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S0020-1693(18)31081-8 DOI: https://doi.org/10.1016/j.ica.2019.04.033 Reference: ICA 18878

To appear in: Inorganica Chimica Acta

**Received Date:** 15 July 2018 **Revised Date:** 10 April 2019 Accepted Date: 15 April 2019



Please cite this article as: C. Cretu, L. Cseh, R. Tudose, A. Bora, S. Matsia, A. Hatzidimitriou, O. Costisor, A. Salifoglou, Piperazine core-containing Schiff ligands define chemical reactivity toward divalent metal ions, Inorganica Chimica Acta (2019), doi: https://doi.org/10.1016/j.ica.2019.04.033

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Piperazine core-containing Schiff ligands define chemical reactivity toward divalent metal ions

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#### Abstract

A series of homologous Schiff bases N,N'-bis[(4-decyloxy-salicylideneamino)-n-propyl]piperazine] (ZOPPH<sub>2</sub>), and N,N'-bis[(4-dodecyloxy-benzylideneamino)-n-propyl]-piperazine (DBPP)(1), based on 1,4-bis(3-amino-propyl)-piperazine (APPZ), were designed and synthesized, with APPZ serving as the piperazine core, bilaterally flanked by extended alkyl chain-containing antennae. Driven by the pursuit of metallomesogenic materials bearing liquid crystalline state properties, chemical reactivity toward divalent metals Co(II) and Cu(II), in alcoholic tetrahydrofuran/dimethylsulfoxide media, led compounds or to All materials were  $[{Co(ZOPP)}(ClO_4)]_2(CH_3OH)(2(CH_3)_2SO(2)) \text{ and } [Cu(APPZ)Cl]Cl(3).$ characterized by elemental analysis, spectroscopic techniques (UV-Visible, FT-IR, NMR where appropriate), molar conductivity, and X-ray crystallography. Physicochemical characterization emphasizes the a) importance of N,O-containing Schiff anchors in metal ion binding, b) significance of the phenolic moiety, on the flanks of the Schiff ligands, in promoting either metal ion complexation or dissociation of the Schiff base at the azomethine moiety junction, thereby altering metal ion chemical reactivity, and c) observed oxidation of Co(II) to Co(III) upon mononuclear complex formation. Hybrid DFT calculations on DBPP and ZOPPH<sub>2</sub> suggest increased reactivity of the Schiff -CH=N- moiety, in the absence of the phenolic moiety, and concurrent metal ion presence, thereby lending credence to the notion of metal-assisted rupture of the specific bond in DBPP and the emergence of specific metal-ligand product(s). Collectively, the data denote the significance of structural features of piperazine-core Schiff antennae ligands in a) promoting chemical reactivity toward transition metals, b) defining metal-ligand complexation and lattice architecture, and c) parameterizing such chemical reactivity into synthetic advances toward new materials with well-defined solid-state architecture, lattice and physicochemical properties.

**Keywords:** Schiff base ligand, coordination complex, cobalt and copper crystal structure, molecular antennae, metal chemical reactivity.

#### **1. Introduction**

Schiff bases have been at the forefront of research over the past decades [1,2]. Interest in their synthesis and emergence in complex organic molecules has stemmed from their natural source of origin and their incipient utilization in cellular processes and pathophysiologies [3,4]. Intimately relevant to their emergence in natural systems is their widespread use in the design and synthesis of new and novel metal-organic materials, exemplifying commensurably new properties as a result of the concurrent metal ion and organic ligand structural-electronic attributes. In such interactive processes, transition metal ions can participate with different oxidation states [5], thereby leading to discrete lattice architectures. Standing out in the family of hybrid binary metal-organic species, comprised of metal ions and appropriately designed organic Schiff ligands, are divalent and trivalent metal ion-Schiff base complexes, including Co(II,III) and Cu(II), which have attracted considerable attention in the field of chemistry [6-9], biology [10], and physics [11-13], due to their extensive practical applications. One such significant application area involves development of liquid crystalline materials, thus drawing in a link between metal ion coordination chemistry and appropriately configured Schiff base ligands [14]. Based on the above grounds, studies [15-17] on the coordination potential of Co(II) with symmetrically structured Schiff bases, derived from salicylaldehyde derivatives and a variety of diamines, have shown that the nature and length of the fragment between the two azomethine groups affect the coordination modes to the cobalt ion [15,16]. Concurrently, increase of the methylene chain length of the diamine moiety bestows adequate flexibility upon those complexes, thereby switching their structure from a planar one toward a distorted or pseudotetrahedral motif [8,12]. To further specify the reactivity of such distinctly configured Schiff bases a) comprised of a common piperazine core, b) bearing well-defined aromatic salicyl aldehyde moieties, and c) containing variable length aliphatic chains, extending out to twelve carbon atoms, toward transition metal ions, two members of the Schiff base family of the aforementioned organic binders were chosen as potential ligands to divalent transition metal ions Co(II) and Cu(II). The latter starting reagents were used in the form of salts to promote chemical reactivity in variable solvent systems.

The employed ligands exhibit long alkyl chains extending bilaterally out of the Schiff azomethine moieties of the piperazine core, while the presence of the phenol moiety on the aromatic ancillary group appears to play an important role in promoting metal ion coordination and chemical

reactivity. These structural features reflect mesomorphic phase characteristics associated with induction of anisotropic fluidity, thereby providing perspective into the pursuit of potential metallomesogenic materials [14,18-20]. Being driven by such a challenge, research efforts were launched to investigate synthetically the ligand structure-specific chemistry toward Co(II) and Cu(II), two metals with broad coordination versatility. In that respect, the collective combination of ligand attributes (alkyl chain length, hydrophobicity, piperazine core, phenol-containing moieties) and metal ion interactions targeted hybrid metal-organic materials exhibiting solid-state architectures, bearing new lattice and electronic properties (e.g. luminescence). The results of the work a) denote the distinct character of metal ion-ligand reactivity through both experimental and theoretical data, b) suggest that metal-Schiff ligand complexation can be pursued effectively in a ligand-structure-specific fashion, c) project the importance of the versatility of the azomethine moiety of the Schiff ligand, seeking organizational role(s) in the coordination to the metal ion and contributing to the arising structural architecture and lattice dimensionality of the emerging molecular metal-ligand assemblies, and d) emphasize the role of the phenolic moiety in modulating the sought after reactivity of N,N'-bis[(4-decyloxy-salicylideneamino)-n-propyl]-N,N'-bis[(4-dodecyloxy-benzylideneamino)-n-propyl]-piperazine piperazine  $(\text{ZOPPH}_2)$ vs (DBPP) by facilitating (dis)assembly of the Schiff ligand and concomitant coordination of the metal ion to the Schiff piperazine core.

#### 2. Experimental

#### 2.1. Materials and methods

Cobalt(II) perchlorate hexahydrate (Co(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O), copper(II) chloride dihydrate (CuCl<sub>2</sub> 2H<sub>2</sub>O), copper(II) perchlorate hexahydrate (Cu(ClO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O) and the organic solvents (tetrahydrofuran (THF), methanol, dimethylsulfoxide, N,N'-dimethylformamide (DMF)) were purchased from Merck or Sigma Aldrich and used without further purification. Ligands ZOPPH<sub>2</sub> and DBPP (**1**) were synthesized according to previously reported procedures [**14,18**].

**Caution!** Cobalt perchlorate is potentially explosive and should be handled in small quantities with due care.

#### **2.1.1 Physical Measurements**

Infrared spectra (KBr) in the range 4000-400 cm<sup>-1</sup> were recorded on a Cary 630 FT-IR spectrophotometer. The simultaneous determination of carbon, hydrogen and nitrogen (%) was

carried out with a ThermoFinnigan Flash EA 1112 CHNS elemental analyzer. The analyzer operation is based on the dynamic flash combustion of the sample at 1800 °C, followed by reduction, trapping, complete GC separation and product detection. The instrument is fully automated and PC controlled via the Eager 300 software. Molar electrical conductivities were measured using a Mettler Toledo FiveEasy plus (FP30) conductivity meter equipped with a Lab conductivity sensor LE740. The solution electronic spectra of all compounds investigated (C =  $10^{-4}$  M) were recorded on an Agilent Cary 60 spectrometer.

#### **2.1.2 Photoluminescence**

Fluorescence spectra were recorded in CHCl<sub>3</sub> (for 1), DMF (for ZOPPH<sub>2</sub> and 2), and MeOH (for 3) solutions ( $C = 10^{-4}$  M) using a Perkin Elmer LS-55 spectrophotometer; the excitation slit was set at 10 and that of the emission at 7.5, while the scanning speed was 100 nm/min. All measurements were carried out at room temperature.

#### 2.1.3 NMR spectroscopy

The NMR spectra were run on a Bruker Avance III 500 spectrometer (500.13 MHz for <sup>1</sup>H, 125.75 MHz for <sup>13</sup>C) in CDCl<sub>3</sub>, at 298 K, using tetramethylsilane (TMS) as internal standard. NMR assignments were carried out on the basis of <sup>1</sup>H, <sup>13</sup>C, DEPT 135 and HSQC (HSQCEDETGPSISP) (2D) NMR spectra.

#### 2.2. Synthesis

Synthesis of  $[{Co(ZOPP)}(ClO_4)]_2(CH_3OH)^2(CH_3)_2SO(2)$ . An ethanolic solution (20 mL) of Co(II) perchlorate hexahydrate, Co(ClO\_4)\_2·6H\_2O, (0.61 g, 1.67 mmol) was added to a stirred solution of ZOPPH<sub>2</sub> (0.60 g, 0.83 mmol) in ethanol (30 mL). The resulting reaction mixture was refluxed for 4 h. A brown solid was obtained by evaporation of the solvent at room temperature. The solid was collected and washed with methanol and hot water. Single crystals suitable for X-ray crystallographic work were obtained by recrystallization from DMSO. Yield: 0.59 g (86 %). Anal. Calcd. for 2, (C<sub>93</sub>H<sub>156</sub>Cl<sub>2</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>19</sub>S<sub>2</sub> M<sub>r</sub> 1943.21): C, 57.48; H, 8.09; N, 5.77. Found: C, 57.41; H, 8.04; N, 5.71.

Molar conductivity (DMF,  $5 \cdot 10^{-4}$  M)  $\Lambda_{M}$ ,  $\Omega^{-1}$ mol<sup>-1</sup>cm<sup>2</sup>: 43; IR (KBr, cm<sup>-1</sup>: 3434 (br, w), 2918 (s), 2840 (s), 1618 (vs), 1606 (vs), 1529 (m), 1488 (m), 1467 (s), 1429 (m), 1367 (m), 1338 (w), 1306 (m), 1268 (w), 1248 (m), 1232 (s), 1213 (m), 1176 (s), 1149 (m), 1117 (m), 1095 (vs), 1079 (vs), 1017 (m), 993 (m), 959 (m), 852 (w), 842 (m), 823(w), 792 (m), 780 (m), 722 (w), 661 (w), 636

(w), 621 (m), 577 (w), 529 (w), 496 (w), 484 (w), 466 (w), 450 (w), 434 (w); UV-Vis (DMF,  $5 \cdot 10^{-4}$ M), ( $\lambda_{max}/nm$  ( $\epsilon/L$  mol<sup>-1</sup>cm<sup>-1</sup>)): 377(5240), 506(420), 578(220), 655(120).

**Synthesis of** [Cu(APPZ)Cl]Cl (**3**). A solution of Cu(II) chloride dihydrate, CuCl<sub>2</sub>·2H<sub>2</sub>O, (0.080 g, 0.48 mmol) in THF (4 mL) was added slowly by diffusion to a solution of APPZ (0.10 g, 0.48 mmol) in DMSO (3 mL). Single crystals suitable for X-ray crystallographic work were obtained from the reaction mixture. Yield: 0.59 g (86 %). Anal. Calcd. for **3**, (C<sub>10</sub>H<sub>24</sub>Cl<sub>2</sub>CuN<sub>4</sub> M<sub>r</sub> 334.78): C, 35.88; H, 7.23; N, 16.74. Found: 35.82; H, 7.25; N, 16.69.

Molar conductivity (MeOH,  $5 \cdot 10^{-4}$  M)  $\Lambda_{M}$ ,  $\Omega^{-1}$ mol<sup>-1</sup>cm<sup>2</sup>: 112; IR (KBr, cm<sup>-1</sup>: 3260 (s), 3219 (s), 3177 (s), 3128 (s),3104 (s), 2934 (s), 2863 (s), 1602 (s), 1467 (s), 1433 (m), 1398 (m), 1346 (m), 1306 (m), 1283 (m), 1256 (m), 1213 (m), 1169 (m), 1147 (s), 1105 (m), 1079 (m), 1027 (s), 981 (m)945 (w), 919 (m), 861 (w), 834 (m), 787 (s), 675 (s), 515 (w), 478 (m), 423 (w). UV-Vis (MeOH,  $5 \cdot 10^{-4}$  M), ( $\lambda_{max}/nm(\epsilon/L mol^{-1}cm^{-1})$ ): 274(6840), 619(282).

#### **2.3. X-Ray structural determination**

Single crystals of DBPP (1) were grown in the reaction mixture [14,18], selected directly from the mother liquor under a microscope and sealed in thin-walled glass capillaries. X-ray quality crystals of compounds 2 and 3 were grown from DMSO and THF-DMSO solutions, respectively. For the structure determination of all compounds, single crystals of the respective compound were mounted on a Bruker Kappa APEX II diffractometer, equipped with a triumph monochromator at ambient temperature. Diffraction measurements were made using graphite monochromated Mo Ka radiation. Unit cell dimensions were determined and refined by using the angular settings of at least 50 high intensity (> $20\sigma(I)$ ) reflections in the range  $10 < 2\theta < 40^{\circ}$ . Intensity data were recorded using  $\varphi$  and  $\omega$  scan modes. The frames collected for each crystal were integrated with the Bruker SAINT software package [21], using a narrow-frame algorithm. Data were corrected for absorption using the numerical method (SADABS) based on crystal dimensions. The structure was solved using the SUPERFLIP [22] package and refined by fullmatrix least-squares method on  $F^2$  using the CRYSTALS package version 14.43 and 14.61 [23]. All non-disordered non-hydrogen atoms have been refined anisotropically. For the disordered non-hydrogen atoms, occupancy factors were first determined with fixed isotropic displacements. Finally, all of them were isotropically refined with fixed occupancy factors.

All hydrogen atoms were found at the expected positions and refined using soft constraints. By the end of the refinement, they were positioned using riding constraints. Crystal data and

structure refinement parameters of **1-3** are presented in **Table 1**. Illustrations were drawn by Diamond 3.1 package [**24**]. The CCDC numbers for compounds are CCDC 743573 (**1**), CCDC 978591 (**2**), and CCDC 1846243 (**3**).

#### 2.4. Computational studies

The molecular structures of APPZ, DBPP (1) and ZOPPH<sub>2</sub> ligands were investigated by means of semi-empirical quantum chemical calculations, involving Austin Model 1 (AM1) [25,26] and Density Functional Theory (DFT), using the Hyperchem 7.52 program [27] and Jaguar module of the Schrodinger package [28]. The AM1 geometry optimization was carried out by using the default parameters as Polak-Ribere algorithm, with the SCF convergence set to 0.0001 kcal/mol and the RMS gradient set to 0.001 kcal/(Åmol) [25,26]. The complete geometric optimization of the AM1 geometries was obtained by applying hybrid DFT with the Becke, three-parameter, Lee-Yang-Parr (B3LYP/6-311++) exchange-correlation functional and the basis set level of theory, 6-31G(d,p) [27]. Ligand geometries were optimized without imposing any symmetry constraints. Further, frequency calculations were done in order to check the true energy minima of the studied ligands. The true minima were confirmed by the absence of any negative frequencies. Based on DFT theory, several electronic properties such as, e.g. heat of formation ( $\Delta H_f^{\theta}$ ) [29], HOMO, LUMO, and HOMO-LUMO gap ( $\Delta E$ ) energies [30,31], the atomic Fukui indices [32], hardness (n), softness (S), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), and global electrophilicity ( $\omega$ ) were computed. These global electronic descriptors are used to describe the reactivity behavior of the chemical system.

#### 3. Results

#### 3.1. Synthesis

Schiff bases, as starting materials, were synthesized according to optimized procedures from their components, i.e. the core-containing piperazine and the corresponding aromatic aldehyde [14,18]. The stoichiometric reactions, under the reaction conditions leading to the synthesis of ligands  $ZOPPH_2$  and DBPP, are shown below:



The piperazine core-containing APPZ ligand, as shown in the above two reactivity schemes, appears to be the key fundamental unit, based on which the two aforementioned ligands rely on and to which the DBPP ligand dissociates upon copper reactivity (vide infra).

Furthermore, the Schiff base metal complex [{Co(ZOPP)}(ClO<sub>4</sub>)]<sub>2</sub>·(CH<sub>3</sub>OH)·2(CH<sub>3</sub>)<sub>2</sub>SO (**2**) and [Cu(APPZ)Cl]Cl (**3**) were synthesized through reactions between cobalt and copper salts and the corresponding ligand, containing the available coordination sites, including the piperazine bridge, employing variable molar ratios in an organic solvent medium. Thus, **2** was synthesized from Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and ZOPPH<sub>2</sub> in ethanol with a 2:1 molar ratio. Previous experience in the lab [**14**] had shown that the hexadentate Schiff base ZOPPH<sub>2</sub> can act as a binucleating ligand through a two (N,O) donor atom set or a bis-tridentate ligand through two (N,N,O) donor atom sets, depending on the involvement of the piperazine core nitrogen in metal coordination, with the piperazine moiety being in the *chair* conformation. Nevertheless, the donor properties, the relatively flexible structure, and the symmetry of similar ligands [**33**] also offer an opportunity to prepare mononuclear complexes with the piperazine moiety in the *boat* conformation. The mononuclear structure of the complex reported herein was supported by molar conductivity measurements and X-ray diffraction. The value of molar conductivity suggests a 1:1 electrolyte-type [**34**] complex.

In an alternative way, Cu(II) chloride reacted with APPZ in a 1:1 molar ratio, in a THF-DMSO medium, leading to the isolation of compound **3**. The isolated material was identified by elemental analysis, FT-IR and X-Ray crystallography. The reaction conditions and stoichiometric reaction associated with the synthesis of **3** are given pictorially in **Scheme 1**:





**Compound 3** 

#### Scheme 1. Synthesis of compound 3

The specific chemical reactivity follows along the line of the synthesis of compound  $[Cu(APPZ)(ClO_4)](ClO_4)$ , which emerged from a similar reaction between  $Cu(ClO_4)_2 \cdot 6H_2O$  and DBPP (1) in THF solution, with a 1:1 molar ratio. The overall stoichiometric reaction and reaction conditions are presented in **Scheme 2**:



**Scheme 2.** Synthesis of [Cu(APPZ)(ClO<sub>4</sub>)](ClO<sub>4</sub>)

It proves that regardless of the solvent system employed, the final product is the same, containing the APPZ core unit of DBPP (vide infra).

#### 3.2. Description of Crystal Structure

 $(C_4H_8N_2)[C_3H_6-N=CH-C_6H_4OC_{12}H_{25}]_2$  (**DBPP**) (1) crystallizes in the triclinic space group Pī. The crystal structure (Fig. 1A) depicts a symmetrical molecule with four potential coordination sites linked to the extended piperazine bridge. The crystal packing of the architecture in 1 is shown in **Fig. 1B**. Crystal data and structure refinement parameters of **DBPP** are presented in

**Table 1**. All relevant bond lengths and angles with their estimated standard deviations are given in **Table 2**. The distance of the derived C=N bond is 1.274(2) Å, in line with typical carbonnitrogen double bonds (1.279 Å). The torsion angle C(7)-N(10-C(8)-C(9) is  $130.4(2)^{\circ}$  [**35**]. The interatomic distances C–C and C–N of the piperazine bridge of 1.500(2) and 1.463(2) Å, respectively, are within the range expected for these single bond types of C–C 1.524 and C–N 1.469 Å, respectively [**35,36**].

The piperazine nitrogen atoms are tetrahedral, as shown by the valence angles around these atoms, in the range of 109°, corresponding to  $sp^3$  hybridization (between 106.81(14)° and 112.55(14)°) [**37**]. The piperazine ring can be thought of as composed of three moieties: plane A composed of N(2)–C(11)–C(12), ring B composed of C(11)–C(12)–C(11)'–C(12)', and plane C composed of  $N(2)^{2}-C(11)^{2}-C(12)^{2}$ . The dihedral angle between planes A and B is 30.89°, equal to that of B and C, and that of A and C is 0°, thus indicating the stable chair conformation of the piperazine ring [38]. The torsion angles  $CCNC_{exo}$ , C(12)-C(11)-N(2)-C(10), of 177.4(1)° indicate that the heterocyclic N substituents are in equatorial positions. All of these arguments support the notion that the geometry of the molecule is characterized by the "chair" conformation of the piperazine core, with the two 4-dodecyloxy-benzylidene moieties pointing away from the diamine bridge [39]. The benzene rings (Structure S1) of two neighboring molecules are arranged in an off-centered parallel displaced manner, with a distance of 2.790 Å between their mean planes. The  $\pi$ - $\pi$  stacking distance is 5.502 Å and the angle between the centroid centroid vector and the normal to the ring plane is 30.68°, thus suggesting the existence of a weak interaction between the slipped interlayers occurring as shown in Fig. 1C [40]. The aforementioned interactions prove that the stability of the crystal package is supported by van der Waals forces between the parallel alkyl chains, hydrogen-bonding, and  $\pi$  stacking interactions.

Compound [{Co(ZOPP)}(ClO<sub>4</sub>)]<sub>2</sub> (CH<sub>3</sub>OH)<sup>-</sup>2(CH<sub>3</sub>)<sub>2</sub>SO (**2**) crystallizes in the monoclinic system, space group C2/c. Fig. 2A shows the crystal structure and the atom numbering scheme of the complex. The position of the molecules in the unit cell can be seen in Fig. 2A. All relevant bond lengths and angles with their estimated standard deviations are given in Table 2.

The compound consists of a well-defined complex unit [Co(ZOPP)], perchlorate counter ions, dimethylsulfoxide and methanol solvent molecules. In view of the fact that there is one methanol CH<sub>3</sub>OH molecule and two molecules of  $(CH_3)_2SO$  per two mononuclear Co(III) assemblies, the molecular formulation of the entire compound is provided through the molecular formula cited

above. The actual mononuclear assembly, however, of the central metal ion remains discrete, and it is used as such throughout the manuscript, reflecting the form of the complex unit [Co(ZOPP)]. The central Co(III) ion is hexacoordinated and the environment can be described as octahedral, with the N<sub>4</sub> set arising from two imino nitrogens and two piperazine nitrogen atoms bordering the basal plane, and two phenolic oxygens in the apical positions. The cobalt ion and the N<sub>4</sub> donor set are almost coplanar, with a 0.010 Å deviation of the cobalt ion from the plane. The Co–N<sub>imino</sub> distances of 1.934(2) and 1.945(2) Å denote bond lengths shorter than Co–N<sub>pip</sub> distances of 1.981(2) and 2.004(2) Å, albeit in the range reported for similar compounds **[41,42]**. The two phenolic oxygen atoms occupy the apical positions, with the Co–O<sub>phenolic</sub> distances being between 1.893(2) and 1.898(2) Å, almost equal, shorter than those reported for similar compounds **[43,44]**. Further, the angles between the apical phenolic oxygen atoms, Co(III) and the donor nitrogen atoms in the basal plane, which should be equal to 90°, are between 87.64(9) and 94.31(9)°. The *trans* angle O(1)–Co(1)–O(2) of 177.68(8)° is close to linearity, emphasizing that both oxygen atoms are placed in the vertices of an almost undistorted octahedron.

The two  $-CH_2-CH_2$  piperazine straps form a double five-membered chelate ring with the Co(II) central ion. As a consequence, the "bite" angle N(2)–Co(1)–N(3) of 73.18(10)° and metal-piperazine nitrogen distances are smaller than those reported for similar compounds [42]. Torsion angles C(12)–C(11)–N(2)–C(10)<sub>propyl</sub> of 164.8(3) – 170.3(2)° can also be noticed. These structural results confirm the *boat* conformation of the piperazine moiety [45] and account for the "reinforced" effect induced by the presence of two straps between the two piperazine nitrogen donors [46,47].

The alkyl chains  $-C_{10}H_{25}$  are disposed almost linearly with respect to the phenyl rings, with the torsion angles C(4)–O(3)–C(25)–C(26) and C(22)–O(4)–C(35)–C(36) being 179.0(3) and 157.9(3), respectively. The perchlorate anion is also present and shows Cl–O bonds ranging from 1.389(3) to 1.425(3) Å. The perchlorate ion is not coordinated to the Co(III) ion and exhibits typical bond angles in the range 102.73(19)–124.8(2)°.

Molecular packing along the *c* axis (**Fig. 2B**) shows a three-dimensional open-framework arrangement, with large ellipsoidal channels/holes of 15.930 x 12.823 Å, filled with ordered solvent molecules. The architecture is held together by van der Waals forces and hydrogen bonds [**48,49**]. Moderate intermolecular hydrogen bonding also occurs between O(11)–H(494)-O(9) (2.932 (5) Å) atoms of methanol and dimethylsulfoxide molecules. The C-H contacts, treated as

Compound [Cu(APPZ)Cl]Cl (3) crystallizes in the monoclinic system, space group P2<sub>1</sub>/n. The crystal structure of the complex (**Fig. 3A**) shows that the DBPP ligand dissociates into the fundamental core APPZ, whereupon the four N atoms of the APPZ are in the same plane (N(1)N(2)N(3)N(4) plane), which is parallel to the *c* axis. The N(1)N(2)N(3)N(4) plane is the base of the pyramid, with the pentacoordinated Cu(II) ion serving as the central metal. The Cl atom sits at the apex of the same pyramid, 2.852 Å away from the base. The piperazine core is in a boat conformation and separated into two dissimilar moieties. The Cu–N<sub>amine</sub> of 2.007(2) and 2.009(2) Å bond lengths are just shorter than the Cu–N<sub>pip</sub> bond distances of 2.057(2) and 2.062(3) Å, but in the range reported for similar compounds [**51**]. The hexagonal Cu(NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N) rings on the two opposite sides of the Cu(II) center have their central CH<sub>2</sub> group residing on different planes. The angles of N-Cu-N are the same for both rings and smaller than 120° (~95°), thereby leading to deformed hexagons. The copper ion is located above the N(1)N(2)N(3)N(4) plane at 0.391 Å.

The position of the molecules in the unit cell can be seen in **Fig. 3B**. Selected bond distances and angles are given in **Table 2**. The molecular packing along the *a* axis (**Fig. 3B**) shows an intercalated array of *zig-zag* molecules. The architecture is held together by van der Waals forces and weak hydrogen bonds between the amine N(4) atom and the chloride Cl(2) ion at 3.258 Å, with an angle N(4)–H(103)<sup>...</sup>Cl(2) of 146.33<sup>o</sup>.

Collectively, compounds 2 and 3 have the main core APPZ fragment unit containing the piperazine moiety in a *boat* conformation. The "bite" angle  $N_{pip}$ -metal ion  $-N_{pip}$  for all of these compounds is around 73°, smaller than 90°, as expected for a "reinforced" effect induced by the presence of two straps between the two piperazine nitrogen donors. This effect leads to a distortion of the central angles, namely  $N_{pip}$ -metal ion- $N_{amino/imino}$  at around 95°, smaller than 120°. The coordination geometry of the metal ions is different in the two assemblies, however the basal plane is the same for all three complexes: the cobalt ion in 2 has an octahedral geometry with the phenolic oxygen atoms in the apical position, whereas the copper ion in 3 has a pyramidal geometry with the equatorial nitrogens, with a 0.010 Å deviation from the plane, whereas the copper ion in 3 is located 0.391 Å above the plane.

#### 3.3. FT-IR spectroscopy

The FT-IR spectrum of **1** shows the characteristic band of the C=N bond at 1637 cm<sup>-1</sup> and intense bands at 2922 and 2851 cm<sup>-1</sup> attributed to CH<sub>2</sub> and CH<sub>3</sub> stretching vibrations belonging to the dodecyloxy-(C<sub>12</sub>) alkyl chains (**Fig. S1A**). The bands around 2750–2850 cm<sup>-1</sup> are assigned to the v(C-H) vibrations of the piperazine fragment [**18**].

The spectrum of **2** provides valuable information on the nature of the functional groups bound to the metal ion (**Fig. S1B**). The strong band at about 1625 cm<sup>-1</sup>, corresponding to the v(C=N) stretching vibrations of the free ligand, is shifted to lower field values in the complex at 1608 cm<sup>-1</sup>. The phenolic v(C-O) stretching vibrations at 1228 cm<sup>-1</sup> in the Schiff base is shifted toward lower frequencies in the complex, at 1213 cm<sup>-1</sup>. This shift confirms the involvement of the phenolic oxygen in the formation of the C-O-M bond. Coordination of the piperazine nitrogens to the Co(III) ion is attested to by the absence of the v(C-H) of N-CH<sub>2</sub> (alkyl) stretching vibration modes at about 2750 cm<sup>-1</sup> in the IR spectrum of the complex [**52**]. Strong vibration bands at 1117–1079 cm<sup>-1</sup> and a sharp medium band at 621 cm<sup>-1</sup> can be attributed to the non-coordinated perchlorate counter ion [**33,53**]. In the low frequency region, new weak bands from the complex spectrum at 529 and 450 cm<sup>-1</sup> can be assigned to the M–O and M–N bonds, respectively.

The spectrum of **3** shows the characteristic bands of the piperazine ligand (APPZ), with changes in the vibration bands due to metal ion coordination (**Fig. S1C**). Thus, the bands in the range  $3260-3104 \text{ cm}^{-1}$  are assigned to the antisymmetric and symmetric v(NH) stretching vibrations of the NH<sub>2</sub> group. The intense band at 1602 cm<sup>-1</sup> is attributed to the  $\delta$ (NH) vibration. The bands at 2934 and 2863 cm<sup>-1</sup> are assigned to the v(CH<sub>2</sub>) mode of the propylene groups. The characteristic bands of the piperazine moiety around 2800–2700 cm<sup>-1</sup> disappear, suggesting involvement of the piperazine nitrogen atoms in metal ion coordination, with piperazine adopting a *boat* conformation [**52**].

#### 3.4. UV-Visible Spectroscopy

The electronic spectrum of the free ligand ZOPPH<sub>2</sub> was recorded in fresh DMF solution (10<sup>-4</sup> M). The spectrum shows two intense bands at 277 and 302 nm, attributable to  $\pi$ - $\pi$ <sup>\*</sup> transitions, and a medium intensity band at 385 nm, corresponding to an n- $\pi$ <sup>\*</sup> transition [54]. The spectrum of DBPP (1) was recorded in chloroform (10<sup>-4</sup> M). It shows an intense band at 270 nm and a shoulder around 296 nm attributed to  $\pi$ - $\pi$ <sup>\*</sup> transitions. In the electronic spectrum of **2**, the d-d transitions characteristic for octahedral Co(III) ion can be observed. Thus, the bands at 506, 578

and 655 nm attributable to  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ ,  ${}^{1}A_{1g} \rightarrow {}^{1}E_{g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  transitions, respectively, are present. The pronounced splitting of  ${}^{1}T_{1g}$ , is indicative of a *trans*-octahedral geometry [**55**,**56**], which was confirmed by the X-ray crystal structure. The position and intensity of these bands indicate an octahedral environment around the Co(III) center [**57**,**58**]. The electronic spectrum of **3** shows a broad band at 619 nm, attributed to a d-d transition, corresponding to a five-coordinate Cu(II) center with a nitrogen-rich coordination environment [**57**].

#### 3.5. NMR spectroscopy

The <sup>1</sup>H-NMR spectra of both ligands (ZOPPH<sub>2</sub> and **1**) [**14,18**] reveal the distinct nature of the emerging compounds through the presence of azomethine protons at 8.13 and 8.19 ppm for ZOPPH<sub>2</sub> and **1**, respectively. New signals appear in the range 1.77-3.60 ppm, attributable to protons from the bis(N-propyl)piperazine unit.

The <sup>1</sup>H-, <sup>13</sup>C-, 1D and 2D-NMR spectra of **2** on single crystals in CDCl<sub>3</sub> are shown in **Fig. S2A-D**). The proton and carbon assignments are presented in **Table 1S**. The HSQC spectrum is used to assign each carbon atom in the aromatic region, but it is very difficult to assign exactly each hydrogen atom to the corresponding carbon atom from the aliphatic chains. From the <sup>1</sup>H-NMR spectrum in solution, it can be seen that the complex molecule is distorted. Because of the twenty hydrogen atoms of the complex there are roughly seven signals at 4.2, 3.71, 3.07-3.2, 2.83, 2.56-2.66, 2.43-2.56, 1.99 ppm, instead of four or maximum five signals (three signals from the propyl chain and one or two from the CH<sub>2</sub> piperazine moiety) corresponding to a symmetrical molecule. This distortion is also confirmed through the HSQC spectrum. All twenty hydrogens are connected to ten carbons, with eight carbons being present in the range 50-60 ppm and two carbon atoms being present at 21.3 ppm. If the molecule were symmetrical, we would only have four signals in the 50-60 ppm range and one signal at 21.3 ppm.

#### 3.6. Photoluminescence

The solution fluorescence spectra (C =  $10^{-4}$  M) of the free ligands ZOPPH<sub>2</sub> and DBPP (1) show emission peaks centered around 436 nm and 394 nm, respectively. They are both attributed to intraligand charge-transfer (ILCT) transitions (**Fig. 4**) [**59**]. It is noted that, under the experimental conditions employed, the spectrum of 1 exhibits enhancement of the emission compared to ZOPPH<sub>2</sub>, thereby denoting the distinct nature of one ligand over the other. Therefore, the presence of the phenolic moiety in the ZOPP ligand appears to cause quenching of the emission [**60,61**]. The spectrum of the Co(III) complex (**2**) shows the same emission

wavelength (437 nm) as the free ligand ZOPPH<sub>2</sub>, with a slight increase in the fluorescence. Fluorescence enhancement through complexation could be attributed to the increase in the rigidity of the ligand, which can minimize the loss of energy through vibrational motions and increase the emission efficiency [62]. Complex 3 shows a similar emission spectrum to the free ligand 1, further exhibiting a decrease in the emission intensity, signifying the presence of the APPZ core bound to the metal center (Table 2S).

#### **3.7.** Computational analysis

The X-ray crystal structure of the DBPP ligand (1) indicates that the piperazine moiety is in the chair conformation. The same conformation was observed for the piperazine core-containing APPZ ligand, which appears to be a key unit in the synthesis of the DBPP and ZOPPH<sub>2</sub> ligands. In order to identify the key structural features responsible for the preferred chair orientation, the lability of the carbon-nitrogen double bond and global chemical reactivity of molecules, the geometric (bond distances and bond angles, Table 3S) and electronic parameters (heat of formation  $(\Delta H_f^{\theta})$ , HOMO and LUMO energies, HOMO-LUMO gap energies ( $\Delta E$ ), the reactivity Fukui indices, hardness ( $\eta$ ), softness (S), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ) and global electrophilicity  $(\omega)$ ) were analyzed in comparison to the experimental results (Figs. S3-S5, Tables 4S-5S). It is well known that the conformational interconversion pathways of a sixmembered ring system are related to the nature, orientation, type, and number of substituents attached to the system [63,64,65]. In this regard, the most stable conformation for the APPZ, DBPP (1), and ZOPPH<sub>2</sub> ligands was found to be the chair conformation, in accordance with the experimental data (section 3.2). As can be seen from the results of AM1 calculations (Table 3S), the chair conformers of all three ligands have the lowest heat of formation ( $\Delta H_{f}^{\,\circ}$  of -9.7782 kcal/mol for APPZ, -136.937 kcal/mol for DBPP and -195.9998 kcal/mol for ZOPPH<sub>2</sub>) compared to the boat conformers; thus, the specific conformation is expected to be significantly populated at room temperature. Moreover, the N-C and C-C bond distances, as well as bond angle values of the piperazine moiety of the title ligands, are in very good agreement with the experimental measurements, with a negligible error of 0.015 for the chair conformers (**Table 3S**). In addition, all semi-empirical method results on the heat of formation values (as derived through AM1, RM1 and PM3 methods, **Table 4S**) have designated the  $ZOPPH_2$  as the most stable ligand in comparison to the APPZ and DBPP ligands. The C=N double bond distance in the DBPP and ZOPPH<sub>2</sub> ligands has values of 1.280 Å and 1.265Å, respectively, which are close to the reported

experimental value of 1.279 Å [66-68]. The small difference between the two measured C=N bond lengths could be ascribed to the presence of the phenolic moiety on the aromatic ring of the ZOPPH<sub>2</sub>. On the other hand, these values could suggest potential lability of the C=N double bond of DBPP compared to ZOPPH<sub>2</sub> under appropriate reaction conditions. The C=N double bond of ZOPPH<sub>2</sub> seems to be slightly stronger than that of the DBPP ligand, requiring high energy to break [29]. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and all descriptors derived from the calculated HOMO and LUMO energies are important stability and chemical reactivity indicators [30-32]; the values for the orbital energies were obtained using hybrid DFT with the B3LYP/6-311++ level of theory (Table 4S). These parameters are considered the main orbitals of chemical stability, indicating the electron-donor or electron-acceptor capacity of a molecule and implicitly its susceptibility to nucleophilic or electrophilic attack. A high HOMO energy value corresponds to a molecule with a strong nucleophile behavior, whereas low LUMO energy values correlate with a strong The HOMO-LUMOs, electrostatic potential, and charge electrophilic character [30,31]. distribution maps of ligands are drawn in Fig. 5 and Figs. S6-S7, respectively. The HOMO orbitals of the DBPP ligand are exclusively located on the piperazine moiety, with the N atoms being the most nucleophilic sites, whereas the LUMO orbitals are distributed around the same fragment (the aromatic ring and the C=N double bond), with the N and C atoms being the most electrophilic sites. In case of the ZOPPH<sub>2</sub> ligand, the HOMO and LUMO orbitals are distributed on the same regions (the phenolic ring and the C=N double bond), indicating the same ability to donate or attract electrons. The charge distribution and electrostatic potential plots of the ZOPPH<sub>2</sub> ligand (Fig. 5c, Figs. S6-S7) indicate high accessibility of the O atom of the phenolic ring, with an excess of negative charge (red color) around and a powerful electrostatic potential created. The HOMO-LUMO gap energy, an important stability index, suggests that the ZOPPH<sub>2</sub> is the most reactive one, whereas the DBPP is slightly more stable during a chemical reaction. The same DBPP stability is evidenced by the slight increase in the hardness value ( $\eta$  of 4.753eV). This DBPP stability, in turn, indicates low chemical reactivity, which could probably mean that the interaction with other molecules would generate very weak bonds. The ZOPPH<sub>2</sub> molecule reactivity is also confirmed by the high value of chemical potential ( $\mu$  of -3.328eV) and low value of chemical hardness (n of 4.637eV). The latter descriptors are significant indicators of the overall reactivity of the molecule. The highest value of electronegativity ( $\chi$  of 3.328eV)

exhibited by the ZOPPH<sub>2</sub> ligand is probably due to the presence of the highly electronegative O atom attached to the aromatic ring compared to the DBPP ligand. These observations confirm once more the superior stability of the ZOPPH<sub>2</sub> complex with a metal ion when compared to the DBPP one. Analysis of the Fukui indices, along with the distribution of charges (**Tables 6S-8S**, **Figs. S3-S5**), projects a more complete image of ligand reactivity. **Tables 7S-8S** indicate that all N, O, and some of the C atoms carry negative charges. This observation recommends these atoms as the negative charge centers, which could donate electron density to the metal atoms, thus forming coordination bonds. The values of Fukui indices, listed in **Tables 7S-8S**, point out that, in both cases, the N and some C atoms are the most susceptible sites for electrophilic or nucleophilic attacks; these sites present the highest values. The information emerging from the theoretical study is consistent with the experimental approaches.

#### 4. Discussion

#### 4.1 Ligand structure-specific metal ion chemical reactivity-The nature of the ligand

Promotion of metal ion chemical reactivity toward Schiff base ligands relies heavily on the chemical characteristics of its anchor groups, defining to a significant extent the a) reactivity toward the metal, and b) details of the binding process in terms of thermodynamics and kinetics. In the present case, the two major Schiff base ligands ZOPPH<sub>2</sub> and DBPP are configured appropriately around a basic piperazine core (APPZ) with bilateral reactive antennae. In the ZOPPH<sub>2</sub> ligand, the flanks to APPZ contain a basic benzene core with two substituents of notable utility to the chemistry toward the employed metal ions: a) an alkyloxy group, with the alkyl chain moiety in para-position with respect to the aldehyde moiety, extending to ten carbon atoms or longer (difference between ZOPPH<sub>2</sub> and DBPP), and b) a phenol moiety in ortho-position with respect to the aldehyde moiety. The most significant difference between ZOPPH<sub>2</sub> and DBPP is the existence of the phenolic anchor group in the former species, thereby affecting profusely metal ion chemical reactivity (vide infra).

Two metal ions, namely Co(II) and Cu(II), were employed in this work, with the products characterized through analytical (elemental analysis, molar conductivity), spectroscopic techniques (FT-IR, UV-Visible, NMR, Luminescence) and X-ray crystallography. Co(II) reacted with ZOPPH<sub>2</sub>, affording the mononuclear Co(III) complex **2**. ZOPPH<sub>2</sub> has the same coordination ability as [N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine] (HBPPH<sub>2</sub>) and acts as an

 $N_4O_2$  hexadentate ligand. The metal center resides in an octahedral environment as attested to through the literature [68]. There, in fact, it is shown that presence of strong  $\pi$ -acceptor constituents, employed in the synthesis of salen complexes, facilitates formation of octahedral Co(III) complexes [8]. In the absence of any additional coligand and by choosing an appropriate diamine with additional donor atoms, aside from the two nitrogens, HBPPH<sub>2</sub> forms mononuclear Co(II) complexes [69,70] with an octahedral geometry, exemplified by an N<sub>4</sub>O<sub>2</sub> set of donor atoms in the ligand. Using the same ligand HBPPH<sub>2</sub> and involving an oxidant agent, such as sodium perchlorate, Kuma reported the formation of a Co(III) complex [69].

#### 4.2 Metal ion oxidation state and reaction conditions in multiparametric systems

The synthetic chemical reactivity of Co(II) and Cu(II) toward the well-defined ligands ZOPPH<sub>2</sub> and DBPP, gave rise to materials with either the same or different oxidation state of the metal center. To that end, the mononuclear assembly in **2** contains an oxidized metal ion center, i.e. Co(III), with the doubly deprotonated ligand wrapped around it. The cationic charge of the metal-organic assembly is counterbalanced by a perchlorate anion. Such events are not unusual in the chemistry of the investigated metal ions. In fact, there are reports of Co(III) complexes containing Schiff base ligands, starting with Co(II)-acetate and pyridine as an ancillary ligand, synthesized and isolated under aerobic conditions [**44**]. Using the same Co(II) salt, Banerjee et al. [**71**] obtained a trinuclear mixed-valence Co(III)-Co(II)-Co(III) complex, the trinuclear complex was allowed to react with hydrazine as a reducing agent. Hariharan et al. [**16**] obtained a Co(II) conflex bound to a Schiff base ligand, using CoCl<sub>2</sub> and a nitrogen atmosphere, to avoid oxidation of Co(II) to Co(III). It appears, therefore, that reaction conditions involve numerous variables that could influence the fate of the reaction pathways and thus the derived product(s).

By the same token, oxidation of Cu(I) to Cu(II) was intensively investigated and can depend on different factors, such as ligand nature, the coordinating solvent(s) or the counter ion, that allow the metal ion to assume tetrahedral coordination when Cu(I) species are stabilized or higher coordination number geometries preferred by Cu(II) species [72-75]. To obtain Cu(I) species, it is also important to employ inert reaction conditions [76,77]. Collectively, the complexity of this multiparametric system of interactions, with factors a) affecting among others the oxidation state of the central metal ion in a complex assembly, and b) exemplified through the employment of

the aforementioned reaction participants, contains a wealth of information at the synthetic and structural level, and is currently under investigation in our labs.

# 4.3 The importance of phenolic OH in the ligand structure. Parameters and consequences in metal ion reactivity

Initially, the investigation was directed toward the effect of phenolic OH in the ligand, when divalent metal ions are presented to it. To that end, when ZOPPH<sub>2</sub> reacts with the divalent Co(II), the integrity of the ligand is maintained upon metal ion coordination. When ZOPPH<sub>2</sub> is presented to Cu(II), the resulting materials are dinuclear complexes with a polymeric or discrete structure, depending on the metal:ligand molar ratio [14]. In fact, hexadentate ZOPPH<sub>2</sub> can act as a binucleating ligand through a two (N,O) donor atom set or a bis-tridentate ligand through two (N,N,O) donor atom sets, depending on the involvement of the piperazine core nitrogen in metal coordination, with the piperazine moiety being in the *chair* or *boat* conformation in the case of mononuclear complexes.

When DBPP (a ligand similar to ZOPPH<sub>2</sub> yet devoid of the phenolic anchor moiety) is used with Cu(II) (vide infra), it appears to break apart in solution, thereby resulting in the formation of the amine constituent (essentially the core structure of the original APPZ ligand), with the latter substrate poised to bind the metal ion in its original oxidation state. A good precedent on such reactivity was previously reported in the literature, exemplifying interactions of Cu(II) toward a similar ligand containing the same core, with the remainder of the structural motif containing no phenolic OH in the o-position of the benzene ring bearing the azomethine –CH=N– moiety [52]. In contrast to that, when Co(II) is presented to that same ligand, complexation does not occur. It appears, therefore, that the presence of the phenolic group facilitates coordination to the metal center, thereby stabilizing that metal ion in its complex assembly (vide infra). Absence of that moiety results in disassembly of the organic ligand in the presence of the metal ion. The above observation is amply shown to emerge in the case of the Cu(II) system, in which the nature of the starting reagent also appears to play a role. To that end, evidence projecting the influence of the two parameters (phenolic moiety and starting reagent) on the chemical reactivity amounting to changes occurring in the ligand structure, in the presence of the metal ion, can be gathered through vibrational spectroscopy. In fact, FT-IR spectra of the materials arising from the reactivity investigation of the Cu-DBPP system, with the copper starting reagent containing NO<sub>3</sub><sup>-</sup> or Cl<sup>-</sup> as a counter ion, seem to be different from those of the Cu-APPZ system (data not shown).

On the contrary, in the case of the  $ClO_4^-$  anion present in the starting material, the emerging Cu-DBPP and Cu-APPZ complexes from the two systems are similar to each other, as noted previously [18]. Toward that end, the FT-IR spectra of the latter two cases reveal that the characteristic bands of the free DBPP ligand are not present, indicating rupture of the imino bonds and formation of N,N,-bis(3-aminopropyl)piperazine perchloratocopper(II) perchlorate, as previously reported [18]. Consequently, it appears that a) upon reaction between DBPP and  $Cu(ClO_4)_2$ , the product emerges different from that of the same reaction employing  $Cu(NO_3)_2$  and  $CuCl_2$  and is identified as  $[Cu(APPZ)(ClO_4)](ClO_4)$ . The fact that the presence of the phenolic moiety does make a difference in the chemical reactivity toward Cu(II), linked to the retention of the integrity of the ligand as a well as the oxidation state of copper upon coordination, has been amply exemplified through the isolation and crystal structure of  $[Cu_9L_6(\mu_3 -$ ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub><sup>·4</sup>CHCl<sub>3</sub> (N,N'-bis[(2-hydroxybenzilideneamino)-propyl]-piperazine (H<sub>2</sub>L)), with the coordinated ligand containing phenolic moieties on both sides of the piperazine ring [78]. Therefore, in the absence of the phenolic moiety, the nature of the Cu(II) starting material appears to be important in the investigated chemical reactivity; b) DBPP breaks apart, at the imino junction, into its constituents in the presence of  $Cu(ClO_4)_2$ . The product of the reaction is the [Cu(APPZ)(ClO<sub>4</sub>)](ClO<sub>4</sub>) complex. The reaction product is confirmed through chemical reactivity of Cu(ClO<sub>4</sub>)<sub>2</sub> and APPZ; and c) the metal binding ability of the core APPZ ligand is confirmed through the emergence of [Cu(APPZ)Cl]Cl in the reaction between  $CuCl_2$  and APPZ. The observed behavior of the chemical reactivity of the two ligands with Cu(II), and more so in the absence of the phenolic OH moiety, appears to be supported by DFT theoretical calculations. In fact, quantum mechanical calculations on DBPP and ZOPPH2 ligands suggest that the -CH=N- bond itself could exhibit a differentially distinct chemical reactivity under appropriate reaction conditions (i.e. presence of a metal ion). Both semi-empirical AM1 and DFT methods point to the lability of the C=N bond, a property that materializes with Cu(II) present in the reaction medium, resulting in the isolation of the Cu-APPZ complex. The importance of that collective theoretical and experimental work on well-defined molecular factors influencing chemical reactivity of the Schiff ligands toward metal ions, testifies to the need of a) identification of such structural and electronic factors guiding the relevant synthetic reactivity toward materials with new applications (e.g. light emission, metallomesogens, liquid crystals), and b) extending further the quest for analytical parametric description and design of organic

substrates-synthons, such as the Schiff ligands employed here, in the exploration of metalspecific interactions, pertaining to other areas of research involving catalytic transformations. Whether or not there is specificity of the chemical reactivity amounting to rupture of the C=N bond by only Cu(II) remains to be seen. Efforts toward establishment of the same or dissimilar reactivity in the presence of Co(II) are currently probed into in our labs.

The collective chemical reactivity in the investigated systems reveals that a) specific structural and electronic factors are involved in the formulation of the products arising when Schiff base ligands, such as the ones reflected into ZOPPH<sub>2</sub>, DBPP, and APPZ, are brought to react with Cu(II) and Co(II); and b) salient structural features of both ligands and metal ions, in conjunction with defined reaction conditions, could be factored into the reactivity patterns leading to structurally distinct isolable crystalline products. To that end, the chemical reactivity of other redox active metal ions is worth looking into when Schiff base ligands with the aforementioned substituent changes in their structure are employed. The accrued knowledge from the employed systems is expected to lay the groundwork for the development of well-defined materials exhibiting distinctly differentiated metal coordination and lattice properties.

#### 5. Conclusions

The synthetic pursuit of potential mesomorphic Schiff base ligands, comprised of a piperazine core and a variably composed alkyloxy-containing salicylaldehyde moiety, led to a family of metal ion binders (ZOPPH<sub>2</sub>, DBPP) reacting in a distinct fashion with divalent Co(II) and Cu(II). The derived title compounds **1-3** reveal that a) in ZOPPH<sub>2</sub> and DBPP, N and O anchors on each side of piperazine bridge generate a symmetrical, conformationally flexible, structure poised to promote metal ion binding; b) the abutting aromatic phenolic moiety stabilizes the arising metallacyclic rings, playing a significant role in the reactivity pursued. In ZOPPH<sub>2</sub>, it facilitates octahedral coordination to the oxidized Co(III) center. When absent (DBPP), the ligand breaks apart in solution in the presence of the metal ion, thereby affording APPZ further coordinating to the metal ion; c) the alkyl chains on the phenolic core contribute to the hydrophobicity of the entire ligand and satisfy the requirements of these bulky substituents into optimally arranged, ordered and oriented metal complex assemblies in the emerging lattice architecture; d) DFT theoretical calculations on the employed ligand structures project a labile azomethine bond, variably influenced by the presence of the metal ion, thus lending credence to the rupture upon

metal ion reactivity in the absence of the phenolic moiety. The specificity of that reactivity with respect to the nature of the metal ion requires further investigation; e) the influence of the starting reagent transition metal and thus the emerging counter ion on the chemical reactivity as well as the (an)aerobic atmosphere conditions are variables that might contribute to the observed reactivity. The aforementioned factors formulate the parametric investigation of the discovered reactivity, meriting further perusal into new well-defined metal-organic materials (metallomesogens) with specified physicochemical profile(s) and are thus currently being investigated in our labs.

#### Acknowledgment

We are thankful to the Romanian Academy of Science, (Project 3.1.) for the financial support (Program No. 3; Project No. 3.1).

#### **Supplementary Material**

CCDC 743573 (1), CCDC 978591 (2), and CCDC 1846243 (3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccde.cam.ac.uk).

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Tables

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 Table 1: Crystallographic data on compounds  $[(C_2H_4N)_2(C_4H_7N)_2(C_6H_4O)_2(C_{12}H_{25})_2]$  (DBPP) (1),

  $[{Co(ZOPP)}(ClO_4)]_2$  (CH<sub>3</sub>OH) 2(CH<sub>3</sub>)<sub>2</sub>SO (2), and [Cu(APPZ)Cl]Cl (3)

Compound	1	2	3
Chemical formula	$C_{48}H_{80}N_4O_2\\$	$C_{93}H_{156}Cl_2Co_2N_8O_{19}S_2$	$C_{10}H_{24}Cl_2CuN_4$
$M_{ m r}$	745.19	1943.21	334.78
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	Pī	C2/c	$P2_{1}/n$
Temperature (K)	295	295	295
<i>a</i> (Å)	5.502 (2)	42.188 (2)	7.9535 (8)
<i>b</i> (Å)	6.672 (3)	13.0685 (6)	14.3181 (15)
<i>c</i> (Å)	32.906(16)	19.8524 (10)	13.5392 (14)
α (°)	85.86 (3)	90	90
β (°)	89.70 (3)	90.153 (3)	101.636 (3)
γ (°)	76.28 (3)	90	90
$V(\text{\AA}^3)$	1170.4 (9)	10945.3 (10)	1510.1 (3)
Ζ	1	4	4
Radiation type	Μο <i>Κ</i> α	Μο <i>Κ</i> α	Μο <i>Κ</i> α
$\mu (mm^{-1})$	0.06	0.45	1.79
Crystal size (mm)	$0.53 \times 0.22 \times 0.12$	$0.26 \times 0.14 \times 0.12$	0.27×0.22×0.15

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Data collection Absorption correction Numerical Numerical Numerical 0.99, 0.99 0.94, 0.95 0.68, 0.76  $T_{\min}, T_{\max}$ Reflections 21356 Measured 34665 83768 12077 3084 Independent 5832 Observed  $[I > 2.0\sigma(I)]$ 2473 2921 6887 0.061 0.025 0.023  $R_{\rm int}$  $(\sin \theta / \lambda)_{max} (\text{\AA}^{-1})$ 0.683 0.643 0.626 Refinement  $R[F^2 > 2\sigma(F^2)]$ 0.043 0.039 0.038  $R_w(F^2)$ 0.083 0.041 0.066 S 1.00 1.00 1.00 6887 No. of reflections 2921 2473 No. of parameters 244 563 154 0.15, -0.15

 $\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$ 

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0.36, -0.52

0.47, -0.43

 Table 2: Bond distances (Å) and angels (°) on compounds  $[(C_2H_4N)_2(C_4H_7N)_2(C_6H_4O)_2(C_{12}H_{25})_2]$  (DBPP) (1),  $[\{Co(ZOPP)\}(ClO_4)]_2$  (CH<sub>3</sub>OH) 2(CH<sub>3</sub>)<sub>2</sub>SO (2), and [Cu(APPZ)Cl]Cl (3).

Bond Distances (Å)								
1								
N(1)—C(7)	1.274 (2)	N(1)—C(8)	1.460 (2)	N(2)—C(10)	1.469 (2)	N(2)—C(11)	1.463 (2)	
N(2)—C(12)	1.469 (2)	C(4)—O(1)	1.346 (2)	O(1)—C(13)	1.441 (2)			
2								
Co(1)—N(1)	1.945 (2)	Co(1)—N(2)	2.004 (2)	Co(1)—N(3)	1.981 (2)	Co(1)—N(4)	1.934 (2)	
Co(1)—O(1)	1.893 (2)	Co(1)—O(2)	1.898 (2)	N(1)—C(7)	1.304 (4)	N(1)—C(8)	1.482 (4)	
N(2)—C(10)	1.459 (4)	N(2)—C(11)	1.486 (4)	N(2)—C(13)	1.460 (4)	N(3)—C(12)	1.446 (4)	
N(3)—C(14)	1.461 (3)	N(3)—C(15)	1.460 (4)	N(4)—C(17)	1.463 (4)	N(4)—C(18)	1.282 (3)	
O(1)—C(2)	1.316 (3)							
	·		Ś	3	·			
Cu(1)—C(11)	2.463 (8)	Cu(1)—N(1)	2.009 (2)	Cu(1)—N(2)	2.062 (3)	Cu(1)—N(3)	2.057 (2)	
Cu(1)—N(4)	2.007 (2)	N(1)—C(1)	1.479 (4)	N(2)—C(3)	1.481 (5)	N(2)—C(4)	1.489 (4)	
N(2)—C(9)	1.478 (4)	N(3)—C(5)	1.483 (4)	N(3)—C(6)	1.485 (4)	N(3)—C(10)	1.475 (5)	
N(4)—C(8)	1.468 (4)	C(1)—C(2)	1.506 (6)	C(2)—C(3)	1.504 (6)	C(4)—C(5)	1.524 (5)	
C(6)—C(7)	1.516 (6)							

Angles (°)								
1								
C(7)—N(1)—C(8)	117.93 (16)	N(1)—C(8)—C(9)	113.02 (16)	C(10)—N(2)—C(11)	112.55 (14)			
C(4)—O(1)—C(13)	119.08 (14)	C(10)—N(2)—C(12)	112.23 (15)	C(9)—C(10)—N(2)	113.41 (16)			
C(11)—N(2)—C(12)	106.81 (14)	$C(12)^{i}$ — $C(11)$ — $N(2)$	106.49 (15)	$C(11)^{i}$ — $C(12)$ — $N(2)$	112.97 (16)			
2								
O(1)—Co(1)—O(2)	177.68 (8)	N(1)—Co(1)—O(1)	89.11 (9)	N(2)—Co(1)—O(1)	93.34 (10)			
N(3)—Co(1)—O(1)	87.99 (9)	N(4)—Co(1)—O(1)	88.82 (9)	N(1)—Co(1)—O(2)	88.74 (10)			
N(2)—Co(1)—O(2)	87.64 (9)	N(3)—Co(1)—O(2)	94.31 (9)	N(4)—Co(1)—O(2)	90.74 (9)			
N(1)—Co(1)—N(2)	92.80 (10)	N(1)—Co(1)—N(3)	165.47 (9)	N(2)—Co(1)—N(3)	73.18 (10)			
N(1)—Co(1)—N(4)	101.20 (9)	N(2)—Co(1)—N(4)	165.87 (9)	N(3)—Co(1)—N(4)	92.97 (9)			
3								
Cl(1)—Cu(1)—N(1)	101.52 (8)	Cl(1)—Cu(1)—N(2)	103.86 (8)	N(1)—Cu(1)—N(2)	94.62 (11)			
Cl(1)—Cu(1)—N(3)	99.96 (8)	N(1)—Cu(1)—N(3)	157.34 (11)	N(2)—Cu(1)—N(3)	73.18 (11)			
Cl(1)—Cu(1)—N(4)	99.24 (8)	N(1)—Cu(1)—N(4)	89.30 (11)	N(2)—Cu(1)—N(4)	155.26 (11)			
N(3)—Cu(1)—N(4)	94.33 (11)	Cu(1)—N(1)—C(1)	119.1 (2)	Cu(1)—N(2)—C(3)	121.3 (2)			
Cu(1)—N(2)—C(4)	99.72 (18)	C(3)—N(2)—C(4)	111.6 (3)	Cu(1)—N(2)—C(9)	104.8 (2)			
C(3)—N(2)—C(9)	110.6 (3)	C(4)—N(2)—C(9)	107.6 (3)	Cu(1)—N(3)—C(5)	99.58 (19)			
etry codes:								
-x+2, -y, -z+1.								

Symmetry codes:

(1) (i) -x+2, -y, -z+1.

#### **Figure captions**

- **Figure 1. A.** Labeled plot of the molecular structure of DBPP (1).
  - **B.** Crystal packing of DBPP (1) in the ac plane.

C. Centroid-centroid interactions between the two neighboring DBPP (1) molecules.

**Figure 2. A.** Labeled plot of the structure of the  $[Co(ZOPP)]^+$  cationic complex assembly in  $[{Co(ZOPP)}(ClO_4)]_2(CH_3OH) \cdot 2(CH_3)_2SO(2).$ 

**B.** Molecular packing along the *c* axis shows a three-dimensional open-framework in **2**.

**Figure 3. A.** Labeled plot of the structure of the  $[Co(APPZ)]^+$  cationic complex assembly in [Cu(APPZ)Cl]Cl (3).

**B.** Molecular packing along the *a* axis shows an intercalated array of *zig-zag* molecules in **3**.

- Figure 4. Solution fluorescence spectra of ligand ZOPPH<sub>2</sub> and compounds 1-3 at room temperature.
- **Figure 5.** The three dimensional HOMO (a) and LUMO orbitals (b), and electrostatic potential (c) plots of the DBPP and ZOPPH<sub>2</sub> ligands















#### **Highlights**

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- Structure-specific Schiff base synthesis leads to discrete metal-organic complexes •
- Piperazine-based Schiff bases with long alkyloxy chains promote metal ion binding •
- Schiff base metal ion binding is linked to adoption of piperazine boat conformation ٠
- Presence-absence of phenol in Schiff base affects metal ion chemical reactivity •
- Piperazine-based Schiff ligands influence metal-ligand complex architecture •

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