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New mononuclear Cu<sup>II</sup> and tetranuclear Cu<sup>II</sup><sub>2</sub>–La<sup>III</sup><sub>2</sub> Schiff base complexes – physicochemical properties

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### Abstract

The new mononuclear inclusion compound  $[CuL \subset (H_2O)]$  (1) and heterotetranuclear  $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$  (2)  $(L = C_{19}H_{18}N_2O_4Br_2)$  complex, derived from the hexadentate Schiff base compartmental ligand *N,N'*-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine, have been synthesized and characterized by elemental analysis, XRF, FTIR, EPR and TG/DSC techniques. Their molecular structures have been confirmed by single crystal X-ray diffraction studies. Compound 1 crystallizes in the triclinic *P*-1 space group with the Cu(II) ion occupying the N2O2 cavity and having a water molecule encapsulated by O–H...O hydrogen bonds in the O2O2 compartment. The tetranuclear complex 2 crystallizes in the monoclinic space group  $P2_1/c$  with only half of the molecule in the asymmetric unit. The inner N2O2 salen-type cavities are occupied by Cu(II) ions, whereas the La(III) ions are present in the open, larger O2O2 space of the Schiff base ligands. The two symmetrically independent heterodinuclear fragments of the molecule are bridged *via* nitrato ions, linking Cu(II) and La(III) ions Magnetic studies for the complexes indicated a weak antiferromagnetic interaction between the copper(II) ions in the crystal lattice of 1 and in the tetranuclear unit of **2**.

*Keywords:* N,O-donors ligand, Compartmental Schiff base, Heteronuclear complex, Inclusion compound, Water encapsulation,

#### 1. Introduction

Complexes of 3d and 3d-4f metal ions with Schiff bases as the main ligands have attracted special attention in view of their numerous applications in bioinorganic chemistry, chemistry. magnetochemistry, separation processes, luminescence, environmental electrochemistry and catalysis [1-8]. Bicompartmental Schiff bases, obtained by the condensation of 3-methoxy/ethoxysalicyladehyde with diamines, have two cavities of different dimensions. Thus, these ligands can bind with one or two metal centers, enabling the successful synthesis of homo- and/or heteronuclear metal complexes with interesting stereochemistries. For heteronuclear 3d-4f compounds, the 3d metal ion occupies the inner N2O2 cavity, whereas all four oxygen atoms of the capacious outer O2O2 cavity coordinate to the 4f center due to the oxophilicity and the larger ionic radius of the lanthanide ions [5-7,9-13]. The ionic radii of the 3d metal ions are smaller compared to 4f metal ions. Therefore, in the 3d coordination compounds the O2O2 compartment of the Schiff base ligand is not a suitable center for coordination of the 3d metal ion and it is expected that these oxygen atoms will not coordinate to a second 3d metal center to form a 3d-3d compounds. The empty cavity may be satisfied by molecules of water (or other solvents), resulting in the formation of an inclusion product [14–20]. This is the first report on the crystal structure of a copper(II) *N*,*N*'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine complex of with an encapsulated water molecule in the O2O2 compartment. In the literature, there are reports on two types of structures of analogues Schiff base complexes with water molecules involved in hydrogen bonds with the oxygen atoms of the O2O2 Schiff base ligand cavity. In the first type of supramolecular structure, the water molecules are completely encapsulated in the O2O2 compartment, usually forming four short intermolecular contacts with all the O atoms. The transition metal ion usually has a coordination number of 4, with an almost planar coordination environment. It is worth noting that water inclusion compounds are formed with ethoxy [17–23] as well as with methoxy derivatives of Schiff base ligands [24-28]. The second type of structure is a "pseudo"-encapsulation. In such structures, the water molecules forming hydrogen bonds with the O2O2 atoms are in fact coordinated to the metal center present in the N2O2 cavity from a neighboring molecule. There are known examples of such coordination compounds with Cu(II) [29], Ni(II) [30], Fe(III) [31] and Mn(II/III) [32] metal ions.

The present investigation concerns the synthesis, molecular and crystal structures, magnetic, spectral and thermal properties of the supramolecular compound  $[CuL \subset (H_2O)]$  (1) and the

coordination compound  $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$  (2) derived from *N*,*N*'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (Scheme 1). In our earlier paper [7] we described the synthesis and physicochemical properties of a heterotrinuclear Cu<sup>II</sup>La<sup>III</sup>Cu<sup>II</sup> compound (the dinuclear cationic complex having nitrates as the counterion), also with *N*,*N*'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine (H<sub>2</sub>L) as a ligand. It is worth noticing that by using the same substrates (H<sub>2</sub>L, copper(II) acetate monohydrate and lanthanide nitrate hexahydrate), but changing the ratio of the reagents and the conditions of the synthesis, we have now obtained the tetranuclear compound  $Cu_2^{II}La_2^{III}$ (2) (an inert complex).

### 2. Experimental

#### 2.1. Synthesis

### 2.1. 1. Materials

The reagents and solvents, *i.e.* 1,3-diaminopropane, 5-bromo-2-hydroxy-3methoxybenzaldehyde,  $Cu(CH_3COO)_2 \cdot H_2O$ ,  $La(NO_3)_3 \cdot 6H_2O$ , ethanol, methanol and DMF, used for synthesis were commercially available from Aldrich Chemical Company and Polish Chemical Reagents. They were used as received without further purification.

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### 2.1.2. N,N'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine, H<sub>2</sub>L

The Schiff base (N,N'-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine,  $C_{19}H_{20}Br_2N_2O_4$ ), abbreviated as  $H_2L$ , was obtained by the 2:1 condensation of 5-bromo-2-hydroxy-3-methoxybenzaldehyde and 1,3-diaminopropane in methanol according to the procedure reported by Maneiro et al. [6].

### 2.1.3. $[CuL \subset (H_2O)]$ (1)

Complex 1 was obtained by the treatment of  $Cu(CH_3COO)_2 \cdot H_2O$  (0.2 mmol, 0.0399g) in MeOH (10mL) with H<sub>2</sub>L (0.2 mmol, 0.0998 g) in 10mL of hot MeOH (about 318 K). As a result, a brown solid appeared. The obtained mixture was stirred for about 30 min, after this time the brown solid was collected by filtration. Recrystallization of this product from dimethylformamide yielded diffraction quality brown crystals.

Yield: 84 mg/72 %. Anal. Calc. (579.73): C, 39.35; H, 3.45; N, 4.83; Cu, 10.97%. Found: C, 39.47; H, 3.34; N, 4.51; Cu, 10.62%. FTIR (KBr, cm<sup>-1</sup>): 3564w, 3516w, 2928w, 2828w, 1612s, 1536m, 1460s, 1320s, 1236s, 1076m, 984w, 848m, 788m, 688m, 572w, 488w, 348w.

### 2.1.4. $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$ (2)

A mixture of the Schiff base  $H_2L$  (0.050 g, 0.10 mmol) and  $Cu(CH_3COO)_2 \cdot H_2O$  (0.0199g, 0.10 mmol) in 15 ml of EtOH was stirred and refluxed for 30 min. A solution of  $La(NO_3)_3 \cdot 6H_2O$  (0.0433 g, 0.10 mmol) in 10 ml EtOH was added and the mixture was refluxed for 15 min and filtered. Diethyl ether was allowed to diffuse slowly into this solution at room temperature and green single crystals were obtained in three weeks.

Yield: 72 mg/80 %. Anal. Calc. (1865.44): C, 27.05; H, 2.57; N, 7.51; Cu, 6.81; La , 14.90 %. Found: C, 27.40; H, 2.56; N, 7.36; Cu, 6.50; La 14.60%. FTIR (KBr, cm<sup>-1</sup>): 3420m, 2928w, 1628s, 1468s, 1384s, 1296s, 1236m, 1076w, 1040w, 840w, 792w, 696w, 568w, 468w.

### 2.2. Methods

The carbon, hydrogen and nitrogen contents in the analysed compounds were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The copper and lanthanum contents were established using an ED XRF spectrophotometer (Canberra–Packard).

The FTIR spectra of the complexes were recorded over the range 4000-200 cm<sup>-1</sup> using an M-80 spectrophotometer (Carl Zeiss Jena). Samples for FTIR spectra measurements were prepared as KBr discs.

The magnetization of powdered samples of the complexes was measured over the temperature range 1.8-300 K using a Quantum Design SQUID MPMSXL–5 magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at a magnetic field of 0.5 T. The SQUID magnetometer was calibrated with a palladium rod sample. Corrections are based on subtracting the sample holder signal and a contribution  $\chi_D$  estimated from Pascal's constants [33].

EPR spectra were obtained using a Bruker Elexsys E 500 spectrometer equipped with an NMR teslameter (ER 036TM) and frequency counter (E 41 FC) at the X-band at room temperature and at about 77 K.

Thermal analyses of the complexes and the Schiff base ligand were carried out by thermogravimetric (TG) and differential scanning calorimetry (DSC) methods using a SETSYS 16/18 analyser (Setaram). The experiments were carried out under an air flow in the temperature range 20-700 °C at a heating rate of 10 °C min<sup>-1</sup>. The samples (5.01 mg (1), 7.78 mg (2) and 5.27 mg (Schiff base ligand)) were heated in Al<sub>2</sub>O<sub>3</sub> crucibles.

The X-ray powder diffraction patterns of the products of the decomposition process were taken on a HZG-4 (Carl–Zeiss, Jena) diffractometer using Ni filtered CuK<sub> $\alpha$ </sub> radiation. The measurements were made within the range  $2\theta = 4-80$  ° by means of the Bragg-Brentano method.

#### 2.3. X-ray crystal structure determination

The X-ray diffraction intensity data for crystals **1** and **2** were collected on an Oxford Diffraction Xcalibur CCD diffractometer with graphite-monochromatized MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) at 100(2) K. Data sets were collected using the  $\omega$  scan technique, with an angular scan width of 1.0°. The programs CrysAlis CCD and CrysAlis Red [34] were used for data collection, cell refinement and data reduction. Empirical absorption correction using spherical harmonics was made for **1** [35] and analytical absorption correction based on the indexing of crystal faces was applied for **2** [36]. The structures were solved by direct methods using SHELXS-97 and refined by the full-matrix least-squares on  $F^2$  using SHELXL-97 [37] (both operating under WinGX [38]). The non-hydrogen atoms were refined with anisotropic displacement parameters. The water H atoms in **1** were found in the Fourier difference map and refined using a riding model with O-H distances of 0.84 Å and  $U_{iso}(H) = 1.2$   $U_{eq}(O)$ . The other hydrogen atoms were placed in calculated positions and treated as riding atoms: C-H = 0.93 - 0.99 Å, with  $U_{iso}(H) = 1.2$   $U_{eq}(C)$  or = 1.5  $U_{eq}(C)$  for methyl H atoms.

The tetranuclear molecule in **2** lies on a center of inversion, with only half of the molecule being symmetrically independent. Bond length restraint was applied by DFIX instructions to 2.00(2) Å for the C20–C21 distance in the ethanol molecule in **2**.

A summary of the data collection conditions and the crystal structure refinement parameters are given in Table 1. The molecular plots were drawn with ORTEP3 for Windows [39].

#### 3. Results and discussion

### 3.1. Infrared spectra

The solid state FTIR spectra of the Schiff base (H<sub>2</sub>L) and its complexes were recorded and compared in order to get some information about the binding of the Schiff base ligand to the Cu(II) and La(III) ions (Figs 1 and 2). The FTIR spectrum of compound **1** (Fig. 1) exhibits two sharp bands at 3564 and 3516 cm<sup>-1</sup> due to the O–H stretching vibrations of the water molecules and one medium intensity band at 1536 cm<sup>-1</sup> corresponding to the bending vibrational mode  $\delta$ (H<sub>2</sub>O) of the water molecules. In hydrated crystals, the asymmetric and symmetric  $\nu$ (OH) stretching vibrations are spread over a considerable range of energies and are normally observed as a broad band. However, because of the encapsulation, the motion of the water molecule in **1** is restricted and the asymmetric and symmetric stretching bands appear separately (Fig. 1) [14-20]. The crystal structure analysis of **1** revealed that the water molecule is encapsulated in the O2O2 compartment through strong O–H…O hydrogen bonds with the phenoxo and methoxy oxygen atoms.

In the FTIR spectrum of 2, the broad medium strong band with a maximum around  $3420 \text{ cm}^{-1}$ may be assigned to the OH stretching vibrations of ethanol molecules, v(OH) [5,7,40,41]. The weak bands at around 2940 and 2840 cm<sup>-1</sup> in the spectra of the ligand and complexes may be attributed to the asymmetric and symmetric stretching vibrations of the  $\nu$ (CH<sub>3</sub>) group from the *methoxy* substituent [8,42]. Four bands near 1468 ( $v_4$ ), 1296 ( $v_1$ ), 1040 ( $v_2$ ) and 840 cm<sup>-1</sup>  $(v_6)$  for 2 may be assigned to the coordinated nitrate groups [43-45]. The strong band attributed to  $\nu$ (C=N) stretching vibrations of the imine nitrogen, present in the free ligand at 1636 cm<sup>-1</sup>, is shifted to lower wavenumbers in **1** and **2**, at 1612 and 1628 cm<sup>-1</sup>, respectively (Figs 1 and 2), confirming the coordination of the nitrogen atom from the azomethine group to the copper(II) ion. This coordination mode is expected to reduce the electron density in the azomethine fragment as a result of the withdrawal of electron density from the nitrogen atom, and as such lowers the C=N absorption frequency [3,5,8,16,41]. A strong band observed at 1253 cm<sup>-1</sup> in the spectrum of the free Schiff base has been assigned to the phenolic stretching vibration  $\nu$ (C–O). On complexation, this band is shifted to a lower frequency of 1236 cm<sup>-1</sup>, indicating coordination through the phenolic oxygen atom [3,4,46]. The occurrence of two bands at *ca*. 572 and 448 cm<sup>-1</sup> in **1** and at *ca*. 568 and 468 cm<sup>-1</sup> in **2**, and their absence in the spectrum of the free Schiff base ligand, give further evidences for M–O and M–N interactions

[16,40,46]. The infrared spectroscopic results are in accordance with the X-ray crystal structure data for **1** and **2**.

### 3.2. Description of the crystal and molecular structure of complex 1

The molecular structure of the mononuclear Cu(II) inclusion compound [CuL $\subset$ (H2O)] (1) (where L = C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Br<sub>2</sub>) is shown in Figure 3. It crystallizes in the triclinic *P*-1 space group. Details of the relevant data collection and refinement are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. In this compound the metal center has a coordination number of 4 and occupies the N2O2 cavity of the salen-type Schiff base ligand. The bond lengths and angles around the Cu(II) ion indicate large deviations from planarity for the coordination polyhedron. The dihedral angle between the (O1Cu1N1) and (O2Cu1N2) planes is 31(1)°. A similar structure was observed in related compounds [11,17,20]. The water molecule in the crystal of **1** is hydrogen bonded to the oxygen atoms inside the O2O2 compartment of the Schiff base ligand. The donor…acceptor distances between the water molecule and the phenoxo and methoxy oxygen atoms are in the range 2.823(4) to 3.236(5) Å (Table 3), indicating that the hydrogen bonds can be considered as moderately strong.

### 3.3. Description of the crystal and molecular structure of complex 2

The tetranuclear complex  $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$  (2) (where  $L = C_{19}H_{18}N_2O_4Br_2$ ) crystallizes in the monoclinic  $P2_1/c$  space group with two symmetrically dependent fragments related to each other by the inversion center. Its crystal structure, along with the atomic numbering scheme, is shown in Figure 4. Details of the relevant data collection and refinement are summarized in Table 1. Selected bond lengths and angles are given in Table 2. The molecule of **2** is composed of two moieties linked by two nitrato groups, both acting as monodentate ligands towards the copper ion from one unit and towards a lanthanum ion from the other unit. The Cu(II) ion adopts a square-based 4+1 coordination mode, the equatorial N2O2 donors being afforded by the Schiff base ligand, while the axial position is occupied by an oxygen atom of bridging nitrate ion. The four atoms of the N2O2 site are almost coplanar and are displaced from the mean plane by less than 0.038 Å. The copper(II) center is 0.113 Å above the mean N<sub>2</sub>O<sub>2</sub> coordination plane. As observed in related compounds, the Cu–N/O

bond lengths are within the usual range of values observed for copper coordinated to Schiff base ligands [11,17,20].

The La(III) ions are deca-coordinated. In addition to the phenolate oxygen atoms, the coordination sphere contains two oxygen atoms of the OMe side arms of the Schiff base, five oxygen atoms of the two bidentate ( $\eta^2$ -chelating) and one bridging nitrato ions, and one oxygen atom of the ethanol molecule. The dihedral angle ( $\alpha$ ) between the (O1Cu1O2) and (O1Ln1O2) planes is *c.a.* 24(1)° (Table 2). The La–O bond lengths depend on the nature of the oxygen atoms. The distances increase in sequence:

phenolato < ethanol < nitrato < methoxo (from 2.526(3) to 2.646(3) Å).

The intramolecular separations Cu1...La1 and Cu1...La1<sup>*i*</sup> (symmetry code: <sup>*i*</sup> -*x*, -*y*, -*z*+1), being *ca*. 3.6 and 6.4 Å, respectively (Table 2), are within the normal range of values for polynuclear Cu–Ln complexes [9,45]. The ethanol O8 atom is involved as a donor in the hydrogen bond with the nitrate O9 atom. The methyl groups interact *via* C–H...O hydrogen bonds with the nitrato O6 oxygen atom. In the crystal structure, weak C–H...O hydrogen bonds are observed between the tetranuclear units (Table 3). Additionally, the presence of Br atoms in the crystal structure results in the formation of intermolecular contacts between the O9 and Br2 atoms, with a separation shorter than the sum of the van der Waals radii (3.297(2) Å).

### 3.4. Magnetic properties

The magnetic susceptibilities of  $[CuL \subset (H_2O)]$  (1) and  $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$  (2) have been measured in the temperature range 1.8–300 K in a 0.5 T applied magnetic field. As shown in the Figure 5, at the room temperature the  $\chi_m T$  product of 1 is equal to 0.835 cm<sup>3</sup> mol<sup>-1</sup> K and it is consistent with only one unpaired electron in magnetically diluted copper(II) complexes [47]. The value of the product  $\chi_m T$  is constant with temperature lowering and reaches 0.427 cm<sup>3</sup> mol<sup>-1</sup> K at 1.8 K. The decrease in the value of  $\chi_m T$  in the low-temperature range is caused by the occurrence of weak antiferromagnetic interactions between the Cu<sup>II</sup> ions in the crystal lattice. The susceptibility data obey the Curie-Weiss law over the temperature range 1.8–300 K with a Curie constant (C) of 0.391 cm<sup>3</sup> K mol<sup>-1</sup> and a Weiss constant ( $\theta$ ) of - 1.1 K. A small, negative value of the Weiss constant could also confirm a small antiferromagnetic exchange coupling between the metal ions in the crystal lattice.

From a magnetic point of view, compound **1** will be considered as a mononuclear compound. In such a situation, the magnetic data were fitted using the susceptibility equation for  $S = \frac{1}{2}$  (eq. 1). To elucidate the significance of the exchange between the copper(II) ions in the crystal lattice, a molecular field correction term was also included, eq. (2) [47,48].

$$\chi_{M} = \frac{N\beta^{2}g^{2}}{3kT}S(S+1)$$

$$\chi_{M}^{corr} = \frac{\chi_{M}}{1 - \frac{2zJ}{N\beta^{2}g^{2}} \cdot \chi_{M}}$$
(1)
(2)

where *N* is Avogadro's number, g – the spectroscopic splitting factor,  $\beta$  – the Bohr magneton, k – Boltzmann constant, zJ' – the intermolecular exchange parameter and z is the number of the nearest neigbours of the Cu<sup>II</sup> center. The least-squares fit of the experimental data using these equations were limited to the temperature range from 1.8 K to 300 K, and leads to zJ' =- 2.98(1) cm<sup>-1</sup> and g = 2.07(1), as indicated by the solid curve in Figure 5. The agreement factor *R* is equal to  $5.52 \times 10^{-4}$ . The criterion used in the determination of the best fit was based on minimization of the sum of the squares of the deviation:  $R = \Sigma (\chi_{exp}T - \chi_{calc}T)^2 / \Sigma (\chi_{exp}T)^2$ . The result of the calculations may be indicative of weak interactions between the copper(II) centers, transmitted through a system of hydrogen bonds in the crystal lattice. This fact is expected in mononuclear magnetically diluted Cu<sup>II</sup> compounds [49].

To confirm the nature of the ground state of **1**, we investigated the variation of the magnetization, M, with respect to the field, at 2 K. The results are shown in Figure 6, where the molar magnetization M is expressed in  $\mu_{\rm B}$  units. As the magnetic field increases, the M vs. H curve is linear over the whole field range and indicates a value of the magnetization close 0.7  $\mu_{\rm B}$  at 5 T. This value is somewhat lower than the simulated value calculated with the Brillouin function for one unpaired electron for the Cu<sup>II</sup> ion.

As depicted in Figure 7 at the room temperature, the  $\chi_m T$  product of **2** is equal to 0.790 cm<sup>3</sup> mol<sup>-1</sup> K. Obviously, this value is equal to the expected value originating from two uncorrelated Cu<sup>II</sup> ( $d^8$ ,  $S = \frac{1}{2}$ ) ions, since no contribution is expected from the non-magnetic La<sup>III</sup> ions ( $f^0$ , S = 0). In this compound, the intramolecular Cu...Cu distance is certainly large and may preclude any significant magnetic interactions between the copper centers in the tetranuclear unit. However, below 10 K, a discernible drop in the  $\chi_m T$  values to 0.668 cm<sup>3</sup> K mol<sup>-1</sup> at 1.8 K was also noted. The thermal dependence of  $\chi_m T$  is characteristic of a small

antiferromagnetic interaction since no maximum appears in the  $\chi_m$  vs *T* curve until 1.8 K. This apparent weak antiferromagnetic interaction may be mediated by the diamagnetic lanthanide(III) center. The examples in the literature [7,50] show that diamagnetic lanthanide(III) centers are capable of mediating magnetic exchange between copper(II) centres in a molecule.

This conclusion is fully confirmed by the magnetization versus field curve of 2 at 2 K (Fig. 6). This measurement shows a saturation value of *ca*. 2  $\mu_{\rm B}$ , which is the expected value for two independent  $S = \frac{1}{2}$  systems with g = 2, and confirm our previous assumption. To estimate the magnitude of the interaction in 2, we used the following equation for the magnetic susceptibility for two exchange coupled copper(II) ions [51]. The data have been fitted to a model which assumes the exchange Hamiltonian to be  $H = -2J\vec{S_1} \cdot \vec{S_2}$ . The susceptibility is then predicted to be:

$$\chi_{m} = \frac{2N\beta^{2}g^{2}}{3kT} \left[ 1 + \frac{1}{3}\exp(-2J/kT) \right]$$
(3)

where the symbols have their usual meaning. Least-squares fitting of the experimental data over the whole temperature range leads to J = -0.37(1) cm<sup>-1</sup>, g = 2.08(2), as indicated by the solid curve in Figure 6. The agreement factor *R* is equal to  $1.29 \times 10^{-5}$  ( $R = \Sigma(\chi_{exp}T - \chi_{calc}T)^2/\Sigma(\chi_{exp}T)^2$ ). The nearest Cu...Cu distance in the tetranuclear unit is 7.730 Å. This fact causes very poor overlap of magnetic orbitals, resulting in very weak antiferromagnetic coupling. Since the Cu<sup>...</sup>Cu distances in the examined compounds are all rather long, it is to be expected that the coupling between the electrons of the Cu<sup>II</sup> ions in the systems will be weak.

### 3.5. EPR spectra

The EPR spectra of a polycrystalline sample of complex 1 at room temperature and 77 K resemble monomeric Cu<sup>II</sup> species, with well-resolved hyperfine features and  $g_{\parallel} > g_{\perp} > g_e$  ( $g_{\parallel} = 2.22$  and  $g_{\perp} = 2.05$ ) (Fig. 8). The spectral features are characteristic of a square-planar geometry and a  $d_x^{2-2}$  ground state for the copper(II) center [53,54].

The polycrystalline EPR spectra of **2**, at both room temperature and liquid nitrogen temperature (77 K), show rhombic spectra with  $g_1 = 2.02$ ,  $g_2 = 2.10$  and  $g_3 = 2.21$ , consistent

with a  $d_x^{2}y^{2}$  ground state for the square pyramidal geometry of the CuN<sub>2</sub>O<sub>2</sub>(O) chromophore [55]. Moreover, in low field part of the spectra the  $\Delta M_s = 2$  transition is observed, which confirms the presence of weak magnetic exchange interactions between the Cu<sup>II</sup> centers [56–59], as detected by the direct magnetic measurements (Fig. 9).

The EPR results are in accord with the X-ray structural data obtained for complexes **1** and **2**, respectively.

### 3.6. Thermal analysis

The thermal behaviors of complexes 1 and 2 were characterized in air atmosphere using thermogravimetric analysis (TG), differential thermogravimetric analysis (DTG) and differential scanning calorimetry (DSC) (Figs 10 and 11). The complexes are stable at room temperature. As shown in Figure 10, on heating over the temperature range 80–100 °C, the change in mass (2.90%) estimated from the TG curve recorded for 1 corresponds to the loss of one water molecule (the theoretical value is 3.10%). The recorded DSC curve reveals the first endothermic peak with a maximum at around 90 °C. The anhydrous complex is stable up to 290 °C. The second endothermic peak recorded on the DSC curve, with a maximum at around 220 °C and without changing the mass on the TG, may indicate the melting of complex 1. The next step for the decomposition of 1 is a gradually loss of mass within the higher temperature range 290-650 °C. It is probably connected with the decomposition of Schiff base ligand, which is accompanied by strong exothermic peaks, seen on the DSC curve. The final product of the decomposition of 1 is CuO, which is formed at around 660 °C. The corresponding mass loss calculated from the TG curve is 14.10% (the theoretical value is 13.70%).

Complex 2 (Fig. 11) is stable on heating up to 150 °C. The first mass loss recorded on the TG curve at a higher temperatures (160-180 °C) is equal to 5.30%, which is connected with the release of two molecules of coordinated ethanol molecules (the theoretical value is 4.90%). This process is accompanied by an endothermic peak, seen on the DSC curve. As the temperature is increased, the TG curve of the heteronuclear compound exhibits a mass loss over a wide temperature range, 290-700 °C, which is accompanied with exothermic peaks seen on DSC curves at around 300 and 530 °C. This may be due to the decomposition of the Schiff base ligand (Figure 11 (inside)). The free Schiff base, on heating in the temperature range 20-700 °C, first melts. This process is confirmed by the recorded DSC and TG curves. The DSC curve shows an endothermic peak with a maximum at about 130 °C which is

connected with no mass loss on the TG curve. At higher temperature, the TG curve exhibits a mass loss in the range 220-700 °C, which is accompanied by exothermic peaks seen on the DSC curves, with maxima at around 280 and 550 °C, connected with the burning of the Schiff base ligand. The decomposition process of  $Cu_{2}^{II}La_{2}^{III}La$  compounds is intricate and it is difficult to distinguish the intermediate solid products. The solid residue obtained during the thermal decomposition of complex **2** is a mixture of La<sub>2</sub>CuO<sub>4</sub> and CuO, which is in accord with results presented by Blake *et al* [60]. The residual mixture percentage, determined from the TG curve, is 25.80%, and this value is fairly coincident with the theoretical one of 26.00%. The final products of the thermal decomposition of **1** and **2** were experimentally verified by phase analysis on the basis of the obtained X-ray diffraction powder patterns.

### Conclusion

Starting from the same Schiff base ligand molecule we have synthesized two coordination compounds with different architectures. The host-guest supramolecular compound  $[CuL=(H_2O)]$  (1) and the novel heterotetranuclear coordination compound  $[Cu_2La_2(L)_2(NO_3)_6(EtOH)_2]$  (2) were obtained. The water molecule found in the crystal structure of 1 is not coordinated to the metal center, but is encapsulated through O–H…O hydrogen bonds to the phenolate and methoxy oxygen atoms as a guest molecule in the O2O2 compartment of the Schiff base ligand. This interesting inclusion property is observed for other transition metal Schiff base complexes. However, little is still known about the factors that determine the formation of host-guest compounds instead of compounds with "pseudo-encapsulated" water molecules that are coordinated to the transition metal center and interact additionally with the oxygen atoms from the outer O2O2 empty cavity of a neighboring molecule. The magnetic susceptibility measurements, as well as the relationship between the magnetic field strength in 1 revealed weak antiferromagnetic interactions between the magnetic Cu<sup>II</sup> centers in the crystal lattice at low temperature.

The inclusion product with the water molecule in the O2O2 compartment is not formed when the lanthanide ions are present in the solution during the synthesis. Determination of the crystal structure of 2 shows that this heterotetranuclear compound consists of two symmetrically dependent moieties with two Schiff base molecules behaving as dianionic hexadentate chelating ligands with two N2O2 and O2O2 donor sites. The Cu(II) and La(III) ions in both parts of the molecule are linked *via* two nitrato bridging ligands. A weak

antiferromagnetic interaction is observed in the tetranuclear compound **2**, between the copper(II) centers and mediated by the diamagnetic lanthanum(III) center.

#### Appendix A. Supplementary data

CCDC 931234 and 931235 contain the supplementary crystallographic data for **2** and **1**, respectively. These data can be obtained free of charge via <u>http://ww.ccdc.cam.ac.uk/conts/retrieving.html</u> or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail deposit@ccdc.cam.ac.uk.

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### **Captions for illustration**

Scheme 1. Chemical structure of the Schiff base ligand H<sub>2</sub>L.

Fig. 1. FTIR spectra of complex 1 and the free ligand  $H_2L$  (inside: part of the FTIR spectra of complex 1 and the  $H_2L$  ligand demonstrating the stretching vibrations of the encapsulated water molecule in 1).

Fig. 2. FTIR spectra of the complex 2 and the ligand  $H_2L$ .

**Fig. 3.** Ortep view with the atom numbering scheme of the mononuclear copper complex with the encapsulated water molecule in the crystal of **1**; the displacement ellipsoids are drawn at the 50% probability level, hydrogen spheres are drawn with an arbitrary radius.

**Fig. 4.** Molecular structure of the tetranuclear  $Cu_2La_2$  complex 2; only half of the molecule is symmetrically independent and it is numbered in the picture; the displacement ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity.

**Fig. 5.** Temperature dependence of the experimental  $\chi_m T(\circ)$  and  $\chi_m(\bullet) vs T$  for complex **1**. The solid line is the calculated curve derived from equations (1) and (2).

**Fig.6.** Field dependence of the magnetization for complex **1** (•) and **2** (•) at 2 K. The dashed line is the Brillouin function for an independent  $S = \frac{1}{2}$  system; the solid line is the Brillouin function curve for two independent  $S = \frac{1}{2}$  of the Cu<sup>II</sup><sub>2</sub>La<sup>III</sup><sub>2</sub> unit.

**Fig. 7.** Temperature dependence of the experimental  $\chi_m T$  ( $\Box$ ) and  $\chi_m$  (**\blacksquare**) *vs T* for complex **2.** The solid line is the calculated curve derived from equation (3).

Fig. 8. EPR (X-band) spectrum of powdered compound 1 at room temperature.

Fig. 9. EPR (X-band) spectrum of powdered compound 2 at room temperature. The inset shows the forbidden line  $\Delta M_S = 2$ .

Fig. 10. TG, DTG and DSC curves of 1 in an air atmosphere.

**Fig. 11.** TG, DTG and DSC curves of **2** (inside TG, DTG and DSC curves of the Schiff base ligand) in an air atmosphere.

























	1	2
Empirical formula	$C_{19}H_{20}Br_2N_2O_5Cu$	$C_{42}H_{48}Br_4N_{10}O_{28}Cu_2La_2$
Formula weight	579.73	1865.44
Temp. (K)	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> -1	$P2_1/c$
<i>a</i> (Å)	9.406(1)	11.683(1)
<i>b</i> (Å)	9.796(1)	11.475(1)
<i>c</i> (Å)	11.508(2)	21.576(1)
α (°)	93.34(1)	90
$\beta$ (°)	111.21(1)	90.14(1)
γ (°)	94.44(1)	90
$V(\text{\AA}^3)$	981.3(2)	2892.5(4)
<i>Z; Z'</i>	2; 1	2; 0.5
Crystal form/colour	needle/brown	plate/green
Crystal size (mm)	0.40 x 0.20 x 0.10	0.40 x 0.35 x 0.25
$D_{\text{calc}} (\text{g cm}^{-3})$	1.962	2.142
$\mu (\text{mm}^{-1})$	5.220	5.032
Absorption correction	multiscan	analytical
$\theta$ range (°)	2.70 - 25.24	3.12 - 25.24
Reflns coll./unique ( $R_{int}$ )	5785/3545 (0.0402)	10169/5218 (0.0156)
Data/restr./parameters	3545/0/270	5218 / 1 / 397
GooF on F <sup>2</sup>	0.815	1.069
$R_{1}, wR_{2} [I > 2\sigma(I)]$	0.0327, 0.0599	0.0291, 0.0699
$R_1, wR_2$ (all data)	0.0579, 0.0629	0.0339, 0.0712
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	0.616 and -0.586	1.506, -0.781

### Table 1

Crystallographic data for crystals 1 and 2.

### Table 2

Selected geometric parameters (Å,  $^{\circ}$ ) in the coordination environments of the metal centers.

1			
bond lengths		angles	
N1-Cu1	1.989(3)	O1-Cu1-O2	86.7(1)
N2-Cu1	1.936(4)	O1-Cu1-N1	92.9(1)
O1-Cu1	1.908(3)	O1-Cu1-N2	156.0(1)
O2-Cu1	1.919(3)	N2-Cu1-O2	92.3(1)
		O2-Cu1-N1	158.2(1)
		N2-Cu1-N1	96.6(1)
2			
bond lengths		angles	
N1-Cu1	1.987(3)	O1-Cu1-O2	78.8(1)
N2-Cu1	1.963(3)	01-Cu1-N1	92.5(1)
O1-Cu1	1.949(3)	01-Cu1-N2	167.4(1)

O2-Cu1	1.974(3)	N2-Cu1-O2	91.7(1)
$O9-Cu1^i$	2.366(3)	N2-Cu1-N1	96.2(1)
Cu1-O9 <sup><i>i</i></sup>	2.366(3)	O2-Cu1-N1	170.5(1)
N3-La1	3.058(4)	O1-Cu1-O9 <sup><i>i</i></sup>	94.0(1)
N4-La1	3.005(4)	O1-La1-O5	76.9(1)
O1-La1	2.526(3)	O2-La1-O4	61.3(1)
O2-La1	2.539(3)	O1-La1-O3	61.1(1)
O3-La1	2.638(3)	O6-La1-O3	75.5(1)
O4-La1	2.646(3)	O10-La1-O3	69.8(1)
O5-La1	2.613(3)	O8-La1-O4	69.8(1)
O6-La1	2.617(3)	O13-La1-O4	71.9(1)
O8-La1	2.536(3)	O1-La1-O12	123.9(1)
O10-La1	2.609(3)	O8-La1-O10	78.2(1)
O12-La1	2.611(3)	O8-La1-O5	135.9(1)
O13-La1	2.580(3)	O10-La1-O6	135.1(1)
Cu1-La1	3.6420(5)	α	24(1)
Cul-Lal <sup>i</sup>	6.4493(8)		

symmetry code: i -x, -y, -z+1.

 $\alpha$  - dihedral angle between the Cu1O1O2 and La1O1O2 planes

### Table 3

Hydrogen bond parameters (Å, °) in 1

D–H···A	D–H	Н…А	D…A	<dha< td=""></dha<>
OW1-H2W01	0.98(5)	2.19(6)	2.972(4)	135
OW1-H2WO3	0.98(5)	1.96(6)	2.823(4)	144
OW1-H1WO2	0.77(7)	2.37(8)	2.968(6)	136
OW1-H1WO4	0.77(7)	2.51(6)	3.236(5)	159

### Hydrogen bond parameters (Å, °) in ${\bf 2}$

D–Н···А	D–H	Н…А	D…A	<dha< th=""></dha<>
08–H8…09 <sup>i</sup>	0.84	1.99	2.734(5)	147
C14–H14…O15 <sup>ii</sup>	0.95	2.42	3.006(5)	120
C18–H18BO15 <sup>iii</sup>	0.98	2.61	3.169(6)	116
C18–H18AO6	0.98	2.65	3.309(6)	125
С19-Н19АО6	0.98	2.57	3.230(6)	125

symmetry codes: <sup>*i*</sup> -*x*, -*y*, -*z*+1; <sup>*ii*</sup> -*x*, *y*-1/2, -*z*+1/2; <sup>*iii*</sup> -*x*, *y*+1/2, -*z*+1/2.



The new compounds [CuL $\subset$ (H<sub>2</sub>O)] (1) and [Cu<sub>2</sub>La<sub>2</sub>(L)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>(EtOH)<sub>2</sub>] (2), derived from *N,N'*-bis(5-bromo-3-methoxysalicylidene)propylene-1,3-diamine, were obtained and their physicochemical properties were investigated. In compound 1, the Cu(II) ion occupies the inner N2O2 salen-type cavity of the Schiff base, whereas the water molecule is encapsulated by O–H...O hydrogen bonds in the larger O2O2 compartment of this ligand. In the bimetallic heterotetranuclear complex 2, the N2O2 cavities of the organic ligand are also occupied by Cu(II) ions, whereas La(III) ions are present in the O2O2 cavities. Moreover, the two symmetrically independent heterodinuclear fragments of this molecule are bridged *via* nitrato ions linking the 3*d* and 4*f* ions. The measurements of variable-temperature magnetic susceptibility as well the relationship between the magnetization and magnetic field strength in 1 and 2 revealed weak antiferromagnetic interactions between the Cu<sup>II</sup> magnetic centers at low temperature.