8-H8B···O12	0.97(4)	2.51(4)	3.389(8)	151(3)	1 - x, $1/2 + y$, $3/2 - z$
2	01W-H20107	0.7400	2.2500	2.812(6)	134.00	
2	06-H10601W	0.9100	1.9900	2.704(7)	134.00	-1 + x, y, z
2	05-H105011	0.67(7)	2.16(7)	2.828(6)	171(7)	
2	05-H205···08	0.92(7)	2.15(7)	3.017(8)	157(5)	
2	06-H206···014	0.72(7)	2.13(7)	2.840(10)	169(6)	



Fig. 3. ORTEP View of the complex 2 with ellipsoids at 30% probability.

bonded to four oxygen atoms, two from each of two "ligands complex", together with two oxygen atoms of perchlorate anions. The four phenoxido oxygen atoms O(1), $O(1)^b$, O(2) and $O(2)^b$ (symmetry operation $^b = 1 - x, 1 - y, 1 - z$) define the basal plane and oxygen atoms of perchlorate ions [O(11) and $O(11)^b]$ coordinate weakly to the elongated side to complete the distorted octahedral geometry around Zn(1). Bond lengths are 2.080(6) Å to O(1), 2.016(5) Å to O(2) and 2.262(6) Å to O(11).

The coordination sphere of terminal Cu(1) atom is penta-coordinated with square-pyramidal geometry. The equatorial plane is formed by the two imine N atoms N(1) and N(2), with the distances



Fig. 4. Intra-molecular and inter-molecular cation– π interactions in complex **2** forms a 1D chain.

1.957(8) and 1.949(8) Å and the two phenoxido O atoms, O(1) and O(2) of the Schiff base with the distances 1.940(5) and 1.935(5) Å, respectively. An oxygen atom O(12) from a perchlorate coordinate to the axial position at 2.561(8) Å (Fig. 6). The r.m.s deviation of the four equatorial donor atoms is 0.163 Å with the metal atom 0.019(1) Å from the plane towards O(12) atom. The Addison parameter (τ) of Cu(1) is 0.01, indicating nearly perfect square planer geometry [40].

The packing of the molecules are controlled by intermolecular cation– π interaction, which forming a 1D polymeric chain with centroid of the phenyl ring Cg···Cu(1) distance of 3.915 Å (Fig. 7).

3.2.4. Complex **4**: $[{CuL^2(ClO_4)} \{ CuL^2(CH_3OH) \} Ni(CH_3OH)_2](ClO_4) \cdot (CH_3OH) \cdot 0.25(H_2O), complex$ **5** $: <math>[(CuL^2) \{ CuL^2(CH_3CN) \} Ni(CH_3CN)_2]$ (ClO₄)₂ and complex **6**: $[(CuL^2)_2Ni(H_2O)_2](ClO_4)_2 \cdot 3H_2O$

The trinuclear structures of **4–6** contain the same two $[CuL^2]$ units, one Ni(II) atom and two perchlorate anions. However, the solvent molecules that coordinate to the central Ni(II) are different; they are methanol, acetonitrile and water for complexes **4–6**, respectively. The ORTEP views of the complexes are shown in Fig. 8. The environment of the nickel ion is distorted octahedral both in the bond distances (Table 6) and bond angles (Table 7).



Fig. 5. Inter-molecular H-bonding interactions to form a 1D polymeric chain in complex 2.



Fig. 6. ORTEP view of the complex 3 with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 5

Bond distances (Å) and angles (°) around the metal centers in complex 3.

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu1-01	1.940(5)	Cu1-012	2.561(8)
Cu1-02	1.935(5)	Zn1-01	2.080(6)
Cu1-N1	1.957(8)	Zn1-02	2.016(5)
Cu1-N2	1.949(8)	Zn1-011	2.262(6)
Atoms	Angle (°)	Atoms	Angle (°)
01-Cu1-O2	80.3(2)	01-Zn1-02	75.1(2)
01-Cu1-N1	92.5(3)	01-Zn1-011	91.9(2)
01-Cu1-N2	167.1(3)	01-Zn1-01 ^b	180.00
01-Cu1-012	86.9(2)	01-Zn1-02 ^b	104.9(2)
02-Cu1-N1	166.5(3)	01-Zn1-011 ^b	88.1(2)
02-Cu1-N2	91.0(3)	02-Zn1-011	91.1(2)
02-Cu1-012	103.4(2)	02–Zn1–011 ^b	88.9(2)
N1-Cu1-N2	97.9(3)	02-Zn1-02 ^b	180.00
012-Cu1-N1	86.0(3)	011-Zn1-011 ^b	180.00
012-Cu1-N2	119.7(2)		

Symmetry operation ^b = 1 - x, 1 - y, 1 - z.



Fig. 7. Cation– π interactions in (**3**) to form a 1D polymeric chain along crystallographic *a* axis.

The hexa-coordinated Ni(II) ions contain four donor atoms of phenoxido oxygen from two terminal $[CuL^2]$ moieties and two *cis*-coordinated methanol (for **4**), acetonitrile (for **5**) and water molecules (for **6**). The bond distances around Ni(II) are in the range of 1.863(10) to 2.093(5) Å for all three complexes. Regarding the angles, three *trans* angles are in the range of 173.8(2)–155.6(4)° and the *cis* angles vary in the range of 74.4(4)–101.5(5)°.

In the three complexes, the coordinating environments of the two [CuL²] moieties are considerably different although they all possess penta-coordinated square-pyramidal geometry. In complex **4**, oxygen atoms of perchlorate ion (O71) and O7 of methanol molecule coordinate to the axial positions of Cu(2) and Cu(1), respectively. In complex **5**, Cu(1) is axially coordinated through O3 of the other [CuL²] moiety and in Cu(2) a nitrogen atom (N7) of acetonitrile molecule is axially coordinated. The penta-coordinated square-pyramidal geometry of both the copper atoms in complex **6** is completed by the axial coordination of the oxygen atom O2 and O2^c (^c = 2 - *x*, *y*, 1/2 - *z*) of two symmetry related [CuL²] units in the molecule.

In the three structures an interesting trend has been found regarding the shape of the trinuclear complexes depending upon the coordinating ability of the solvent molecules which are ciscoordinated to central Ni(II) atom. In complex 4, the av. Ni(II)-OHCH₃ distance of 2.065 Å is the longest one and the terminal Cu(II) atoms are not connected by the phenoxido oxygen atoms as is evident from the long separation (2.976(5)Å) between them. Consequently, the shape of the molecule is angular. Whereas, in 6 the av. Ni–OH₂ distance (1.915 Å) is the shortest and the terminal Cu(II) are linked together through double μ_3 -phenoxido bridge with a bond distance of 2.590(8) Å that makes the shape of the molecule triangular. On the other hand, in complex 5, the av. Ni(II)-NCCH₃ distance (2.048 Å) is intermediate and the two terminal Cu(II) are joined together through only one μ_3 -phenoxido bridge with longer bond distance of 2.726(11) Å. These differences in bridging modes is also reflected in Cu-...Cu distances which are 4.027(2), 3.897(5) and 3.501(3) Å for complexes **4–6**, respectively. Therefore, we may infer that in these complexes, shorter is the *cis* Ni(II)–S (S = solvent) distances, the two terminal $[CuL^2]$ units come closer forming more in number as well as stronger bridges between them.

3.2.5. Complex 7: $[{CuL^2(H_2O)}_2(CuL^2)Zn](ClO_4)_2 H_2O$

The structure of **7** contains a discrete, independent $[{CuL^2(H_2 - O)}_2(CuL^2)Zn]^{2+}$ cation and two perchlorate anions. The structure of the cation is shown in Fig. 9. The selected bond lengths and angles are summarized in Table 8. The structure of the $[{CuL^2(H_2 - O)}_2(CuL^2)Zn]^{2+}$ cation involves two $[CuL^2(H_2 O)]$ and one $[CuL^2]$ moieties surrounding a zinc cation. The zinc ion is six-coordinate being bonded to three pairs of oxygen atoms from each 'ligand complex'. Thus the zinc ion bridges three copper atoms each



Fig. 8. ORTEP View of the complexes 4-6 (left to right) with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

through two phenoxido oxygen atoms. The environment of the Zn(II) ion can be described as a considerably distorted octahedron. There are four short Zn–O bonds to O(1), O(4), O(5) and O(6) with distances in the range 1.990(6)–2.087(6) Å, and two longer bonds Zn–O(2) = 2.561(7) and Zn–O(3) = 2.269(6) Å. The bond angles also show significant deviations from the ideal octahedral geometry. Thus, the *trans* angles are lower than 180° (168.6(2)°, 176.2(2)° and 141.0(2)°, Table 8) and the *cis* angles vary in a wide range (from 67.1(2)° to 112.1(2)°, Table 8). The distances between the Zn and three Cu(II) are almost equal (Zn(1)···Cu(1) = 3.074(2) Å, Zn(1)···Cu(2) = 3.098(2) Å and Zn(1)···Cu(3) = 3.150(2) Å). The Cu···Cu distances are 3.683(2) (for Cu(1)···Cu(2)), 5.687(3) (for Cu(1)···Cu(3)) and 6.026(3) Å (for Cu(3)···Cu(2)).

The geometry of Cu(3) and Cu(2) in the two $[CuL^2(H_2O)]$ moieties is best described as square pyramidal with the four coordinating atoms from the di-anionic Schiff base ligand in the basal plane and a weakly coordinated water molecule in one of the axial sites. The metal atoms Cu(3) and Cu(2) deviated from the N₂O₂ basal plane 0.124(1) and 0.003(1) Å, respectively towards the axially coordinated water molecule. The Addison parameters [40] 0.15 for Cu(3) and 0.01 for Cu(2) indicate that the distortion towards the trigonal bipyramid geometry of Cu(3) is greater than Cu(2). In the remaining [CuL²] unit, both the axial positions of copper atom Cu(1) are vacant. Thus the geometry around Cu(1) is square planar. The r.m.s. deviation (0.205 Å) of donor atoms from their mean plane indicates a tetrahedral distortion. The metal atom is 0.001(1) Å from this plane. The tetrahedral distortion is also appar-

Table 6	6					
Bond d	listances (<i>I</i>	Å) around	the metal	centers i	n complexes	4-6.

Atoms	Complex 4 Distances	Complex 5 Distances	Complex 6 Distances
Cu1-01	1.930(5)	1.906(11)	1.784(8)
Cu1-02	1.934(6)	1.909(10)	1.766(10)
Cu1-N1	1.981(7)	1.951(12)	1.811(14)
Cu1–N2	1.967(7)	1.956(16)	1.831(10)
Cu1-07/03/02 ^c	2.426 (8)	2.726(11)	2.590(8)
Ni1-01	2.029(5)	2.035(10)	1.863(10)
Ni1-02	2.086(5)	2.081(12)	2.002(8)
Ni1-03	2.093 (5)	2.092(10)	-
Ni1-04	2.024(5)	2.006(9)	-
Ni1-05/N5/01W	2.073(6)	2.061(17)	1.915(11)
Ni1-06/N6	2.057(5)	2.035(12)	-
Cu2-03	1.935(5)	1.925(9)	-
Cu2-04	1.916(5)	1.919(10)	-
Cu2–N3	1.938(7)	1.947(15)	-
Cu2-N4	1.979(7)	1.925(11)	-
Cu2-071/N7	2.567(11)	2.78(2)	-

Symmetry operation c = 2 - x, y, 1/2 - z for complex **6**.

ent from the dihedral angles (17.07°) between the two planes, N(1)-Cu(1)-O(1) and N(2)-Cu(1)-O(2) compare with 0° for a perfectly square-planar arrangement and 90° for a perfect tetrahedral arrangement.

A CSD search reveals that at least 25 trinuclear homometallic Cu(II) complexes with salen type N_2O_2 donor ligands have been reported. Of them, 21 are linear and rests are bent. It is to be noted that the coordination sphere of the central Cu(II) is very important to determine the shape of the molecule. When the central copper atom is bonded only with the four oxygen atoms of two ligand complexes in a square planar environment, the geometry is

 Table 7

 Bond angles (°) around the metal centers in complexes 4–6.

Atoms	4	5	6
	Angles	Angles	Angles
O(1)-Cu(1)-O(2)	81.1(2)	81.4(4)	82.5(4)
$O(1)-Cu(1)-O(7)/O(3)/O(2)^{c}$	97.0(2)	70.8(4)	71.8(4)
O(1)-Cu(1)-N(1)	88.7(3)	91.6(5)	90.2(6)
O(1)-Cu(1)-N(2)	170.2(3)	160.8(5)	166.5(5)
$O(2)-Cu(1)-O(7)/O(3)/O(2)^{c}$	107.8(3)	67.2(4)	66.6(3)
O(2)-Cu(1)-N(1)	161.1(3)	163.2(5)	164.7(5)
O(2)-Cu(1)-N(2)	89.1(2)	90.5(5)	89.9(5)
$O(7)/O(3)/O(2)^{c} - Cu(1)-N(1)$	89.1(3)	96.1(4)	98.3(4)
$O(7)/O(3)/O(2)^{c} - Cu(1)-N(2)$	86.0(3)	121.9(4)	115.3(4)
N(1)-Cu(1)-N(2)	100.6(6)	100.4(6)	99.7(6)
O(3)-Cu(2)-O(71)/ N(7)	95.5(3)	89.2(5)	-
O(3)-Cu(2)-O(4)	81.9(2)	83.8(4)	-
O(3)-Cu(2)-N(3)	89.6(2)	88.7(5)	-
O(3)-Cu(2)-N(4)	162.1(2)	172.3(5)	-
O(4)-Cu(2)-N(3)	168.2(2)	171.9(4)	-
O(4)-Cu(2)-N(4)	89.7(2)	89.2(5)	-
O(4)-Cu(2)-O(71)/N(7)	83.3(3)	90.6(5)	-
O(71)/N(7)-Cu(2)-N(3)	89.4(3)	92.3(6)	-
O(71)/N(7)-Cu(2)-N(4)	99.2(3)	93.9(5)	-
N(3)-Cu(2)-N(4)	100.7(3)	98.2(5)	-
O(1)-Ni(1)-O(2)	75.2(2)	74.4(4)	74.5(4)
O(1)-Ni(1)-O(3)/O(3)/O1W	88.8(2)	84.2(4)	101.5(5)
O(1)-Ni(1)-O(4)/O(4)/O1W ^c	158.6(2)	157.3(4)	96.0(5)
$O(1)-Ni(1)-O(5)/O(5)/O(1)^{c}$	97.3(2)	96.7(5)	155.6(4)
O(1)-Ni(1)-O(6)/O(6)/O(2) ^c	98.4(2)	96.2(4)	86.4(4)
O(2)-Ni(1)-O(3)/O(3)/O1W	84.3(2)	79.0(4)	98.3(4)
O(2)-Ni(1)-O(4)/O(4)/O1W ^c	88.6(2)	89.0(4)	169.4(5)
O(2)-Ni(1)-O(5)/O(5)/O(2) ^c	95.6(2)	170.3(5)	76.9(3)
O(2)-Ni(1)-O(6)	173.0(2)	94.5(5)	-
O(3)-Ni(1)-O(4)	75.6(2)	77.5(4)	-
O(3)-Ni(1)-O(5)	173.8(2)	96.8(5)	-
O(3)-Ni(1)-O(6)	93.0(2)	173.1(5)	-
O(4)-Ni(1)-O(5)	98.1(2)	98.7(5)	-
O(4)-Ni(1)-O(6)	96.9(2)	100.4(4)	-
O(5)-Ni(1)-O(6)	87.9(2)	90.0(5)	-
01W-Ni(1)-01W ^c	-	-	88.0(5)

Symmetry operation c = 2 - x, y, 1/2 - z for complex **6**.



Fig. 9. $_{\mbox{\scriptsize ORTEP}}$ View of the complex 7 with ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

Table 8

Bond distances (Å) and angles (°) around the metal centers in complex 7.

Atoms	Distance (Å)	Atoms	Distance (Å)
Cu1-01	1.951(6)	Cu3-06	1.971(6)
Cu1-N1	1.983(8)	Cu3-N5	1.991(9)
Cu1-N2	1.966(7)	Cu3-N6	1.945(9)
Cu1-02	1.934(7)	Cu3-08	2.466(11)
Cu2-03	1.896(6)	Zn1-01	1.990(6)
Cu2-04	1.939(6)	Zn1-02	2.561(7)
Cu2-N3	1.969(8)	Zn1-03	2.269(6)
Cu2-N4	1.959(9)	Zn1-04	2.002(6)
Cu2-07	2.697(18)	Zn1-05	2.087(6)
Cu3-05	1.934(6)	Zn1-06	2.076(6)
Atoms	Angle (°)	Atoms	Angle (°)
01-Cu1-02	83.3(3)	05-Cu3-N5	89.9(3)
01-Cu1-N1	90.1(3)	05-Cu3-N6	170.1(3)
01-Cu1-N2	166.4(3)	08-Cu3-N5	93.0(4)
02-Cu1-N1	165.4(3)	08-Cu3-N6	84.5(4)
02-Cu1-N2	91.7(3)	N5-Cu3-N6	99.9(4)
N1-Cu1-N2	97.5(3)	02-Zn1-06	168.6(2)
03-Cu2-04	81.9(3)	03-Zn1-04	71.8(2)
03-Cu2-N3	90.5(3)	03-Zn1-05	176.2(2)
03-Cu2-N4	168.2(3)	03-Zn1-06	103.4(2)
03-Cu2-07	102.8(5)	04-Zn1-05	104.8(3)
04-Cu2-N3	168.8(3)	04-Zn1-06	112.1(2)
04-Cu2-N4	90.1(3)	05-Zn1-06	76.0(2)
04-Cu2-07	88.4(5)	01-Zn1-02	67.1(2)
N3-Cu2-N4	98.6(3)	01-Zn1-03	83.0(2)
015-Cu2-N3	85.2(5)	01-Zn1-04	141.0(2)
015-Cu2-N4	85.7(5)	01-Zn1-05	100.8(2)
06-Cu3-08	104.6(3)	01-Zn1-06	102.3(2)
06-Cu3-N6	89.0(3)	02-Zn1-03	72.1(2)
06-Cu3-N5	161.1(3)	02-Zn1-04	76.9(2)
05-Cu3-08	93.9(3)	02-Zn1-05	109.3(2)
05-Cu3-06	82.0(2)		

invariably linear. Moreover, when both the axial positions are coordinated either by two weakly coordinating monodentate ligands and by the bridging bidentate ligands the geometry is also linear. However, if only one monodentate ligand coordinates to an axial position of the central copper, its geometry may distort towards trigonal bipyramidal and consequently the structure becomes bent [23]. The structure can also be bent if the anionic coligands are strongly coordinating and occupy the equatorial positions [24,42]. On the other hand, when the central metal ion is not a Cu(II) and is hexa-coordinated, the coordination of two ligands other than the four phenoxido atoms determine its geometry. A bidentate bridging coligand that usually links the terminal metal atom to the central one, coordinates to the *trans* positions of the central atom and the structure becomes linear [43]. However, the monodentate coligands usually coordinate to the *cis* positions of the central atom making the structure angular or triangular. In the present system, two axial positions of central Cu(II) atom in complex **1** are weakly coordinated by two perchlorate oxygen atoms and in **3** the perchlorate ions act as bridging bidentate ligands between terminal Cu(II) and central Zn(II). Hence, both the molecules are linear. On the other hand, in complexes **2** and **4–6**, in addition to the phenoxido oxygen atoms, two monodentate solvent molecules (water in **2** and **6**, methanol in **4** and acetonitrile in **5**) coordinate to the *cis* positions of the central metal ion and consequently the molecules are angular or triangular.

The star-shaped tetra-nuclear complexes MCu₃ in which the hetero atom, M, is surrounded by three "metalloligands" of Cu(II) are less common in monoatomic brides and are usually formed with polyatomic bridging ligands such as oxalate, oxamato, oximato etc. Using Cu(II) complexes of salen type di-Schiff bases as metalloligands, six examples of single atom oxido bridged star-shaped tetra-nuclear complexes have been reported. These examples include three with $M = Na^+$ [20,44,45], one with $M = K^+$ [46] and one for each with Cd^{2+} [17] and Mn^{2+} [21]. Four of these complexes are constituted by the "metalloligands" [CuL²] and other two by aother metalloligand [Cu(acacen)] (where $[acacen]^{2-} = N,N'$ -ethylenebis(acety1acetoniminato)). There is no example of star-shaped tetranuclear ZnCu₃ complex according to the CCDC database (updated to December 2012) with any type bridging ligands. Therefore, complex 7 of this article is the first known example of star-shaped ZnCu₃ complex.

4. Conclusions

The isolation of the seven complexes using neutral Cu(II) complexes of N,N'-bis(salicylidene)-1,3-propanediamine (H₂L¹) and *N*,*N*'-bis(α -methylsalicylidene)-1,3-propanediamine (H₂L²) as metalloligands shows that this approach is very useful for the synthesis of homo- and hetero-metallic complexes utilizing the bridging capability of the phenoxido oxygen of the Schiff bases. Among these seven complexes, six (1-6) are trinuclear, indicating that these species are formed most commonly as was also found earlier. The shape of the trinuclear species may vary from linear to triangular depending upon various factors e.g. coordination mode of the anionic coligand, coordination ability of the solvent molecules, nature of the central metal ion etc. The other complex (7) which is formed by coordination of three [CuL²] to a central Zn(II), is a rare type of star-shaped tetranuclear species. We fail to isolate such a star-shaped complex with Cu(II) or Ni(II) as central metal ion. Moreover, [CuL¹] does not produce such tetranuclear species with none of the metal ion used here. Therefore, both the central metal ions and the Schiff bases are important in determining the nuclearity of the species obtained by this approach.

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Appendix A. Supplementary data

CCDC 897775, 897776 and 932598–932602 contain the supplementary crystallographic data for compounds **1**, **2** and **3-7**,

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.

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