

# Synthesis and structural study of the mixed copper(II)/lanthanum(III) complex with the bicompartamental ligand $H_2L = 2,2'$ -{propane-1,2-diyl bis[nitrilomethylylidene ]}bis(6-methoxyphenol)

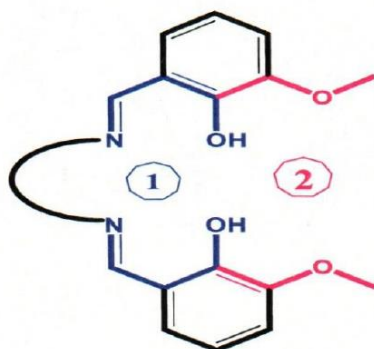
## Abstract

The neutral hetero-trinuclear compound 3d-4f,  $[Cu(II)La(III)Cu(II)]$  was obtained with the “brick by brick” method and it crystallizes in the monoclinic system with a space group of  $P2_1/n$ . The asymmetric unit of the structure of  $[Cu_2(\mu-L_2)La(NO_3)_2]$  contains two molecules of the dideprotonated ligand  $L^{2-}$ , two  $Cu(II)$  ions, one  $La(III)$  ion and two bidentate nitrate anions. In the structure of the trinuclear complex, the two  $Cu(II)$  ions and the  $La(III)$  ion are bridged by two phenolate oxygen atoms. The  $Cu(II)$  ion has a square planar geometry with the basal plane formed by two imine nitrogen atoms and two phenolic oxygen atoms. The  $La(III)$  ion, which occupies the largest open site of the Schiff base ligand, is bonded to two phenolate oxygen atoms and two methoxy oxygen atoms of the ligand and two oxygen atoms of a bidentate nitrate group from each ligand. The  $La(III)$  cation is located in the planar cavity defined by the two phenolate oxygen atoms and the two methoxy oxygen atoms. The positive charge of  $Cu(II)$  and  $La(III)$  ions is balanced by the deprotonated  $L^{2-}$  ligand, perchlorate and nitrate anions. The duodecaordinated  $La(III)$  ion coordination polyhedron is described as a severely distorted icosahedron or dodecahedron.

**Keywords :** Schiff bases, crystal structure, hetero-trinuclear complex, uodecaordinated

## 1. Introduction

Since the exploration of new properties, bicompartamental Schiff bases derived from o-vanillin are widely used to prepare homo and heteronuclear 3d-3d, 3d-3f, 3d-ns complexes [1, 2], they are often represented as a ligand with two differently sized pockets.



*Scheme 1. Representation of the structure of a bicompartamental Schiff base*

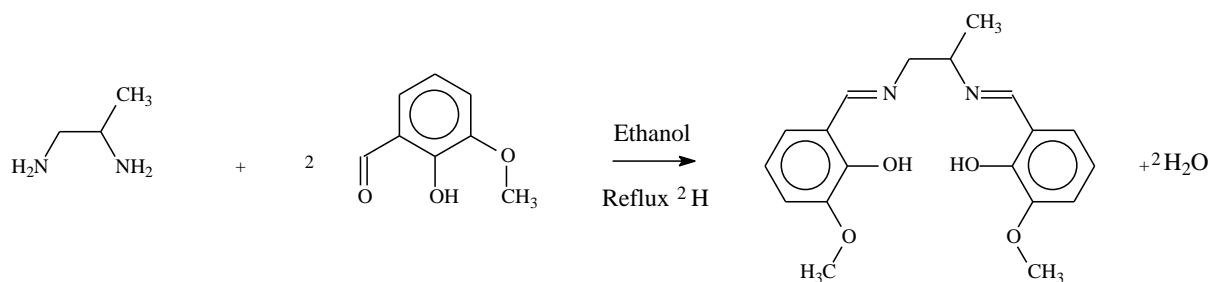
The inner  $[N_2O_2]$  coordination sphere of these ligands is more suitable for hosting a d-block metal ion [3] whereas the larger  $[O_2O_2]$  chamber better accommodates an f- or s-block ion. The corresponding complexes have been the subject of several in-depth studies due to their remarkable properties in the field of electron storage [3], magnetism [1,4,5], catalysis [4,6], electrochemistry [7], in luminescence [7-10], in biochemistry [10] and in biology [11]. They can be used in particular as nonlinear optical materials [1,7], but also as magnetocaloric materials [12] for design coolers that meet environmental standards as well as energy efficiency. There are a large number of examples of 3d-4f heteronuclear complexes in the literature, while only a limited number of 3d-ns examples are studied [3]. Due to their fascinating structural diversities, they are promising candidates for explaining some difficult-to-understand properties in 3d-4f aggregates.

## **2. Materials and Methods**

### **2.1. Starting materials and instrumentations**

Ortho-vanillin and 1,2-diaminopropane were commercial products (Aldrich) and were used without further purification. Solvents were of reagent grade and were purified by the usual methods. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the  $4000-400\text{ cm}^{-1}$  region. The  $^1\text{H}$  NMR spectra were recorded at 300 MHz and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra at 75 MHz on a Bruker AC-300 instrument.

### **2.2. Synthesis of 2,2'-{propane-1,2-diyl bis[nitrilomethylylidene ]}bis(6-methoxyphenol)**



*Scheme 2. Ligand synthesis reaction scheme*

Dissolve 3.04g (20 mmol) of o-vanillin in ethanol then add 0.9 mL (10 mmol) of 1,2-diaminopropane. The orange-yellow mixture obtained is heated under reflux with magnetic stirring for 2 hours. Filter and air dry. Yellow-orange precipitate obtained is washed with diethyl ether. The mass obtained is 2.23 g.

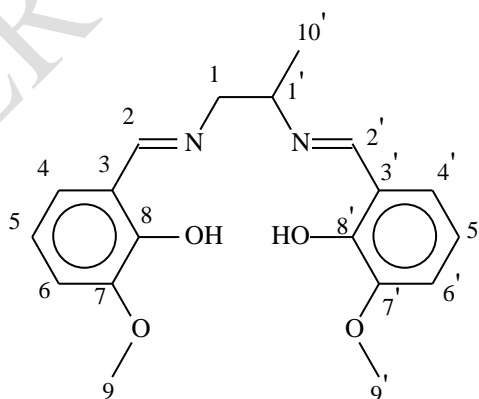
Yield : 65.5%

Molar mass : 342 g/mol

**NMR  $^1\text{H}$**  : ( $\delta$ , ppm) : 13.65 (s, 2H, Ar-OH), 8.30 (s, 2H, HC=N), 6.92-6.75 (m, 6H, Ar-H), 3.79-3.86 (m, H<sub>1</sub>, H<sub>1'</sub>), 3.71 (s, 6H, -CH<sub>3</sub>), 1.40 (3H -CH<sub>3</sub>-CH).

**NMR  $^{13}\text{C}$**  : ( $\delta$ , ppm) : 65.20 (C<sub>1</sub>), 55.9 (C<sub>1'</sub>), 166.5 (C<sub>2</sub> ; C<sub>2'</sub>), 148.08 (C<sub>3</sub> ; C<sub>3'</sub>), 123.14 (C<sub>4</sub> ; C<sub>4'</sub>), 118.28 (C<sub>5</sub> ; C<sub>5'</sub>), 118.00 (C<sub>6</sub> ; C<sub>6'</sub>), 151.40 (C<sub>7</sub> ; C<sub>7'</sub>), 154.6 (C<sub>8</sub>; C<sub>8'</sub>), 64.49 (C<sub>9</sub> ; C<sub>9'</sub>), 20.25 (C<sub>10'</sub>).

**IR  $\text{H}_2\text{L}$** :  $\nu(\text{cm}^{-1})$  : 1625 (s) (C=N) ; 3196 (m) (HC=N) ; 3190 (m) (OH), (1466-1358) (m) (C=C) ; 1249 (m) (C-O), 2931 (m) (C-H).

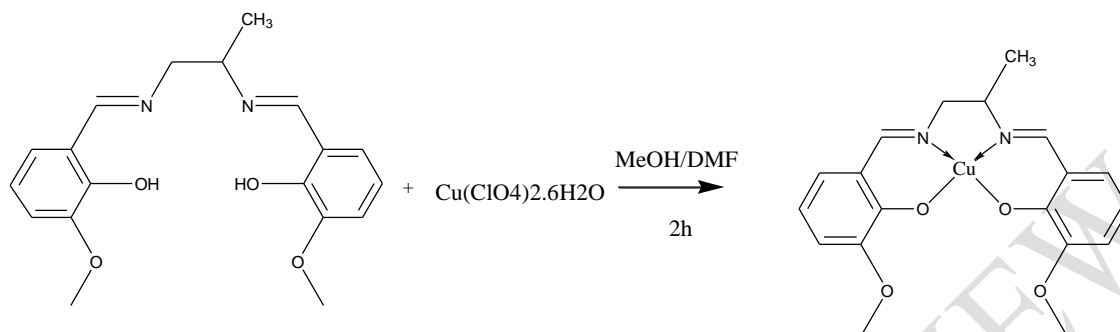


*Scheme 3. Numbering of carbon atoms*

## 2.3. Synthesis of the complexes

### 2.3.1. Complex of copper (II)

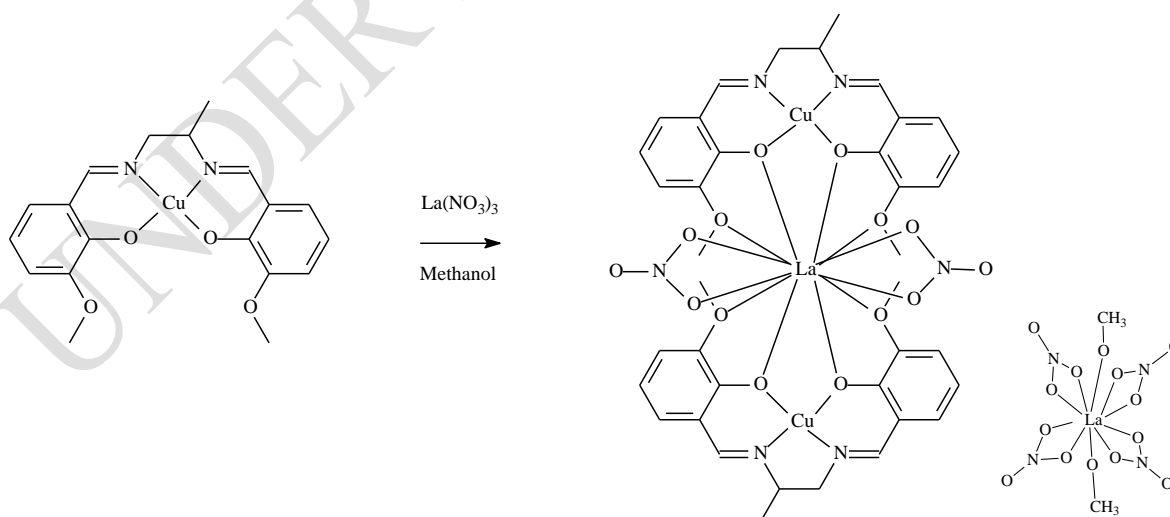
In a 100 mL flask, dissolve 0.1 g (0.3 mmol) of the **H<sub>2</sub>L** ligand in DMF then add 0.11 g (0.3 mmol) of copper perchlorate hexahydrate  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  previously dissolved in methanol. The mixture is stirred for 2 hours and it turns dark green. The latter is filtered and then left to slowly evaporate. After a month, crystals of dark green color are obtained.



*Scheme 4. Reaction scheme for the synthesis of the copper (II) complex*

### 2.3.2. Complex of the mixed Cu(II)/La(III) ions

In a 100 mL flask, dissolve 0.1 g (0.3 mmol) of the **H<sub>2</sub>L** ligand in DMF. Then add 0.11 g (0.3 mmol) of copper perchlorate hexahydrate  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  previously dissolved in methanol. Mixture A obtained is stirred for 2 hours and it becomes dark green. Introduce 0.1 g (0.3 mmol) of lanthanum nitrate into a crystallizer containing a minimum of methanol. The solution is filtered directly into the test tube containing mixture A without color change. After three weeks of slow evaporation of the mixed  $\text{Cu}^{2+}/\text{La}^{3+}$  complex, brown crystals are obtained.



*Scheme 5. Reaction scheme for the synthesis of the copper (II)/lanthanum (III) complex*

## 2.4. X-ray crystallography

Details of the crystal structure solution and refinement are given in table 1. Single-crystal X-ray diffraction data were measured on a Rigaku Oxford Diffraction Super Nova diffractometer at the MoKa radiation. Data collection reduction and multiscan ABSPACK correction were performed with CrysAlisPro (Rigaku Oxford Diffraction). The crystal structures including the anisotropic displacement parameters were refined with SHELXL-2013. Molecular graphics were generated using Diamond and ORTEP-3.

### 3. Results and Discussion

#### 3.1. General study

The  $^1\text{H}$  proton NMR spectrum of **H<sub>2</sub>L** shows three singlets, one doublet and multiplets. The singlets pointed at 3.71 and 13.65 ppm represent (CH<sub>3</sub>-O) and Ar-OH, respectively. The multiplet in the 3.79-3.85 ppm region represents the H1, H1' protons. Aromatic protons appear as multiplets in the range of 6.92 to 6.75 ppm [13].

The  $^{13}\text{C}$  NMR spectrum of **H<sub>2</sub>L** shows a signal at 166.5 ppm which represents the carbon atom of the imine C=N. The signals plotted at 151.40 and 64.49 ppm represent the aromatic carbon of phenol and methoxy, respectively.

The infrared spectrum of the ligand shows bands corresponding to  $\nu(\text{O-H})$  peaked at 3190  $\text{cm}^{-1}$ . The band pointed at 1625  $\text{cm}^{-1}$  is attributed to  $\nu(\text{C=N})$  confirming the formation of the ligand [14]. The band pointed at 1249  $\text{cm}^{-1}$  attributed to  $\nu(\text{C-OPh})$ . The vibration band observed around 3400  $\text{cm}^{-1}$  can be attributed to  $\nu(\text{HO})$  of H<sub>2</sub>O.

#### 3.2. Study of complexes

During coordination, the band due to C=N passes to low frequencies for the two complexes. For compounds (1) and (2) the vibration bands of C=N are respectively pointed at 1617 and 1600  $\text{cm}^{-1}$ . The broad band of average intensity that appears in the 3190  $\text{cm}^{-1}$  range is due to the O-H stretching vibration of the phenolic and alcoholic OH groups. The phenolic C-O stretch shifts towards low frequencies for both complexes at 1239 and 1220  $\text{cm}^{-1}$  respectively for compounds (1) and (2). The presence of the band around 1100  $\text{cm}^{-1}$  characteristic of an ionic perchlorate group shows the existence of a perchlorate playing the role of counter-anion. The conductivity measurements carried out in DMF indicate values which are those of electrolytes of type 1:1 for the complex (1), for the fresh solution and 15 days later, which confirms the spectroscopic data [15]. Molar conductance value of 81 and 88  $\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$  in DMF 15 days after is indicative of 1:1 electrolyte for complex 1.

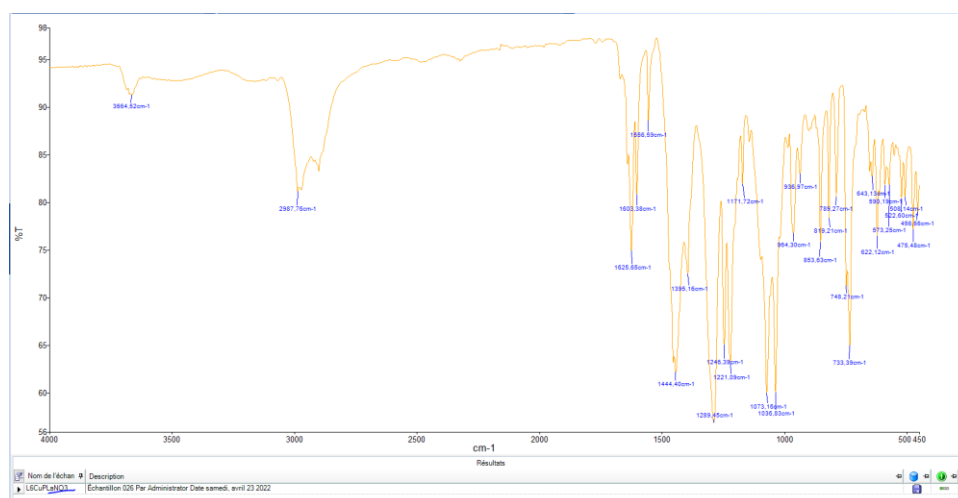
For the complex 2 obtained with lanthanum (III) nitrate, the presence of bands around 1420 and 1320  $\text{cm}^{-1}$  shows in figure 1 that there is presence of a nitrate group. They are

respectively due to  $\nu(\text{N=O})$  ( $\nu_1$ ) and  $\nu_{\text{as}}(\text{NO}_2)$  ( $\nu_5$ ) of the coordinated nitrate group. The separation  $\Delta\nu = \nu_1 - \nu_5$  is used as a selection criterion between a monodentate nitrate group and a bidentate nitrate group,  $\Delta\nu$  increasing with the mode of coordination. The value of  $\Delta\nu = 111 \text{ cm}^{-1}$  clearly indicates that the nitrate group is bidentate [16]. No band characteristic of an uncoordinated nitrate group is observed at  $1380 \text{ cm}^{-1}$ .

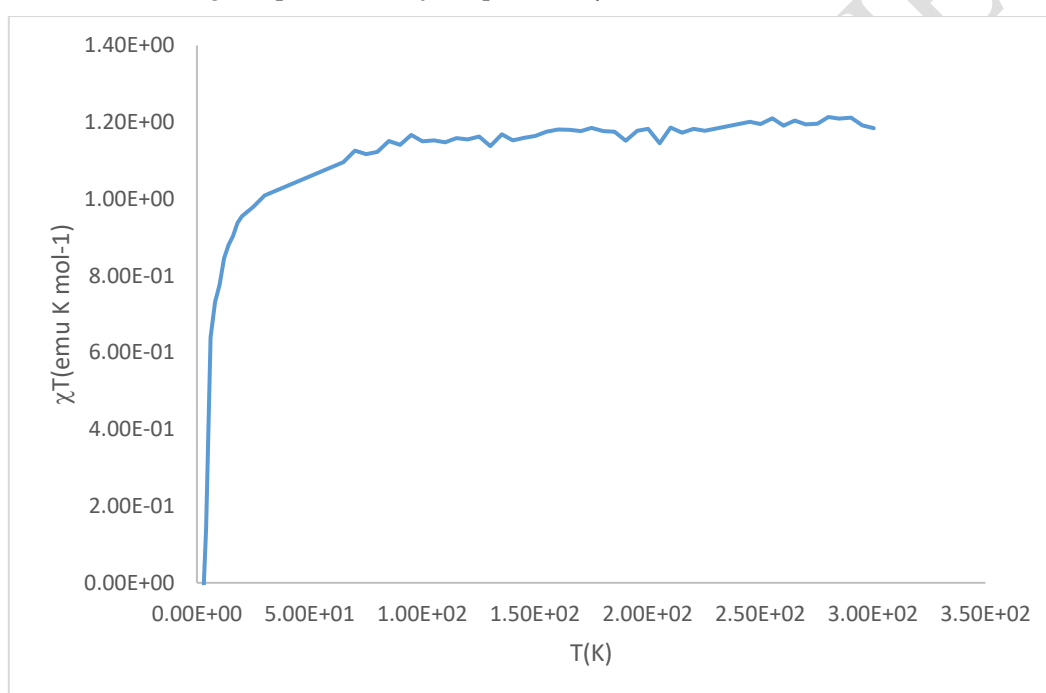
Magnetic study of the complex **2**, the curve  $\chi T$  as a function of the temperature of the mixed complex is shown in figure 2. For this mixed complex  $[\text{Cu}_2(\mu\text{-L})_2\text{La}(\text{NO}_3)_2]_2\text{La}(\text{NO}_3)_4$ , the value of the product  $\chi T$  at the temperature ambient is  $1.2 \text{ emu K mol}^{-1}$ . We observe a growth rate of the product  $\chi T$  with the increase in temperature from 2-300 K. It shows a moderate antiferromagnetic interaction between copper (II) ions and lanthanum (III) ion. For this complex  $[\text{Cu}_2(\mu\text{-L})_2\text{La}(\text{NO}_3)_2]_2\text{La}(\text{NO}_3)_4$ , the value of the product  $\chi T$  at room temperature is  $1.2 \text{ emu K mol}^{-1}$ . When cooling from 300 K to 50 K, the product  $\chi T$  decreases steadily. After cooling, the product  $\chi T$  decreases regularly, with a faster descent below 50 K. Below 50 K, it decreases more rapid descent, which suggests an antiferromagnetic interaction between the different metal centers. Indeed, this behavior clearly indicates that antiferromagnetic interactions are active within the complex, with a small percentage of paramagnetic impurities for residual paramagnetism at low temperatures.

The magnetic analysis was then carried out using and a satisfactory fit, shown in figure 2. It was obtained using the Van Vleck equation drawn by the Hamiltonian:  $\hat{H} = J [\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3]$ , (where the two copper (II) ions are identified by  $\hat{S}_1$  and  $\hat{S}_3$  while the lanthanum (III) ion by  $\hat{S}_2$ ). It is interesting to note that in this approach the ground state cannot be diamagnetic, so a meaningful model must include a correction to account for possible zero field splitting effects and/or intermolecular interactions:  $\chi = \frac{\chi_M}{1 - \chi_M \theta}$ , where  $\chi_M$  the molar magnetic susceptibility,

is calculated on the basis of Van Vleck equation and  $\theta$  is a phenomenological parameter which simulates the zero effects of the field and/or intermolecular interactions. The best correlation of the values obtained with the experimental data of the hetero-trinuclear complex ( $\text{Cu}^{2+}\text{La}^{3+}\text{Cu}^{2+}$ ) is including a small fraction of paramagnetic impurities, with the best values adjustment:  $g = 2.124 \pm 0.005$ ,  $J = -13.12 \pm 0.4 \text{ cm}^{-1}$ ,  $\theta = -0.85 \pm 0.04 \text{ K}$  ( $g$  is parameter of Zeeman). In order to understand the coupling behavior, it is important to note that the Cu(II) and La(III) centers are linked by two bridging  $\mu\text{-O}_{\text{phenolate}}$  atoms. The magnetic behavior of the complex is governed by copper since lanthanum is diamagnetic.



**Fig. 1. Spectrum IR of complex  $[Cu_2(\mu-L)_2La(NO_3)_2]_2La(NO_3)_4$**



**Fig. 2.  $\chi T = f(T)$  of complex  $[Cu_2(\mu-L)_2La(NO_3)_2]_2La(NO_3)_4$**

### 3.3. Crystallography

The Cu (II) ion complex (**1**) crystallizes in the triclinic system in space group P-1 with unit cell parameters  $a = 7.8726(2) \text{ \AA}$ ,  $b = 11.8907(4) \text{ \AA}$ ,  $c = 14.5266(4) \text{ \AA}$ ,  $\alpha = 62.243(3)^\circ$ ,  $\beta = 83.036(2)^\circ$ ,  $\gamma = 88.469(2)^\circ$ . In the copper (II) complex, the geometry around the metal ion is described as a distorted square plane. In the structure of the mononuclear complex the Cu(II) ion is coordinated by two imine nitrogen atoms and two phenoxo oxygen atoms, originating from the deprotonated Schiff base ligand. There is also the presence of two neighboring solvent molecules and an uncoordinated perchlorate anion. The copper (II) ion has a distorted square-planar geometry.

The Cu(II) ion is coordinated by two imine nitrogen atoms, N1A and N2A and two phenolic oxygen atoms, O2A and O3A from the deprotonated Schiff base ligand. There are also two neighboring solvent molecules and a non-coordinating perchlorate anion. A 90° deviation of bond angles involving chelation is observed : (O2ACu1AN1A = 95.4° ; O3ACu1AN1A = 173.6° ; N2ACu1AN1A = 85.5° ; N4ACu1AN5A = 86.9°). There is also a 180° deviation of the bond angles involving chelation (O10BCu1BN4B = 173.9° and O9BCu1BN5B = 178.0°). The relevant bond distances are : d(Cu1BO10B) = 1.917 Å, d(Cu1BN5B) = 1.901 Å, d(Cu1BN4B) = 1.921 Å. The coordination environment around the Cu(II) center is Jahn-Teller elongation as expected for a distorted square planar d<sup>9</sup> ion. A Jahn-Teller distortion is predicted whenever a nonlinear symmetric molecule has degenerate orbitals and has unequal electron occupancy in these degenerate orbitals. Of course, this is most often discussed in the context of octahedral complexes, but it also occurs in other species-it's a general effect [17]. The Cu-O distances are 1.883 and 1.905 Å while the Cu-N distances are between 1.904 and 1.915 Å. These values are lower than those observed for the copper complex obtained with the ligand 4-chloro-6-hydroxymethyl-2-((3-aminopropylimino)methyl)phenol (Jiang et al, 2009). The sum of the angles around the Cu(II) ion is 360.8°. This fact indicates that there are very weak distortions of the square planar geometry around the Cu(II) ion.

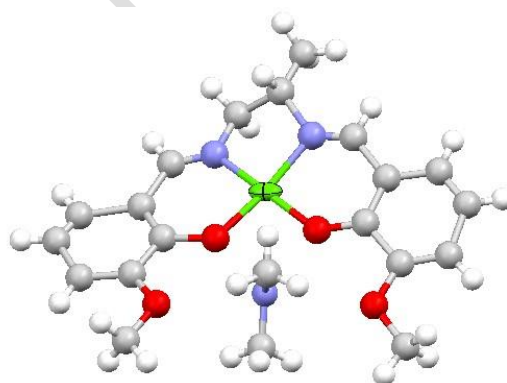
Our attention arises from the ability of multinuclear copper (II) enzyme similarities to activate molecular oxygen and the dependence of their optoelectric, magnetic properties on their molecular structures. Many studies have shown well-established magneto-structural correlations and predominant magnetic interactions between the metal centers in most of the known polynuclear copper (II) complexes are antiferromagnetic. Herein, we present one trinuclear copper(II) complex derived from a new Schiff base ligand based on the dianion of 4-chloro-6-(hydroxymethyl)-2-((3-aminopropylimino)methyl)-phenol: Synthesis, structure, spectroscopic and magnetic properties [18].

Moreover, d-Block transition metal(II)-lanthanide(III) (3d-4f) hetero-trinuclear [Cu(II)<sub>2</sub>Ln(III)] (Ln = La and Ce) complexes [Cu<sub>2</sub>La(L)(η<sup>2</sup>-NO<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>].2CH<sub>3</sub>OH (1) and [Cu<sub>2</sub>Ce(L)(η<sup>2</sup>-NO<sub>3</sub>)<sub>3</sub>(CH<sub>3</sub>OH)<sub>2</sub>].2CH<sub>3</sub>OH (2) are described, both of which are formed by a flexible symmetrical bis(salamo)-type ligand H<sub>4</sub>L. The crystal structures of 1 and 2 were determined by single-crystal X-ray diffraction analyses. In 1 and 2, each Cu(II) ion (Cu1 or Cu2) is located in the N<sub>2</sub>O<sub>2</sub> cavity of an (L)<sup>4-</sup> unit, while the apex is occupied by one oxygen atom of the coordinated methanol molecule, forming a penta-coordinated square pyramidal geometry. The lanthanide(III) (La or Ce) ion is located in the O<sub>6</sub>-donor coordination sphere of the completely deprotonated (L)<sup>4-</sup> unit and coordinated with the other six oxygen atoms of the

three nitrate ligands to form a twelve-coordinated icosahedron. The twelve-coordinated La(III) ion of 1 is surrounded by the O<sub>12</sub>-donor coordination atoms (O1, O2, O5, O6, O9, O10, O11, O12, O14, O15, O17 and O18), forming an icosahedron. Six oxygen atoms (O1, O2, O5, O6, O9 and O10) come from the deprotonated (L)<sup>4-</sup> unit, and the other six oxygen atoms (O11, O12, O14, O15, O17 and O18) come from the three bidentate chelated nitrate ligands [19]. We are going to compare some values of angles and distances between this complex and the one we are studying.

**Table 1 : Selected interatomic bond distances and bond angles around Cu(II) and La(III)**

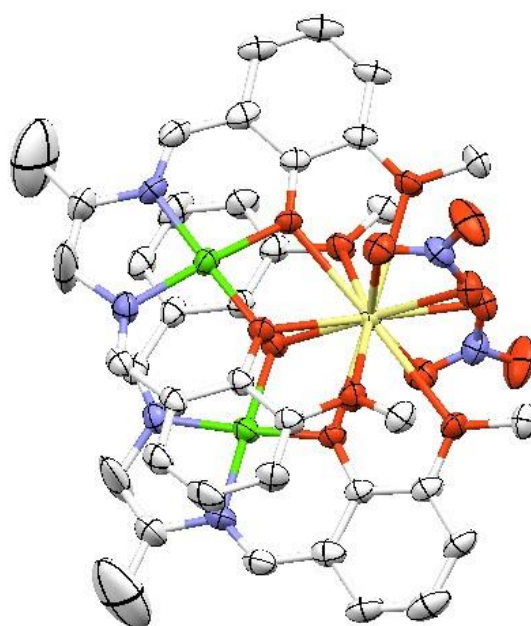
Distances in Å	Selected angles (°)	Selected angles (°)
La1AO5A 2.625	O13BLa1BO9B 179.2	O2ALa1AO1A 108.28
La1AO6A 2.704	O4ALa1AO2A 110.79	O3ACu1AN1A 173.6
Cu1AN1A 1.915	O4ALa1AO6A 65.51	O3ALa1AO4A 57.25
Cu1AN2A 1.904	O4ALa1AO5A 67.13	O6ALa1AO5A 47.7
Cu1AO3A 1.905	O1ALa1AO5A 124.2	O3ALa1AO5A 120.44
La1BO12B 2.734	O3ALa1AO2A 72.88	O4ALa1AO1A 129.08
La1AO2A 2.569	N2ACu1AO3A 95.2	O2ACu1AN1A 95.4
La1AO3A 2.534	N3AO5ALa1A 98.9	O3ACu1ALa1A 43.67
Cu1AO2A 1.883	O2ACu1AO3A 84.3	N2ACu1AN1A 85.5
Cu1BO10B 1.917	N4ACu1AN5A 86.9	O10BCu1BN4B 173.9
Cu1BN5B 1.901	O9BCu1BN5B 178.0	O2ACu1AN2A 177.0
Cu1BN4B 1.921	O2ACu1ALa1A 44.57	N2ACu1ALa1A 135.9



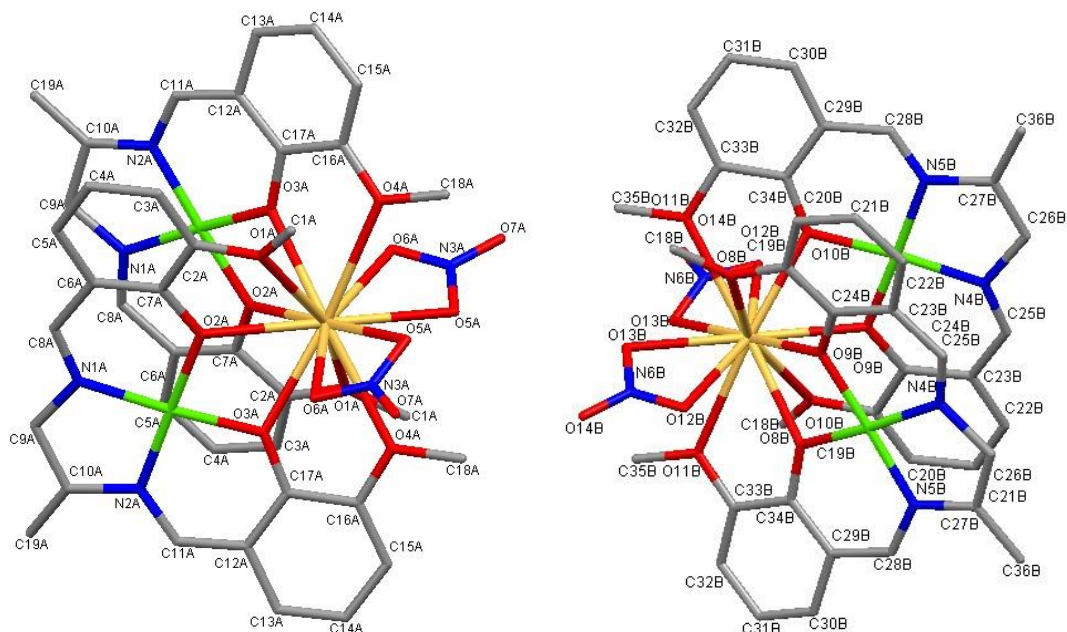
*Fig. 3. Complex 1 with solvent*

<b>Table 2 : Crystal data and structures refinement for complex 2</b>	
Empirical Formula	C <sub>74</sub> N <sub>16</sub> O <sub>42</sub> H <sub>32</sub> Cu <sub>4</sub> La <sub>3</sub>

Formula weight / g.mol <sup>-1</sup>	522.716
Crystal system	Monoclinic
Space group	P2/n
a/Å	13.0910(4)
b/Å	29.2635(9)
c/Å	14.3617(5)
α/°	90
β/°	92.181(3)
γ/°	90
Volume/Å <sup>3</sup>	5497.82(3)
Z	24
ρ <sub>calc</sub> /cm <sup>3</sup>	3.789
μ/mm <sup>-1</sup>	6.971
F(000)	5914.4
Radiation	Mo Kα (λ = 0.71073)
θ range for data collection /°	5.56 à 58.84
Index ranges	-18 ≤ h ≤ 17, -39 ≤ k ≤ 39, -19 ≤ l ≤ 19
Reflections collected	73099
Independent reflections	13641 [R <sub>int</sub> = 0.0362. R <sub>sigma</sub> = 0.0314]
Data/restraints/parameters	13641/0/651
GOF	1.505
Final R Indices [I > 2 σ (I)]	R <sub>1</sub> = 0.0932. wR <sub>2</sub> = 0.3493
R Indices (all data)	R <sub>1</sub> = 0.1395. wR <sub>2</sub> = 0.4388



*Fig. 4. ORTEP diagram of complex 2*

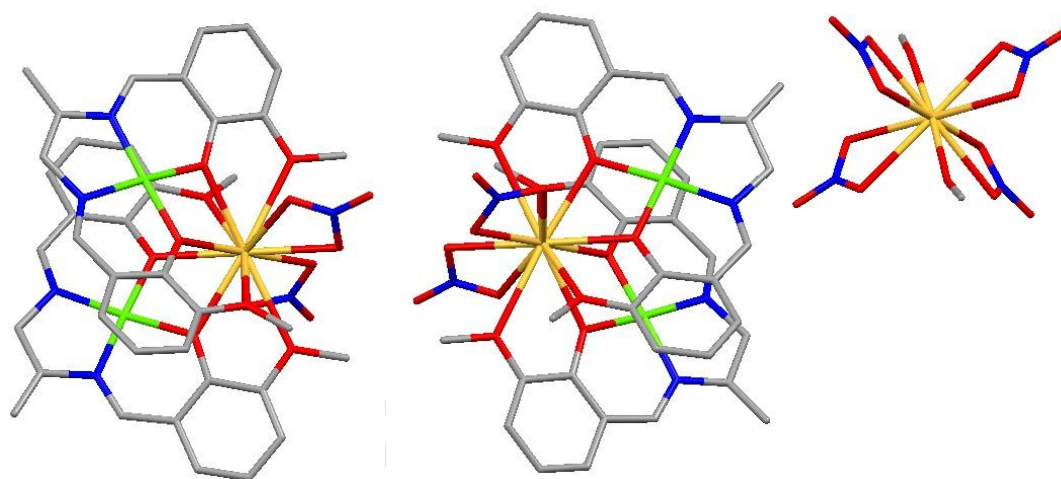


**Fig. 5. ORTEP diagram of complex 2 with labels**

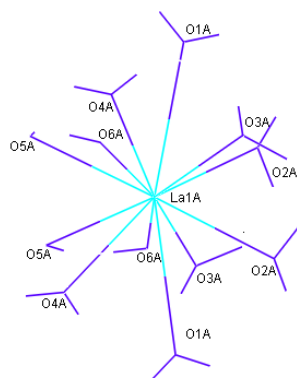
The neutral hetero-trinuclear compound  $[\text{Cu}(\text{II})_2\text{La}(\text{III})]$  was obtained with the “brick by brick” method and it crystallizes in the monoclinic system with a space group of  $P2_1/n$ . The asymmetric unit of the structure of  $[\text{Cu}_2(\mu\text{-L}_2)\text{La}(\text{NO}_3)_2]$  contains two molecules of the dideprotonated ligand  $\text{L}^{2-}$ , two  $\text{Cu}(\text{II})$  ions, one  $\text{La}(\text{III})$  ion, one perchlorate ion and two bidentate nitrate anions. In the structure of the dinuclear complex **2**, the  $\text{Cu}(\text{II})$  ion and the  $\text{La}(\text{III})$  ion are bridged by two phenolate oxygen atoms. The  $\text{Cu}(\text{II})$  ion has a square planar geometry with the basal plane formed by two imine nitrogen atoms and two phenolic oxygen atoms. The cisoid angles around the  $\text{Cu}(\text{II})$  ion, which are in the range  $[84.3^\circ\text{-}85.5^\circ]$ , deviate significantly from their ideal values of  $90^\circ$ .

The diagonal basal angles respectively  $\text{O}3\text{ACu}1\text{AN}1\text{A}=173.6^\circ$  and  $\text{O}2\text{ACu}1\text{AN}2\text{A}=177.0^\circ$  deviate slightly from the ideal values of  $180^\circ$ . The copper (II) ion lies almost in the plane defined by the  $\text{N}_2\text{O}_2$  site. The bond distance values are  $1.904 \text{ \AA}$  for  $d(\text{Cu}1\text{AN}2\text{A})$  and  $1.915$  for  $d(\text{Cu}1\text{AN}1\text{A})$  and the  $\text{Cu-O}$  distances  $1.883 \text{ \AA}$  and  $1.905 \text{ \AA}$ , are different. The  $\text{Cu-O}$  distances are  $1.883$  and  $1.905 \text{ \AA}$  while the  $\text{Cu-N}$  distances are  $1.904$  and  $1.915 \text{ \AA}$ . This fact indicates that there are distortions of the square planar geometry around the  $\text{Cu}(\text{II})$  ion. The  $\text{La}(\text{III})$  ion, which occupies the largest open site of the Schiff base ligand, is bonded to two phenolate oxygen atoms and two methoxy oxygen atoms of the ligand and two oxygen atoms of a bidentate nitrate group from each ligand. The  $\text{La-O}_{\text{phenoxo}}$  bond distances are on the order of  $2.534 \text{ \AA}$ - $2.569 \text{ \AA}$ . The distances between the  $\text{La}(\text{III})$  cation and the two oxygen atoms of bidentate nitrate  $d(\text{La}1\text{AO}5\text{A}) = 2.625 \text{ \AA}$  ;  $d(\text{La}1\text{AO}6\text{A}) = 2.704 \text{ \AA}$  show that the geometry is

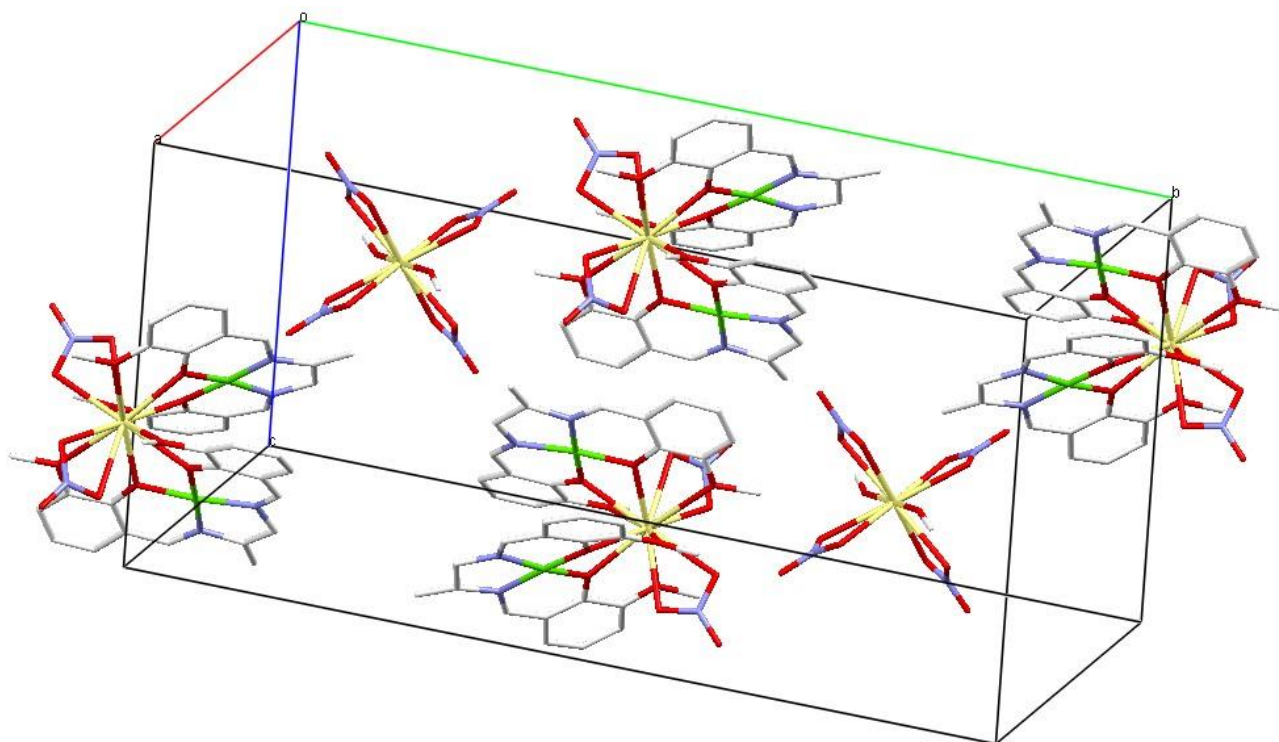
distorted. The La(III) cation is located in the planar cavity defined by the two phenolate oxygen atoms and the two methoxy oxygen atoms. The Cu-La distance is 3.543 Å. The positive charge of Cu(II) and La(III) ions is balanced by the deprotonated  $L^{2-}$  ligand and nitrate anion. The duodecaordinated La(III) ion coordination polyhedron is described as a severely distorted icosahedron or dodecahedron. The angles around the La(III) ion are very different: ( $O5ALa1AO6A = 47.7^\circ$  ;  $O5ALa1AO4A = 67.13^\circ$  ;  $O2ALa1AO4A = 110.79^\circ$  ;  $O3ALa1AO4A = 57.25^\circ$  ;  $O6ALa1AO4A = 65.51^\circ$  ;  $O3ALa1AO1A = 63.16^\circ$  ;  $O2ALa1AO1A = 108.28^\circ$  ;  $O5ALa1AO1A = 124.2^\circ$ ). For our complex the O-La-O angle varies between 47.1 and 179.2° while for the complex  $[Cu_2La(L)(\eta^2NO_3)_3(CH_3OH)_2] \cdot 2CH_3OH$  (1) [19] this angle of bonds varies between 56.2 and 160.3°. The La-O distance of bonds varies between 2.524 and 2.807 Å while for the complex  $[Cu_2La(L)(\eta^2-NO_3)_3(CH_3OH)_2] \cdot 2CH_3OH$  (1) this distance of bonds varies between 2.539 and 2.928 Å. These values are therefore comparable.



*Fig. 6. Complete structure of complex 2 by capped sticks*



*Fig. 7. Coordination scheme of La(III)*



*Fig. 8. The packing of the compound in the crystal structure*

#### 4. Conclusion

This work allowed us to synthesize and characterize a new isolated bicompartamental flexible ligand as well as its copper (II) complexes. From spectroscopic and physico-chemical methods we were able to demonstrate the formation of ligand. We also determined certain structures by X-ray diffraction. Thus we have isolated a copper (II) complex and a mixed hetero-trinuclear complex  $[\text{Cu(II)}_2\text{La(III)}]$ . The bicompartamental nature of the ligand has made it possible to house an element of the first transition series in the first compartment as well as a lanthanide in the second more open compartment by the “brick by brick” method. The Cu(II) ions in complex 2 are located in the  $\text{N}_2\text{O}_2$  cavities of the completely deprotonated  $(\text{L})^{2-}$ . The duodecacoordinated La(III) ion coordination polyhedron is described as a severely distorted icosahedron or dodecahedron with bidentate chelation occurs with the two nitrate ligand to form. The magnetic data of complex 2 indicate that antiferromagnetic coupling occurs via the phenoxo bridge.

**In memory of Dr Mouhamadou Moustapha SOW**

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