



Syntheses, crystal structures, thermal and magnetic properties of new heterotrinnuclear Cu^{II}–Ln^{III}–Cu^{II} complexes incorporating N₂O₄-donor Schiff base ligands

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ABSTRACT

New heterotrinnuclear complexes [Cu₂La(H₂hamp)₂(NO₃)₂H₂O]NO₃·6MeOH (**1**), [Cu₂Pr(H₂hamp)₂(NO₃)₃]·6MeOH (**2**), [Cu₂Nd(H₂hamp)₂(NO₃)(MeOH)₂](NO₃)₂·H₂O (**3**) where H₂hamp is the dideprotonated forms of the *N,N'*-bis(2,3-dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane were obtained in the reaction of the Schiff base ligand with the respective salts of Cu^{II} and Ln^{III}. The compounds **1–3** crystallize in the monoclinic space group *P2₁/n*. The X-ray structures of **1–3** show the central Ln^{III} ion surrounded by two CuH₂hamp units, so that Ln^{III} and Cu^{II} ions are linked by phenoxido bridging groups. The compounds **1–3** are stable at room temperature and their decomposition processes proceed in the similar way. The temperature dependence of the magnetic susceptibility and the field-dependent magnetization indicated that the interaction between Cu^{II} and Ln^{III} ions (Ln = Pr and Nd) is antiferromagnetic.

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1. Introduction

N,N'-Bis(2,3-dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane (abbreviated as **H₄hamp**) is the salicylaldimine derivative with hydroxyl groups in the 3- and 3'-position which contains six potential donor atoms. The Cambridge Structural Database [1] includes only several compounds with the above Schiff base: the tetranuclear complex [U₄(L₂)₂(H₂L₂)₂(py)₂O][CF₃SO₃]₂ reported by Salmon et al. that contains a U₄ tetrahedron held by a central, μ-oxo ion and eight bridging oxygen atoms from the N₂O₄-donor ligands. In the crystal structure of this compound the two Schiff base ligands in the asymmetric unit display different conformations, either slightly curved with an uranium atom in the inner N₂O₂ site or very strongly folded with an uranium atom bound to the outer O₄ site, with further bridging in both cases [2]. Salmon et al. described also heterodinuclear Cu^{II}/Ni^{II}–U^{IV} anionic complexes [Hpy][CuL⁵(py)UCl₃] and [Hpy][NiL⁵(py)UCl₃], respectively. Results of X-ray analysis show that 3d transition metal ions occupy the smaller N₂O₂ cavity of the Schiff base ligand whereas uranium atoms place the bigger O₄ one. The copper(II)/nickel(II) and uranium(IV) ions are bridged by the two oxygen atoms of the salicylidene fragments [3]. **H₄hamp** was also used by Ephritikhine, Girerd et al. for the synthesis of heterotrinnuclear 3d–5f–3d

complexes of the general formula [{ML(py)}₂U] (M = Co, Ni, Zn) or [{CuL(py)}M'CuL] (M' = U, Th, Zr). In the series of obtained complexes a weak antiferromagnetic coupling was observed between the Ni(II) and the U(IV) ions, while a ferromagnetic interaction was revealed between the Cu(II) and U(IV) ions [4,5]. Chaudhury et al. reported a rare type of all-oxido heterotrimetallic compound [L³{(Re^VO)(OCH₃)}{(V^VO)(OCH₃)(μ-OCH₃)₂}. In its crystal structure the smaller N₂O₂ compartment of the hexadentate Schiff base ligand is occupied by rhenium(V) whereas two vanadium(V) centres are accommodated in the more flexible and larger O₄ compartment. The solvent CH₃OH plays a crucial role as it supplies the –OCH₃ donor groups, both bridging and monodentate, to stabilize vanadium in the +5 oxidation state [6].

Herein we report syntheses, structures, spectroscopic, thermal and magnetic properties of the new heterotrinnuclear complexes [Cu₂La(H₂hamp)₂(NO₃)₂H₂O]NO₃·6MeOH (**1**), [Cu₂Pr(H₂hamp)₂(NO₃)₃]·6MeOH (**2**), [Cu₂Nd(H₂hamp)₂(NO₃)(MeOH)₂](NO₃)₂·H₂O (**3**) with the N₂O₄ Schiff base compartmental ligand *N,N'*-bis(2,3-dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane (**H₄hamp**).

2. Experimental

2.1. Materials

The chemicals: 2,3-dihydroxybenzaldehyde, 2,2-dimethyl-1,3-propanediamine, Cu(CH₃COO)₂·H₂O, La(NO₃)₃·6H₂O, Pr(NO₃)₃·5H₂O,

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$\text{Nd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and CH_3OH (solvent) were of analytical reagent grade. They were purchased from commercial sources and used as received without further purification.

2.2. Synthesis of the **H₄hamp**

The Schiff base ligand ($\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$) was synthesized by the 2:1 condensation reaction between 2,3-dihydroxybenzaldehyde (1.38 g, 10 mmol) and 2,2-dimethyl-1,3-propanediamine (0.51 g, 5 mmol) in hot methanol (50 ml) following the procedure reported in the literature [7,8]. The compound was separated as orange needles and recrystallized twice from methanol. The empirical formula and the molecular weight are $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_4$ and 342.00 g/mol respectively. Yield 84%. Analytical data (%), Calcd: C, 66.60; H, 6.43; N, 8.19. Found: C, 66.50; H, 6.30; N, 8.10.

2.2.1. General procedure of preparation of complexes

The heterotrinary compounds **1**, **2** and **3** were prepared as follows: the solution of copper(II) acetate ($\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ 0.4 mmol, 0.0799 g) in methanol (10 mL) was added dropwise to the stirred solution of **H₄hamp** (0.4 mmol, 0.1368 g) in methanol (20 mL) to produce a green coloured mixture. The reaction mixture was stirred for 30 min at 45 °C. Next, the freshly prepared solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0860 g), $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0870 g) or $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0877 g) in methanol (5 mL) was added slowly to the mixture with constant stirring and the resulting deep green solution was stirred for another 30 min. A small amount of precipitate that appeared was filtered off. Green single crystals suitable for X-ray diffraction analysis were formed at 4 °C (in a refrigerator) after several weeks.

2.2.1.1. $[\text{Cu}_2\text{La}(\text{H}_2\text{hamp})_2(\text{NO}_3)_2\text{H}_2\text{O}]\text{NO}_3 \cdot 6\text{MeOH}$ (**1**). The empirical formula and the molecular weight are $\text{C}_{44}\text{H}_{66}\text{N}_7\text{O}_{24}\text{Cu}_2\text{La}$ and 1343.04 g/mol, respectively. Yield 29%. Analytical data (%), Calcd: C, 38.33; H, 4.71; N, 7.45; Cu, 9.67; La, 10.56. Found: C, 38.10; H, 4.60; N, 7.20; Cu, 9.50; La, 10.20.

2.2.1.2. $[\text{Cu}_2\text{Pr}(\text{H}_2\text{hamp})_2(\text{NO}_3)_3] \cdot 6\text{MeOH}$ (**2**). The empirical formula and the molecular weight are $\text{C}_{44}\text{H}_{64}\text{Cu}_2\text{N}_7\text{O}_{23}\text{Pr}$ and 1327.03 g/mol respectively. Yield 24%. Analytical data (%), Calcd: C, 39.79; H, 4.82; N, 7.38; Cu, 9.58; Pr, 10.62. Found: C, 39.80; H, 4.60; N, 7.10; Cu, 9.30; Pr, 10.40.

2.2.1.3. $[\text{Cu}_2\text{Nd}(\text{H}_2\text{hamp})_2(\text{NO}_3)(\text{MeOH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**3**). The empirical formula and the molecular weight are $\text{C}_{40}\text{H}_{50}\text{Cu}_2\text{NdN}_7\text{O}_{20}$ and 1220.21 g/mol, respectively. Yield 26%. Analytical data (%), Calcd: C, 39.34; H, 4.10; N, 8.03; Cu, 10.42; Nd, 11.82. Found: C, 39.80; H, 4.15; N, 7.90; Cu, 10.20; Nd, 11.60.

2.3. Methods

The contents of carbon, hydrogen and nitrogen in the complexes were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser. The contents of copper and lanthanides were established using ED XRF spectrophotometer (Canberra-Packard). The FTIR spectra of compounds were recorded over the range of 4000–400 cm^{-1} using M-80 spectrophotometer (Carl Zeiss Jena). Samples for FTIR spectra measurements were prepared as KBr discs. Thermal analyses of complexes **1**, **2** and **3** and the **H₄hamp** were carried out by the thermogravimetric (TG) and differential scanning calorimetry (DSC) methods using the SETSYS 16/18 analyser (Setaram). The experiments were carried out under air flow in the temperature range of 20–1000 °C (compounds) and 20–700 °C (Schiff base) at a heating rate of 10 °C min^{-1} . The samples 7.68 mg (**1**), 7.79 mg (**2**), 7.67 mg (**3**) and 7.54 mg (**H₄hamp**) were heated in Al_2O_3 crucibles. The TG–FTIR of the title compounds was recorded using the TGA

Q5000 analyzer TA Instruments, New Castle, Delaware, USA, interfaced to the Nicolet 6700 FTIR spectrophotometer (Thermo Scientific). The complex samples were put in an open platinum crucible and heated from ambient temperature to 1000 °C. The analysis was carried out at a heating rate of 20 °C min^{-1} under nitrogen at flow rate of 20 mL min^{-1} . To reduce the possibility of gasses condensing along the transfer line, the temperature in the gas cell and transfer line was set to 250 and 240 °C, respectively. Gas analysis was performed by matching the spectra against those from the spectrum library Nicolet TGA Vapor Phase of the software Ominic together with the literature sources. The X-ray powder diffraction patterns of the products of decomposition process were collected at room temperature on an Empyrean PANanalytical automated powder diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54187 \text{ \AA}$) over the scattering angular range $2\theta = 20\text{--}120^\circ$. Magnetic susceptibility measurements were performed on finely ground crystalline samples over the temperature range 1.8–300 K at magnetic field 0.1 T using a Quantum Design SQUID-VSM magnetometer. Field dependences of magnetization were measured at 2 K in an applied field up to 5 T. Corrections are based on subtracting the sample – holder signal and contribution χ_D estimated from the Pascal's constants [9,10].

2.4. X-ray crystal structure determination

The X-ray diffraction intensities for **H₄hamp** were collected at 100 K on Oxford Diffraction Xcalibur CCD diffractometer with the graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal data for **1–3** were collected at 120 K on SuperNova X-ray diffractometer equipped with Atlas S2 CCD detector using the mirror-monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). All data were collected using the ω scan technique, with an angular scan width of 1.0°. The programs CrysAlis CCD, CrysAlis Red and CrysAlisPro [11,12] were used for data collection, cell refinement and data reduction. The structures were solved by direct methods using SHELXS-2013 and SHELXS-97 and refined by the full matrix least-squares on F^2 using SHELXL-2013 [13] implemented in the WinGX software package [14] and SHELXL-97 implemented in OLEX2 [15]. All non-hydrogen atoms with except of the two disordered nitrate N and O atoms in complexes were refined with anisotropic displacement parameters. The hydrogen atoms residing on carbon atoms were positioned geometrically and refined applying the riding model [$\text{C–H} = 0.93\text{--}0.97 \text{ \AA}$ and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5 U_{\text{eq}}(\text{C})$]. The hydrogen atom at one of the hydroxyl group in **H₄hamp** is disordered over two positions: at O3 and N2 atoms. They were located in the difference Fourier map and then refined using riding model (with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ or $1.2 U_{\text{eq}}(\text{N})$). The other hydrogen linked to O and N atoms in **H₄hamp** were also found from the difference Fourier map and refined isotropically. Some of methanol and water molecules in **1–3** were refined isotropically, as well as the disordered nitrate ion in the crystal **3**. The disorder is over two positions around inversion center with sof's being 0.5. The crystallographic and refinement data for this compound are summarized in the Tables 1 and S1 (Supplementary materials).

3. Result and discussion

3.1. Infrared spectra

In order to obtain some information about binding mode of the N_2O_4 -donor ligand to Cu(II) and Ln(III) ions the FTIR spectra of the complexes **1–3** were compared with the spectrum of the free Schiff base (**H₄hamp**) (Table 2). All heterotrinary coordination compounds show similar FTIR spectral features exhibiting a strong band at 1620 cm^{-1} attributable to $\nu(\text{C}=\text{N}_{\text{imine}})$, which is shifted 20 cm^{-1} lower than that in the spectrum of the **H₄hamp** ligand,

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