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**Linear trinuclear copper(II)-alkali/alkaline earth metal compounds
derived from a compartmental ligand**

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ABSTRACT

The work in this investigation deals with syntheses, crystal structures and ESI-MS positive of five compounds of composition $[(\text{Cu}^{\text{II}}\text{L})_2\text{Na}^{\text{I}}](\text{ClO}_4)$ (**1**), $[(\text{Cu}^{\text{II}}\text{L})_2\text{K}^{\text{I}}](\text{ClO}_4)$ (**2**), $[\{\text{Cu}^{\text{II}}\text{L}(\text{H}_2\text{O})\}\text{Ca}^{\text{II}}(\text{Cu}^{\text{II}}\text{L})](\text{ClO}_4)_2$ (**3**), $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Sr}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH})_{0.6}\}](\text{ClO}_4)\cdot 1.2\text{MeOH}$ (**4**) and $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Ba}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH})\}](\text{ClO}_4)\cdot \text{MeOH}$ (**5**), where $\text{H}_2\text{L} = \text{N,N}'\text{-bis}(3\text{-ethoxysalicylidene})\text{-1,4-butanediamine}$. The s-block metal ion in all of these five compounds occupies an O_8 (four phenoxo and four ethoxy) site provided by two L^{2-} ligands. While Na^{I} , K^{I} and Ca^{II} are eight-coordinated, Sr^{II} and Ba^{II} are nine-coordinated due to additional coordination by an oxygen atom of a bridging perchlorate ligand. In all of **1–5**, the two Cu^{II} and M^{II} are positioned in almost linear way ($\text{Cu}^{\text{II}}\text{-M}^{\text{II}}\text{-Cu}^{\text{II}}$ angle range = $168.24\text{--}175.39^\circ$). The geometries of the coordination environments have been understood from SHAPE analyses. A disagreement has been observed for the first time between the results of SHAPE analyses and Addison's geometric parameter for the pentacoordinated environment. Some interesting structural features regarding composition, metal-ligand bond lengths and twisting of the aromatic rings have been observed. UV-Vis spectra indicates two d-d absorption of copper(II) centers in each of the five compounds. ESI-MS positive reveals the appearance of some tri/di/mononuclear ions.

Keywords: Heterometallic; s-block metal ions; Structural resemblance; Addison parameter; Schiff base ligand

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1. Introduction

Heterometallic complexes have been extensively explored. A major reason for such exploration is the development of the area of molecular magnetism [1–9]. Another major objective has been to mimic the structures/functions of metallo-proteins having heterometallic active sites [10–13]. A third major objective has been to explore the structural aspects, which includes the following: (i) The variation in nuclearity and structure in the same or closely similar ligand systems by changing the heterometallic combinations [14–21]; (ii) Weak interaction directed self-assemblies including cocrystals [14–18,21]. It is worth mentioning that the paramagnetic-diamagnetic and even diamagnetic-diamagnetic heterometallic systems deserve attention to explore the various types of structural aspects.

Notably, the following Schiff base ligands have been extensively utilized to derive varieties of heterometallic complexes: [2+1] condensation products of an aromatic hydroxyaldehyde (e.g. salicylaldehyde [22–37], 2-hydroxyacetophenone [31,32,37,38–40], 2-hydroxypropiophenone [41–43], 3-methoxysalicylaldehyde [31,44–65], 3-ethoxysalicylaldehyde [14–21,31,45,57,66–81]) and a diamine (e.g. ethylenediamine, 1-methylethylenediamine, 1,1-dimethylethylenediamine, 1,2-diaminocyclohexane, *o*-phenylenediamine, 1,3-diaminopropane, 2,2-dimethyl-1,3-diaminopropane, 1,4-diaminobutane). The synthetic approach involves the isolation of a mononuclear complex (of Cu^{II} or Ni^{II} in most cases) as a metallo-ligand which is then treated with a second metal salt to produce a heterometallic compound. Several copper(II)/nickel(II)–second metal ions complexes have been reported from the said family of ligands, where the second metal ion is a member of various blocks of the periodic table (s-, p-, d-, d¹⁰, 4f-, 5f-). The types of systems include dinuclear, trinuclear

(sandwiched and closely linear), tetranuclear including stars, other types of oligonuclear clusters, polymers, discrete and polymeric cocrystals, etc.

We have been working in the above mentioned general area for almost two decades. We have observed that the types of above mentioned ligands with two carbon atoms between the two imine nitrogen atoms have been much more explored in comparison to those ligands having four carbon atoms between the two imine nitrogen atoms [22–28,82–87]. Therefore, we thought to explore the ligand systems with four carbon atoms between the two imine nitrogen atoms and, interestingly, a series of rare family of $M^{II}Cu^{II}_3$ stars ($M = Zn, Cu, Ni, Mn, Cd$) were obtained from salicylaldehyde-1,4-diaminobutane ligand [27,28]. The $Cu^{II}Cu^{II}_3/Ni^{II}Cu^{II}_3/Mn^{II}Cu^{II}_3$ stars in this series exhibit interesting magnetic properties as well. Therefore, we anticipated to get some interesting features with respect to structures or properties in heterometallic complexes from other such ligands. It may be mentioned that metal complexes derived from 3-ethoxysalicylaldehyde-1,4-diaminobutane ligand (Scheme 1) is yet unknown, although its single crystal structure has been reported [88]. As an attempt to explore the metal complexes from this particular ligand for the first time, we chose alkali and alkaline metal ions as the second metal ions. Accordingly, we have isolated five copper(II)-s block metal ion complexes. Herein, we report the syntheses, crystal structures, ESI-MS positive and interesting structural features of those five compounds of composition $[(Cu^{II}L)_2Na^I](ClO_4)$ (1), $[(Cu^{II}L)_2K^I](ClO_4)$ (2), $[\{Cu^{II}L(H_2O)\}Ca^{II}(Cu^{II}L)](ClO_4)_2$ (3), $[(Cu^{II}L)(\mu-ClO_4)Sr^{II}\{Cu^{II}L(MeOH)_{0.6}\}](ClO_4) \cdot 1.2MeOH$ (4) and $[(Cu^{II}L)(\mu-ClO_4)Ba^{II}\{Cu^{II}L(MeOH)\}](ClO_4) \cdot MeOH$ (5).

2. Experimental Section

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

2.1. Materials and Physical Measurements

All the reagents and solvents were purchased from the commercial sources and used as received. The mononuclear metallo-ligand, [Cu^{II}L], was synthesized by the reported procedure [28]. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. FT-IR spectra were recorded in the region 400–4000 cm⁻¹ on a Bruker-Optics Alpha-T spectrophotometer with samples as KBr disks. Electronic spectra were obtained by using a Shimadzu UV-3600 spectrophotometer. The electrospray ionization mass spectra were recorded on a Waters Xevo G2 QTOF Mass Spectrometer.

2.2. Syntheses

$[(Cu^{II}L)_2Na^+](ClO_4)$ (**1**), $[(Cu^{II}L)_2K^+](ClO_4)$ (**2**), $[\{Cu^{II}L(H_2O)\}Ca^{II}(Cu^{II}L)](ClO_4)_2$ (**3**), $[(Cu^{II}L)(\mu-ClO_4)Sr^{II}\{Cu^{II}L(MeOH)_{0.6}\}](ClO_4)\cdot 1.2MeOH$ (**4**) and $[(Cu^{II}L)(\mu-ClO_4)Ba^{II}\{Cu^{II}L(MeOH)\}](ClO_4)\cdot MeOH$ (**5**)

These five compounds were prepared following a general procedure, as follows: A methanol solution (5 mL) of the corresponding hydrated metal perchlorate (0.1 mmol) was dropwise added to a stirred suspension of [Cu^{II}L] (0.090 g, 0.2 mmol) in acetonitrile (10 mL). Then the mixture was heated to obtain almost a clear solution. The mixture was filtered and the filtrate (reddish brown for **1** and **2** and green for **3–5**) was kept at room

temperature for slow evaporation. After a few days, brown (for **1** and **2**) or green (for **3–5**) crystalline compounds containing diffraction quality crystals that deposited were collected by filtration, washed with cold 1:1 methanol-acetonitrile and dried in vacuo.

Data for **1**: Yield: 0.076 g (75%). Anal Calc. for $C_{44}H_{52}N_4O_{12}ClCu_2Na$: C, 52.09; H, 5.17; N, 5.52. Found: C, 51.79; H, 5.25; N, 5.61. Selected FT-IR data on KBr (cm^{-1}): $\nu(C=N)$, 1612vs; $\nu(ClO_4)$, 1088vs and 622w.

Data for **2**: Yield: 0.074 g (72%). Anal Calc. for $C_{44}H_{52}N_4O_{12}ClCu_2K$: C, 51.28; H, 5.09; N, 5.44. Found: C, 50.97; H, 4.96; N, 5.35. Selected FT-IR data on KBr (cm^{-1}): $\nu(C=N)$, 1612vs; $\nu(ClO_4)$, 1082vs and 622w.

Data for **3**: Yield: 0.092 g (80%). Anal Calc. for $C_{44}H_{54}N_4O_{17}Cl_2Cu_2Ca$: C, 45.99; H, 4.74; N, 4.88. Found: C, 46.21; H, 4.81; N, 4.77. Selected FT-IR data on KBr (cm^{-1}): $\nu(C=N)$, 1614vs; $\nu(ClO_4)$, 1087vs and 624w; $\nu(H_2O)$, 3475w.

Data for **4**: Yield: 0.105 g (84%). Anal Calc. for $C_{45.8}H_{59.2}N_4O_{17.8}Cl_2Cu_2Sr$: C, 44.50; H, 4.83; N, 4.53. Found: C, 44.25; H, 4.94; N, 4.57. Selected FT-IR data on KBr (cm^{-1}): $\nu(C=N)$, 1617vs; $\nu(ClO_4)$, 1098vs and 623w.

Data for **5**: Yield: 0.103 g (80%). Anal Calc. for $C_{46}H_{60}N_4O_{18}Cl_2Cu_2Ba$: C, 42.75; H, 4.68; N, 4.34. Found: C, 43.01; H, 4.77; N, 4.41. Selected FT-IR data on KBr (cm^{-1}): $\nu(C=N)$, 1621vs; $\nu(ClO_4)$, 1098vs and 624w.

2.3. Crystal structure determination of **1–5**

The crystallographic data for **1–5** are summarized in Table 1. X-ray diffraction data were collected on a Bruker-APEX II CCD diffractometer at 296(2) K using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were processed using the SAINT [89]. All data were corrected for Lorentz-polarization effects and multi-scan absorption correction were made using SADABS [90]. The structures were solved by

direct methods in SHELXS-97 [91] and refined by full-matrix least-squares based on F^2 using SHELXL-2015 [92] within Olex2 [93].

All of the non-hydrogen atoms were refined anisotropically. While all of the hydrogen atoms were located geometrically and refined using a riding model. All 5 structures contained disorder. In all cases the occupancies of the disordered pairs or sets of atoms were determined by refining the occupancies with their sum set to equal 1 and refined occupancies are given in brackets below along with details of the disordered atoms and restraints or constraints applied. In the case of **1** one of the carbons of the dimine moiety (C10) was disordered over two positions (73:27) and two carbons of one of the ethoxy groups were also disordered over two positions (83:17). For both sets of disordered atoms restraints were applied to maintain sensible geometric and thermal parameters. For **2** one of the carbons of the dimine moiety (C9) was disordered over two positions (54:46), restraints were applied to maintain similar C-C distances in the dimine backbone. In **3** two of the ethoxy groups were disordered over two positions (74:26 and 54:46), the geometric parameters were restrained to sensible values while the thermal parameters were restrained or constrained to maintain reasonable values. In addition, both of the free ClO₄ ions showed disorder (52:48 and 62:38), the Cl-O bond lengths were restrained to similar values and the thermal parameters were also restrained to be similar. The structure of **4** showed disorder in three of the ethoxy groups (57:43, 59:41 and 57:43), one of the dimine backbones (89:11) and the free ClO₄ (63:37). In addition, the occupancy of the coordinated MeOH refined to 60% at which it was subsequently fixed. Restraints were applied to maintain sensible geometric and thermal parameters for all of the disordered atoms. The lattice of **4** also contained disordered methanol solvent (~2.3 methanol per unit cell) that could not be sensibly modelled, the Squeeze routine within Platon [94] was used to remove the contribution of this electron density. The structure of **5**

showed disorder in two of the ethoxy groups (54:46 and 66:34), the coordinated ClO₄ (76:24), the free ClO₄ (90:10) and one of the methanol in the lattice (51:49), restraints were applied to the bond lengths and restraints and constraints were applied to some of the thermal parameters.

The final refinement converged at the R_1 ($I > 2\sigma(I)$) values of 0.0363, 0.0411, 0.0522, 0.0550 and 0.0344 for **1–5**, respectively.

3. Results and discussion

3.1. Syntheses and characterization of **1–5**

The trinuclear Cu^{II}M^{I/II}Cu^{II} compounds **1–5** were readily obtained in good yield on treating 2 equivalents of the metallo-ligand [Cu^{II}L] with 1 equivalent of hydrated perchlorate salts of sodium(I), potassium(I), calcium(II), strontium(II) and barium(II) in methanol. Notably, the same compounds **1–5** were obtained by changing the metallo-ligand : perchlorate salt ratio to 1:1, revealing the tendency of the ligand L²⁻ to stabilize trinuclear Cu^{II}M^{I/II}Cu^{II} systems (M^I = Na^I and K^I; M^{II} = Ca^{II}, Sr^{II}, Ba^{II}).

The characteristic C=N stretching vibration appears as a band of very strong intensity in the range 1612–1621 cm⁻¹ for **1–5**. A very strong absorption in the range 1082–1098 cm⁻¹ and a weakly intense band in the range 622–624 cm⁻¹ for **1–5** arise due to the presence of perchlorate. A weakly intense broader band at 3475 cm⁻¹ in the spectrum of **3** may be assigned to the water molecule in this compound.

UV-Vis spectra of the methanol solution of **1–5** were recorded in the wavelength range 200–900 nm. The spectra of 2×10⁻³ (M) solutions in the range 550–900 nm and of 2×10⁻⁵ (M) solutions in the range 200–500 nm are shown, respectively, in Fig. 1 and Fig. S1. The spectral parameters are listed in Table S1. All the compounds show three bands in

the UV region; overall ranges for the three bands in the five compounds are 229–237 nm, 281–284 nm and 361–383 nm. Among these three bands, the two higher energy bands can be assigned to $\pi \rightarrow \pi^*$ transitions and the lowest can be assigned to phenolate \rightarrow Cu^{II} LMCT transition. At around 610 nm (range 607–614 nm; Table S1), there is a band for **2–5** and a shoulder for **1**. Again, all the five compounds have significant absorbance at around 750 nm, which can be taken as a shoulder for the Ca^{II} (**3**) and Sr^{II} (**4**) compounds. Clearly, two d-d absorptions of Cu^{II} centers appear in all the five compounds because of appreciable distortion of the copper(II) geometry and the presence of two types of copper(II) centers.

3.2. ESI-MS (positive) studies of **1–5**

ESI-MS (positive) of the methanol solutions of **1–5** have been recorded. The observed and simulated spectra are shown in Fig. S2 (for **1**), Fig. S3 (for **2**), Fig. S4 (for **3**), Fig. S5 (for **4**) and Fig. S6 (for **5**). The species appeared in the spectra of all of **1–5** are listed in Table 2 (without drawing) and Table S2 (with drawing). The line-to-line separation in a peak for the dipositive and monopositive ions are 0.5 and 1.0, respectively.

Corresponding to the original composition in terms of nuclearity, one or more trinuclear $[\text{Cu}^{\text{II}}_2\text{M}^{\text{I/II}}]^{+/2+}$ species appear in the spectra of all the five compounds; the types of composition of such species are $[(\text{Cu}^{\text{II}}\text{L})_2\text{Na}^{\text{I}}]^+$ (**IV**) for the Cu^{II}₂Na^I compound **1**, $[(\text{Cu}^{\text{II}}\text{L})_2\text{K}^{\text{I}}]^+$ (**V**) for Cu^{II}₂K^I compound **2**, $[(\text{Cu}^{\text{II}}\text{L})_2\text{Ca}^{\text{II}}]^{2+}$ (**VI**) for Cu^{II}₂Ca^{II} compound **3**, $[(\text{Cu}^{\text{II}}\text{L})_2\text{Sr}^{\text{II}}]^{2+}$ (**VII**) for Cu^{II}₂Sr^{II} compound **4** and $[(\text{Cu}^{\text{II}}\text{L})_2\text{Ba}^{\text{II}}]^{2+}$ (**VIII**) and $[(\text{Cu}^{\text{II}}\text{L})_2\text{Ba}^{\text{II}}(\text{ClO}_4)]^+$ (**IX**) for Cu^{II}₂Ba^{II} compound **5**. Notably, sodium(I) containing ion of composition $[(\text{Cu}^{\text{II}}\text{L})_2\text{Na}^{\text{I}}]^+$ (**IV**) appears not only in the spectra of the sodium(I) analogue **1** but also in the spectra of the other four compounds **2–5**. Another species, a dinuclear ion containing copper(II) and sodium(I) of composition $[\text{Cu}^{\text{II}}\text{LNa}^{\text{I}}]^+$ (**III**) appears in the spectra of the Na^I (**1**), K^I (**2**) and Sr^{II} (**4**) analogues. The spectra of **2**, **3** and **4** exhibit a

dicopper(II) ion of composition $[(\text{Cu}^{\text{II}}\text{L})_2\cdot\text{H}^+]^+$ (**II**). Finally, a monocopper(II) ion of composition $[\text{Cu}^{\text{II}}\text{L}\cdot\text{H}^+]^+$ (**I**) is observed in the spectra of all the five compounds.

3.3. Description of crystal structures of 1–5

The crystal structures of the five compounds $[(\text{Cu}^{\text{II}}\text{L})_2\text{Na}^{\text{I}}](\text{ClO}_4)$ (**1**), $[(\text{Cu}^{\text{II}}\text{L})_2\text{K}^{\text{I}}](\text{ClO}_4)$ (**2**), $[\{\text{Cu}^{\text{II}}\text{L}(\text{H}_2\text{O})\}\text{Ca}^{\text{II}}(\text{Cu}^{\text{II}}\text{L})](\text{ClO}_4)_2$ (**3**), $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Sr}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH})_{0.6}\}](\text{ClO}_4)\cdot 1.2\text{MeOH}$ (**4**) and $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Ba}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH})\}](\text{ClO}_4)\cdot\text{MeOH}$ (**5**) are shown in Fig. 2–6, respectively. The structures reveal that these are trinuclear $\text{Cu}^{\text{II}}\text{M}^{\text{I}}\text{Cu}^{\text{II}}$ ($\text{M} = \text{Na}$ for **1** and K for **2**) or $\text{Cu}^{\text{II}}\text{M}^{\text{II}}\text{Cu}^{\text{II}}$ ($\text{M} = \text{Ca}$ for **3**, Sr for **4** and Ba for **5**) compounds containing two deprotonated compartmental Schiff base ligands, L^{2-} . The $\text{N}(\text{imine})_2\text{O}(\text{phenoxo})_2$ compartment of each of the two L^{2-} ligands is occupied by a copper(II) ion in all of **1–5** to form two $[\text{Cu}^{\text{II}}\text{L}]$ moieties. These two mononuclear copper(II) moieties are placed in such a way that an O_8 site ($(\text{O}(\text{phenoxo})_2\text{O}(\text{ethoxy})_2)_2$) is generated, which, in turn, accommodates the mono or divalent s-block metal ion (Na^{I} , K^{I} , Ca^{II} , Sr^{II} and Ba^{II} for **1–5**, respectively) to form a nearly linear $\text{Cu}^{\text{II}}\text{M}^{\text{I/II}}\text{Cu}^{\text{II}}$ trinuclear system (the $\text{Cu}^{\text{II}}\text{-M}^{\text{I/II}}\text{-Cu}^{\text{II}}$ angles in **1–5** are, respectively, 169.11° , 169.06° , 175.39° , 172.63° and 168.24°). Clearly, four phenoxo and four ethoxy oxygen atoms of two L^{2-} are coordinated to the second or central metal ion. **1** as well as **2** contains one perchlorate moiety, while each of **3–5** contains two perchlorate moieties. The perchlorate moiety in **1** and **2**, both perchlorate moieties in **3** and one of the two perchlorate moieties in **4** and **5** is or are present as anion(s), while the second perchlorate moiety in the latter two compounds acts as a bridging ligand to one copper(II) ion and the central metal ion (Sr^{II} or Ba^{II}). Due the bridging perchlorate ligand in **4** and **5**, the Sr^{II} center in **4** and Ba^{II} center in **5** are nine-coordinated, while the Na^{I} , K^{I} and Ca^{II}

centers in **1**, **2** and **3**, respectively, are eight-coordinated. Both copper(II) centers in both **1** and **2** and one copper(II) center (Cu2) in **3** are four-coordinated, while the second copper(II) center (Cu1) in **3** and both copper(II) centers in both **4** and **5** are pentacoordinated; the fifth coordination position is satisfied by a water oxygen atom for Cu1 in **3**, fractional (0.6) methanol oxygen atom for Cu2 in **4**, one methanol molecule in **5** and one bridging perchlorate oxygen atom for Cu1 in **4** and **5**. While **1–3** contain no solvent of crystallization, **4** and **5** have, respectively, 1.2 and 1.0 methanol molecules as solvent of crystallization.

The results of SHAPE [95,96] analyses on the copper(II) coordination environment in **1–5** are listed in Tables S3 and S4. As already mentioned, two copper(II) centers in both **1** and **2** and one copper(II) center (Cu2) in **3** are tetracoordinated. For both copper(II) centers in each of **1** and **2**, two largest bond angles are deviated significantly from the ideal square planar geometry (by around 24–33° in **1** and by around 25–35° in **2**), revealing significant tetrahedral distortion from square planar geometry. SHAPE [95,96] analyses reveal that although the ‘best ideal’ geometry is square planar for the copper(II) centers in **1** and **2**, the deviation from the ‘best ideal’ geometry is significant (range is 6.123–6.601; deviation should be zero for the ideal case); the geometries should be considered as around 57.8–59.4% square planar and around 40.6–42.2% tetrahedral. In contrast, the two largest bond angles (*ca.* 162 and 165°) for Cu2 environment in **3** are much less deviated from the ideal values, revealing much less tetrahedral distortion. In fact, a SHAPE [95,96] analysis reveals smaller deviation (value = 1.955) from square planar geometry and around 23% weightage of tetrahedral geometry.

The Addison’s geometric parameter, τ ($\alpha - \beta / 60$, where α is the largest angle and β is the second largest angle in the coordination environment) values of the pentacoordinated copper(II) centers, Cu1 in **3**, Cu1 and Cu2 in **4** and Cu1 and Cu2 in **5**,

are, respectively, 0.19, 0.24, 0.14, 0.28 and 0.34 (Table S4), indicating that the geometry in all these cases should be taken as distorted square pyramidal [97]. A SHAPE [95,96] analysis on the Cu1 environment in **3** also reveals that ‘most ideal’ is square pyramidal (Table S4). In contrast, SHAPE analyses reveal that the geometries of the other four pentacoordinated cases (Cu1 and Cu2 in both **4** and **5**) are trigonal bipyramidal, revealing a contradiction between SHAPE [95,96] analyses and Addison’s geometric parameter.

The selected bond lengths and angles for the copper(II) centers in **1–5** are listed in Tables 3, and S5–S7. The Cu–N(imine) bond distances for a particular copper(II) environment are clearly longer than the corresponding Cu–O(phenoxo) bond distances. In contrast the Cu–O(water/methanol/perchlorate) bond distance for the pentacoordinated copper(II) center is significantly longer, as expected due to Jahn-Teller distortion.

SHAPE [95,96] analyses for the coordination environment of the s-metal ion have also been carried out (Tables S8 and S9). The analyses reveal that the ‘most ideal’ geometry for the octa-coordinated Na^I in **1** and K^I in **2** is cube, although the deviation from the ‘most ideal’ geometry from the ideal cube is significantly greater, 6.576 and 7.287, respectively. On the other hand, a SHAPE [95,96] analysis reveals that ‘most ideal’ geometry for the octa-coordinated Ca^{II} center in **3** is biaugmented trigonal prism and the deviation value (3.616) here is much smaller than those in the cases of Na^I or K^I. SHAPE [95,96] analyses on the nine-coordinated environment of Sr^{II} in **4** and Ba^{II} in **5** reveal that the ‘most ideal’ geometry in both cases is muffin with deviation values 3.304 and 6.162, respectively.

The selected bond lengths and the ranges of bond angles around the central metal ion in **1–5** are listed in Table 3, while the individual bond angles in the environments are listed in Tables S10 and S11. The order of ionic radii (*r*) of the central metal ion in **1–5** is K^I (8-coordinated; *r* = 1.51 Å) > Ba^{II} (9-coordinated; radius = 1.47 Å) > Sr^{II} (9-

coordinated; $r = 1.31 \text{ \AA}$) $>$ Na^{I} (8-coordinated; $r = 1.18 \text{ \AA}$) $>$ Ca^{II} (8-coordinated; $r = 1.12 \text{ \AA}$) [98]. However, the similar trend in the corresponding bond distances does not in general take place in **1–5**. It is not surprising because of the following reasons: (i) There exists a difference in coordination number of the central metal ion – octa-coordinated in **1–3**, nine-coordinated in **4** and **5**; (ii) One perchlorate moiety bridges one copper(II) and the central metal ion in **4** and **5**, while no such bridge is present in **1–3**; (iii) There exists a difference in coordination geometry – the ‘most ideal’ geometry is cube for Na^{I} and K^{I} , biaugmented trigonal prism for Ca^{II} and muffin for Sr^{II} and Ba^{II} . Anyway, as environments of Na^{I} and K^{I} are similar, as are those of Sr^{II} and Ba^{II} , the following trends are at least expected for the corresponding bond lengths: $\text{Ba}^{\text{II}}\text{–O} > \text{Sr}^{\text{II}}\text{–O}$ and $\text{K}^{\text{I}}\text{–O} > \text{Na}^{\text{I}}\text{–O}$. In fact, all corresponding bond lengths in **4** and **5** follow the expected order of $\text{Ba}^{\text{II}}\text{–O} > \text{Sr}^{\text{II}}\text{–O}$. Regarding K^{I} in **2** and Na^{I} in **1**, the bond lengths involving K^{I} in **2** is significantly longer than those involving Na^{I} in **1** for some bonds (M–O1, M–O2, M–O5, M–O6, M–O8) but not for all the bonds; surprisingly, one K–O bond length (M–O3) is only slightly longer (by 0.042 \AA) and two K–O bond lengths (M–O4, M–O7) are even shorter (by 0.024 \AA and 0.0104 \AA , respectively) than the corresponding Na–O bond lengths.

As K^{I} (8-coordinated; $r = 1.51 \text{ \AA}$) is significantly larger than that of Na^{I} (8-coordinated; $r = 1.18 \text{ \AA}$) and the two metal ions occupy the similar O_8 site, it is expected that the overall twisting of the two molecules would be different. On the contrary, the twisting may be taken as practically identical, as evidenced by the close values of dihedral angles between the two aromatic rings in each of the two ligands in the two compounds (54.76° and 59.31° in **1**; 55.18° and 55.68° in **2**). In each of **4** and **5**, one can expect appreciably different amount of twisting in two $\text{Cu}^{\text{II}}\text{M}^{\text{II}}$ parts as there is a bridging perchlorate in one part but no such bridge in the second. In fact, such an expected situation occurs in the Ba^{II} analogue **5** where the dihedral angle (62.76°) between the two phenyl

rings of one L^{2-} (perchlorate bridge part) is much greater than that (23.96°) in the second part. In contrast, two parts of the Sr^{II} analogue **4** are more or less similarly twisted (the dihedral angle values are 42.09° and 42.30°). Regarding twisting of the Ca^{II} analogue **3** it is least twisted in this series of five compounds; the dihedral angles between the aromatic rings of each of the two ligands are the smallest, 29.39° and 25.37° .

As the arrangement of the three metal ions in all of **1–5** is nearly linear with the s-block metal ion as the central member (*vide supra*), it is obvious that these compounds are not sandwiched systems, which can also be understood from almost perpendicular disposition of the two $O(\text{phenoxo})_2O(\text{ethoxy})_2$ compartments; the range of the dihedral angle between the two least squares O_4 planes in **1–5** is 81.02° – 88.19° .

3.4. Significant aspects in the composition and structures of **1–5**

Previously published copper(II)–s block metal ion and nickel(II)–s block metal ion complexes derived from single- or double-compartmental Schiff base ligands are listed in Tables S12 and S13 in Supporting Information. The ligands mentioned in Tables S12 and S13 are illustrated in Table S14. Sixteen ligands ($H_2L^I - H_2L^{XVI}$) have been previously utilized to isolate copper(II)–s block metal ion complexes. Of those, complexes of only one s-block metal ions are known for nine ligands ($H_2L^I, H_2L^{II}, H_2L^{IV}, H_2L^V, H_2L^{IX}, H_2L^X, H_2L^{XI}, H_2L^{XV}$ and H_2L^{XVI}), so there is no scope of comparison of second metal ion dependent composition or structure in these cases. On the other hand, systems with more than one s block metal ions have been derived or have been possible to derive from remaining seven ligands ($H_2L^{III}, H_2L^{VI}, H_2L^{VII}, H_2L^{VIII}, H_2L^{XII}, H_2L^{XIII}$ and H_2L^{XIV}). The similarities and differences of the copper(II)–s-block metal ion and nickel(II)–s-block metal ion complexes for different s-block metal ions are concisely mentioned in Table S15. In some cases, similarities in nuclearities are observed in the compounds or the basic

units of the compounds for the following s-block metal ions: (i) Na^I and K^I (Sl. No. 2, 5 and 7 in Table S15); (ii) K^I and Cs^I (Sl. No. 3); (iii) Rb^I and Cs^I (Sl. No. 9); (iv) Na^I and Ca^{II} (Sl. No. 3 and 9) (v) Li^I, Na^I and Mg^{II} (Sl. No. 6 and 9); (vi) Na^I, K^I and Ca^{II} (Sl. No. 4); (viii) Na^I and Sr^{II} (Sl. No. 1); (ix) Rb^I and Ba^{II} (Sl. No. 6). In some cases, differences in nuclearities are observed in the compounds or the basic units of the compounds for the following s-block metal ions: (i) Any of Na^I, K^I and Cs^I compounds are different from another (Sl. No. 8); (ii) Na^I and K^I compounds are similar but those are different from Cs^I analogue (Sl. No. 5 and 7); (iii) Na^I analogue is different from Ca^{II} analogue (Sl. No. 4); (iv) Li^I, Na^I and Mg^{II} compounds are similar and Rb^I and Cs^I compounds are similar but the two sets are different (Sl. No. 9); (v) Na^I, K^I and Ca^{II} compounds are similar but those are different from Ba^{II} system (Sl. No. 4); (vi) Li^I, Na^I and Mg^{II} compounds are similar and Rb^I and Ba^{II} compounds are similar but the two sets are of different types and also these two sets are different from K^I analogue (Sl. No. 6); (vii) Na^I and Ca^{II} compounds are similar and K^I and Cs^I compounds are similar but the two sets are of different types and these two sets are also different from Ba^{II} analogue (Sl. No. 3).

Copper(II)–s-block metal ion or nickel(II)–s-block metal ion complexes for a particular single- or double-compartmental ligand may be similar for some s-block metal ions but should be different for other s-block metal ions, as previously observed and as expected due to the combined effects of the differences in ionic radii and charges (+1 or +2). Anyway, based on ionic radii and charges of the s-block metal ions as well as based on the literature reports, it is unlikely that the types or nuclearities of copper(II)–s-block metal ion or nickel(II)–s-block metal ion complexes with all of Na^I, K^I, Ca^{II}, Sr^{II} and Ba^{II} will be similar (e. g., it is not expected that small monpositive ion Na^I and large dipositive ion Ba^{II} will form closely similar compounds). Such a similarity can only be possible if an average (intermediate) site is somehow created which can accommodate all

of Na^I, K^I, Ca^{II}, Sr^{II} and Ba^{II} more or less similarly. Such a situation occurs in the five title compounds (they are similar as all are trinuclear and approximately linear Cu^{II}M^{I/II}Cu^{II} systems).

Three 3-ethoxysalicylaldehyde-diamine ligands, namely, 3-ethoxysalicylaldehyde-ethylenediamine (H₂L^{XII} in Tables S12–S15) [15–18,66,67], 3-ethoxysalicylaldehyde-1,2-diaminocyclohexane (H₂L^{XIII} in Tables S12–S15) [19] and 3-ethoxysalicylaldehyde-o-phenylenediamine (H₂L^{XIV} in Tables S12–S15) [20,21] were previously utilized to prepare a number of copper(II)/nickel(II)-s block metal ion complexes but definitely the similarity observed herein was not taken place in those systems. Possibly, the presence of four carbon atoms between the two imine nitrogen atoms in H₂L and the accompanied distortion (already discussed) in the copper(II) environment in the N(imine)₂O(phenoxo)₂ compartment allow the two L²⁻ ligands to approach in such a way that an average (intermediate) O(phenoxo)₂O(ether)₂ site is created which can accommodate all of Na^I, K^I, Ca^{II}, Sr^{II} and Ba^{II} approximate in the same way.

It is worth mentioning that a number of trinuclear Cu^{II}M^{I/II}Cu^{II} or Ni^{II}M^{I/II}Ni^{II} compounds from single- or double-compartmental Schiff base ligands are known (M^{I/II} are s-block metal ions) [15–19,21,34,37,38,44,46,48,66]. As listed in Table S16, few of them are linear [18,19,44,46,48] and most of them are sandwiched [15–19,21,34,37,38,44,46,66]. So, the linear trinuclear Cu^{II}M^{I/II}Cu^{II} compounds in this investigation don't represent any new type of structure. However, close similarity of copper(II)-s-block metal ion complexes for all of Na^I, K^I, Ca^{II}, Sr^{II} and Ba^{II} is the interesting aspect that is being focused herein.

From the structural resemblance in **1–5** (derived from 3-ethoxysalicylaldehyde-1,4-diaminobutane) and that in the previously reported M^{II}Cu^{II}₃ stars (derived from salicylaldehyde-1,4-diaminobutane; M = Zn, Cu, Ni, Mn) [27,28], it seems that the

presence of four carbon atoms between the two imine nitrogen atoms and accompanied distortion in the copper(II) environment in the $N(\text{imine})_2O(\text{phenoxo})_2$ compartment facilitate different types of metal ions to behave more or less similarly from structural point of view.

4. Conclusions

The major and interesting outcomes from this investigation may be summarized as the following: (i) All the five copper(II)-s-block metal ion complexes (**1–5**) obtained on reacting $[\text{Cu}^{\text{II}}\text{L}]$ with the salts of five s-block metal ions (Na^{I} , K^{I} , Ca^{II} , Sr^{II} , Ba^{II}) are almost similar; (ii) The results of SHAPE analyses and the values of Addison's geometric parameter regarding square pyramidal versus trigonal bipyramidal geometry are not matched; (iii) $\text{Na}^{\text{I}}-\text{O} \approx \text{K}^{\text{I}}-\text{O}$ and even $\text{Na}^{\text{I}}-\text{O} > \text{K}^{\text{I}}-\text{O}$, although the two metal ions occupy the same O_8 site.

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Appendix A. Supplementary data

Crystallographic data of **1–5** in CIF format, Tables S1–S16 and Figs. S1–S6. CCDC reference number 1825135–1825139 for **1–5**, respectively, contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Figure Captions

Fig. 1. Part of the UV-Vis spectra of 2×10^{-3} (M) methanol solutions of compounds **1–5**.

Fig. 2. Crystal structure of $[(\text{Cu}^{\text{II}}\text{L})_2\text{Na}^+](\text{ClO}_4)$ (**1**). One perchlorate anion and hydrogen atoms are omitted for clarity.

Fig. 3. Crystal structure of $[(\text{Cu}^{\text{II}}\text{L})_2\text{K}^+](\text{ClO}_4)$ (**2**). One perchlorate anion and hydrogen atoms are omitted for clarity.

Fig. 4. Crystal structure $[\{\text{Cu}^{\text{II}}\text{L}(\text{H}_2\text{O})\}\text{Ca}^{\text{II}}(\text{Cu}^{\text{II}}\text{L})](\text{ClO}_4)_2$ (**3**). Two perchlorate anions and hydrogen atoms, except those of coordinated water molecule, are omitted for clarity.

Fig. 5. Crystal structure of $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Sr}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH}_{0.6})\}](\text{ClO}_4) \cdot 1.2\text{MeOH}$ (**4**). One perchlorate anion, except coordinated perchlorate anion, solvated methanol molecules and hydrogen atoms are omitted for clarity.

Fig. 6. Crystal structure of $[(\text{Cu}^{\text{II}}\text{L})(\mu\text{-ClO}_4)\text{Ba}^{\text{II}}\{\text{Cu}^{\text{II}}\text{L}(\text{MeOH})\}](\text{ClO}_4) \cdot \text{MeOH}$ (**5**). One perchlorate anion, except coordinated perchlorate anion, solvated methanol molecule and hydrogen atoms are omitted for clarity.