Polyhedron 144 (2018) 225-233

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

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



^a Department of General and Coordination Chemistry, Maria Curie-Sklodowska University, Maria Curie-Sklodowska sq. 2, 20-031 Lublin, Poland ^b Department of Crystallography, Maria Curie-Sklodowska University, Maria Curie-Sklodowska sq. 3, 20-031 Lublin, Poland

ARTICLE INFO

Article history: Received 21 November 2017 Accepted 23 January 2018

Keywords: Schiff base N₂O₄-donor ligand Heterotrinuclear complex Phenoxo bridge 3d–4f complex

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 $[U_4(L_2)_2(H_2L_2)_2(py)_2O]$ [CF₃SO₃]₂ reported by Salmon et al. that contains a U_4 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 O_4 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 heterotrinuclear 3d-5f-3d

ABSTRACT

New heterotrinuclear complexes $[Cu_2La(H_2hamp)_2(NO_3)_2H_2O]NO_3 \cdot 6MeOH$ (1), $[Cu_2Pr(H_2hamp)_2(NO_3)_3]$. 6MeOH (2), $[Cu_2Nd(H_2hamp)_2(NO_3)(MeOH)_2](NO_3)_2\cdot H_2O$ (3) where H_2hamp 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 $P2_1/n$. 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.

© 2018 Elsevier Ltd. All rights reserved.

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 $[L^3((Re^VO)(OCH_3))\{(V^VO)(OCH_3)(\mu-OCH_3)\}_2]$. 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 heterotrinuclear complexes $[Cu_2La(H_2hamp)_2(NO_3)_2H_2O]NO_3\cdot 6MeOH$ (1), $[Cu_2Pr(H_2hamp)_2(NO_3)_3]\cdot 6MeOH$ (2), $[Cu_2Nd(H_2hamp)_2(NO_3)(MeOH)_2](NO_3)_2\cdot H_2O$ (3) with the N₂O₄ Schiff base compartmental ligand *N*,*N*'-bis(2,3dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane (**H_4hamp**).

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,





Check fo

^{*} Corresponding author. E-mail address: beata.cristovao@poczta.umcs.lublin.pl (B. Cristóvão).

 $Nd(NO_3)_3 \cdot 5H_2O$ 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 ($C_{19}H_{22}N_2O_4$) 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 $C_{19}H_{22}N_2O_4$ 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 heterotrinuclear compounds **1**, **2** and **3** were prepared as follows: the solution of copper(II) acetate (Cu(OAc)₂·H₂O 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 La (NO₃)₃·6H₂O (0.2 mmol, 0.0860 g), Pr(NO₃)₃·6H₂O (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. $[Cu_2La(H_2hamp)_2(NO_3)_2H_2O]NO_3 \cdot 6MeOH$ (1). The empirical formula and the molecular weight are $C_{44}H_{66}N_7O_{24}Cu_2La$ 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. $[Cu_2Pr(H_2hamp)_2(NO_3)_3]$ ·6MeOH (**2**). The empirical formula and the molecular weight are $C_{44}H_{64}Cu_2N_7O_{23}Pr$ 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. $[Cu_2Nd(H_2hamp)_2(NO_3)(MeOH)_2](NO_3)_2 \cdot H_2O(3)$. The empirical formula and the molecular weight are $C_{40}H_{50}Cu_2NdN_7O_{20}$ 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 **H**₄**hamp** 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 (**H**₄**hamp**) were heated in Al₂O₃ 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 CuK α radiation ($\lambda \alpha$ = 1.54187 Å) over the scattering angular range $2\theta = 20-120^\circ$. 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 $\gamma_{\rm D}$ 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 MoK α radiation (λ = 0.71073 Å). Crystal data for 1-3 were collected at 120 K on SuperNova X-ray diffractometer equipped with Atlas S2 CCD detector using the mirrormonochromatized CuK α radiation (λ = 1.54184 Å). 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 leastsquares 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 [C—H = 0.93–0.97 Å and with $U_{iso}(H) = 1.2$ or 1.5 $U_{eq}(C)$]. The hydrogen atom at one of the hyrdroxyl group in **H**₄hamp 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 $U_{iso}(H) = 1.5 U_{eq}(O)$ or 1.2 $U_{eq}(N)$). 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 N₂O₄-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 (**H**₄**hamp**) (Table 2). All heterotrinuclear coordination compounds show similar FTIR spectral features exhibiting a strong band at 1620 cm⁻¹ attributable to $v(C=N_{imine})$, which is shifted 20 cm⁻¹ lower than that in the spectrum of the **H**₄**hamp** ligand,

Table 1	
Crystal data and structure refinement details for 1-3.	

Identification code	1	2	3
Empirical formula	C44H66N7O24Cu2La	C44H64N7O23Cu2Pr	C40H50N7O20Cu2Nd
Formula weight	1343.04	1327.03	1220.21
T (K)	120.0(1)	120.0(1)	120.0(1)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	13.1508(4)	13.1445(4)	14.9951(5)
b (Å)	20.1662(6)	20.2259(6)	17.8574(6)
<i>c</i> (Å)	21.4930(9)	21.4443(7)	18.2642(6)
β (°)	104.022(4)	104.175(3)	103.726(3)
$V(\text{\AA})^3$	5530.2(3)	5527.6(3)	4751.0(3)
Ζ	4	4	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^3)$	1.6130	1.5945	1.7058
$\mu (\mathrm{mm}^{-1})$	7.503	8.275	9.989
F(000)	2732.2	2695.4	2447.7
Crystal size (mm)	$0.35 \times 0.22 \times 0.2$	$0.35\times0.28\times0.25$	$0.3\times0.25\times0.08$
Reflections collected	68078	37633	33684
Independent reflections	9673 [R _{int} = 0.0757, R _{sigma} = 0.0333]	9980 [<i>R</i> _{int} = 0.0802, <i>R</i> _{sigma} = 0.0583]	9822 [<i>R</i> _{int} = 0.0768, <i>R</i> _{sigma} = 0.0611]
Data/restraints/parameters	9673/7/717	9980/4/705	9822/13/647
Goodness-of-fit on F^2	1.048	1.034	1.032
Final R indexes $[I > 2\sigma(I)]$	$R_1 = 0.0417$, $wR_2 = 0.1075$	$R_1 = 0.0523, wR_2 = 0.1385$	$R_1 = 0.0601$, $wR_2 = 0.1609$
Final R indexes [all data]	$R_1 = 0.0436, wR_2 = 0.1101$	$R_1 = 0.0581$, $wR_2 = 0.1455$	$R_1 = 0.0728$, $wR_2 = 0.1809$
Largest difference in peak and hole (e $Å^{-3}$)	1.74/-1.13	1.69/-1.27	2.40/-1.92
CCDC No.	1584666	1584667	1584669

(1640 cm⁻¹). It indicates a decrease in the C=N bond order due to the coordinate bond formation between the Cu(II) ion and the imine nitrogen lone pair of the Schiff base [16–20]. The strong peak characteristic of phenolic v(C-O) stretching vibration band observed at 1240 cm⁻¹ for the **H**₄hamp is observed as a doublet in the FTIR spectra of complexes 1–3 and occurs at 1256 and 1220 cm⁻¹, indicating the involvement of the phenolic oxygen atoms in the metal-ligand bonding [19,21]. The bands attributed to asymmetric and symmetric stretching vibrations of the methyl group, $v(CH_3)$ are presented at around 2960 cm⁻¹ and 2860 cm⁻¹. In the FTIR spectra of **1–3** the characteristic frequencies of nitrate groups acting as mono- and bidentate ligands overlap and occur

at about 1468 cm⁻¹, 1312–1304 cm⁻¹, 1096 cm⁻¹ and 784 cm⁻¹ [22]. The presence of a broad band at about 3400 cm⁻¹ characteristic of v(O–H) stretching vibrations is associated with coordinated and/or solvated water/methanol molecules, but unfortunately it interferes with the observation of protonated hydroxyl groups of the organic ligand [8,16–20].

3.2. Crystal and molecular structure

The slow crystallization of the **H**₄**hamp** from methanol resulted in formation of crystals suitable for X-ray structural analysis. Its molecular structure is displayed in Fig. 1. The structure of N_i .

Table 2 Selected spectroscopic data of the H_4 hamp, $Cu^{II}-La^{II}-Cu^{II}$ (1), $Cu^{II}-Pr^{III}-Cu^{II}$ (2) and $Cu^{II}-Nd^{III}-Cu^{II}$ (3).

H₄hamp	1	2	3	Proposed assignments
-	3424 m	3432 w	3436 w	v(O-H) + v(C-H)
3204 m	-	-	-	$v(O-H) \leftrightarrow v(N-H)$
_	2956 w	2960 w	2956 w	$v(CH_3)_{as}$
_	-	-	2860 w	$v(CH_3)_s$
1640 vs	1620 vs	1620 vs	1620 vs	v(C=N)
1548 m	1568 m	1568 m	1568 m	v(C=C)
1464 s	1468 vs	1468 s	1468 s	$v(C=C) + v(N=O)_{comp.}$
1384 m	1384 s	1384 w	1384 s	sc(C-H) + v(CCC))
1352 m	-	-	-	δ(O —H)
_	1308 s	1312 s	1304 s	$v(C-N) + \omega(C-H) + v(N-O)$
_	1256 s	1256 s	1256 s	v(C-O)
1240 vs	1220 s	1220 s	1220 m	$v(C-O) + \delta(O-H)$
1184 vs	1168 w	1168 w	1168 w	v (C-C) + tw(C-H)
1080 w	1096 w	1096 w	1096 w	$\delta (C-H) + v(N-O)$
1056 w	1048 w	1044 w	1048 w	skeletal
-	972 w	972 w	-	$\rho(C-H) + CH_2 + \delta(CCC)$
896 w	-	-	-	γ(O —H)
848 m	864 m	864 m	864 m	$\delta(C-N=C)$
784 w	784 w	784 w	784 w	γ (C—H) + ν (N—O)
740 vs	740 s	740 s	740 s	γ(C — H)
644 w	648 m	648 m	628 w	δ (C=C) + ring deform.
612 w	620 w	620 w	612 w	ring deform.
_	532 w	536 w	536 w	v(M-O)
	-	-	524 w	γ(C — H)
500 w	496 m	500 s	504 w	γ(C—H)
-	364 w	364 w	364 w	v(M—N)

vs - very strong, s - strong, m - medium, w - weak, br - broad, v - stretching, δ - deformation in plane, sc - scissoring, ω - waggining, tw - twisting, ρ - rocking, γ - deformation out of plane, as - asymmetric, sym - symmetric.



Fig. 1. ORTEP view with the atom numbering scheme of H_4 hamp. Displacement ellipsoids are drawn at the 30% probability level. The site-occupation factors of the disordered H atom is 0.58(6) at hydroxy O3 atom and 0.42(6) at N2 atom.

bis(2,3-dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane has been previously reported by Aguiari et al. [7] and Bermejo et al. [8]. Both X-ray measurements of single crystals were made at room temperature. Aguiari and co-workers synthesized crystals of H₄hamp where one half contained a protonated nitrogen atom (zwitterionic form) whereas in the second dihydroxybenzaldimine moiety the hydrogen atom was located on the oxygen atom. The C-N distances are practically identical (Table S2) and indicates double character of these bonds [7]. The compound described by Bermejo and co-workers crystallizes in the phenol-imine/ketoamine form [8]. The X-ray analysis of **H**₄**hamp** prepared by us was performed at 100 K. Similar to previously described structures the N₂O₄-ligand has a non-planar conformation. The dihedral angles between the plane formed by two aromatic rings (C1–C6/ C14–C19) is 47.6(1)°. The C7–N1 (1.296(3)Å) and C2–O1 (1.295 (2) Å) lengths have intermediate values between single and double C-O (1.362 Å and 1.222 Å) and C-N (1.339 and 1.279 Å) bond distance [23]. The shortened C2–O1 distance and the slightly longer C7-N2 bond indicates that in this half of the molecule the stabilization of the zwitterionic form occurs. The similar value of related bonds for the zwitterionic forms of Schiff base was reported earlier [24–27]. In the second dihydroxybenzaldimine moiety the N2–C13 and C15–O3 bonds are equal to 1.283(3) and 1.336(3) Å, respectively. This can indicate that the hydrogen atom is delocalized between the two positions, i.e., partly bound to oxygen and nitrogen atoms (Fig. S1). The position of hydroxyl and amine H-atom was determined from the difference Fourier map and their occupancies were refined complementarily. The site occupancy factors for H atoms attached to O3/N2 atoms were 0.58(6)/0.42(6).

Single-crystal X-ray studies of the coordination compounds **1–3** revealed that $[Cu_2La(H_2hamp)_2(NO_3)_2H_2O]NO_3 \cdot 6MeOH$ (**1**), $[Cu_2Pr(H_2hamp)_2(NO_3)_3] \cdot 6MeOH$ (**2**), $[Cu_2Nd(H_2hamp)_2(NO_3)(MeOH)_2]$ (NO₃)₂·H₂O (**3**) where H₂hamp = C₁₉H₂₀N₂O₄ is a dianion of *N*,*N'*-bis(2,3-dihydroxybenzylidene)-1,3-diamino-2,2-dimethylpropane crystallize in the monoclinic space group *P*2₁/*n*. Details for the structure solution and refinement are summarized in Table 1. The selected bond distances and angles are listed in Tables 3 and 4. Although compounds **1–3** crystallize in the same space group and the crystal unit cell dimensions are similar they are not

isostructural. The main differences between **1**. **2** and **3** originate in the nature of the polynuclear species (cationic (1, 3) versus neutral (2)), the kind and amount of solvent molecules in the outer coordination sphere and the type of ligands coordinated to copper(II). The structures of 1-3 presented in Figs. 2-4 show the that the coordination modes of the Schiff base ligands toward the lanthanide(III) and copper(II) ions are the same. The central Ln^{III} ion is surrounded by two Cu(H₂hamp) units, so that the Ln^{III} and Cu^{II} ions are linked by phenoxido bridging groups. In the all complexes 1-3 the Ln^{III} ion is ten-coordinated by eight atoms originated from two H₂hamp ligands and two O atoms coming from the bidentate (η^2 -chelating) nitrate ion (Fig. S2). The external hydroxyl groups of the Schiff base ligands closing the outer compartment O₂O₂ are undeprotonated and they are involved in the intra- and intermolecular hydrogen bonds (Table S3). The Ln–O bond lengths vary from *ca*. 2.47 Å for phenoxy groups presented inside the coordination cavity of the Schiff base ligand, through the protonated hydroxy groups closing this compartment up to ca. 2.68 Å for less coordinated nitrate groups (Table 3). The fivecoordinated Cu^{II} ions are in a square pyramidal environment, the N₂O₂ atoms of the Schiff base ligands defining the basal plane with the Cu–N and Cu–O bond distances in the range of 1.957(5)–1.997 (3) Å and 1.923(3)-1.979(3) Å, respectively (Table 3) while oxygen atoms coming from different species: aqua and nitrate ion (1). nitrate ions (2) and methanol molecules (3), respectively occupy the apical position (Fig. S2). The intramolecular separations Cu1...Ln1/Cu2...Ln1 and Cu1...Cu1/Cu2...Cu2 are within the normal range of values for similar heteronuclear Cu^{II}–Ln^{III} complexes, being *ca.* 3.62–3.68 Å and 7.11–7.18 Å, respectively [28–35].

In order to check the influence of the kind of substituents in the benzene ring on the structure and properties of the coordination compounds some structural parameters (Cu—N, Cu—O_{phen}, Ln—O_{phen}, Ln—O_{hydroxy}, Cu…Ln) of the obtained complexes **1–3** with **H**₄**hamp** were compared with ones (Cu—N, Cu—O_{phen}, Ln—O_{phen}, Ln—O_{methoxy/ethoxy}, Cu…Ln) of chosen heteronuclear Cu^{II}—Ln^{III} compounds synthesised with *N*,*N*'-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diamino-2,2-dimethylpropane (Tables 3 and S4). The aforementioned ligands are

Table 3
Bond lengths and selected intramolecular distances for crystals 1-3.

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
1			2			3		
La1	01	2.520(3)	Pr1	01	2.479(3)	Nd1	01	2.478(4)
La1	02	2.548(3)	Pr1	02	2.514(3)	Nd1	02	2.474(4)
La1	03	2.572(3)	Pr1	03	2.526(4)	Nd1	03	2.526(4)
La1	04	2.595(3)	Pr1	04	2.498(4)	Nd1	04	2.489(4)
La1	05	2.520(3)	Pr1	05	2.492(3)	Nd1	05	2.525(4)
La1	06	2.552(2)	Pr1	06	2.518(3)	Nd1	06	2.473(4)
La1	07	2.569(3)	Pr1	07	2.535(3)	Nd1	07	2.539(4)
La1	08	2.521(3)	Pr1	08	2.560(4)	Nd1	08	2.496(4)
La1	09	2.654(3)	Pr1	09	2.627(4)	Nd1	09	2.665(5)
La1	010	2.677(3)	Pr1	010	2.619(4)	Nd1	010	2.555(5)
Cu1	01	1.930(3)	Cu1	01	1.979(3)	Cu1	01	1.926(5)
Cu1	02	1.963(3)	Cu1	02	1.942(3)	Cu1	02	1.951(4)
Cu1	N1	1.987(3)	Cu1	N2	1.990(4)	Cu1	N1	1.974(6)
Cu1	N2	1.968(3)	Cu1	N1	1.979(4)	Cu1	N2	1.969(6)
Cu1	020	2.736(5)	Cu1	014	2.432(3)	Cu1	012	2.771(6)
Cu2	05	1.979(3)	Cu2	05	1.923(3)	Cu2	05	1.963(4)
Cu2	06	1.944(3)	Cu2	06	1.960(3)	Cu2	06	1.924(4)
Cu2	N3	1.982(3)	Cu2	N3	1.982(4)	Cu2	N3	1.957(5)
Cu2	N4	1.997(3)	Cu2	N4	1.962(4)	Cu2	N4	1.975(6)
Cu2	015	2.449(3)	Cu2	020	2.785(4)	Cu2	013	2.680(6)
Cu1	La1	3.6679(6)	Cu1	Pr1	3.6393(7)	Cu1	Nd1	3.617(1)
Cu2	La1	3.6776(5)	Cu2	Pr1	3.6403(6)	Cu2	Nd1	3.635(1)

Table 4

Bond angles for 1-3.

Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
1				2				3			
Cu1	01	La1	110.3(1)	Cu1	01	Pr1	108.9(1)	Cu1	01	Nd1	109.8(2)
Cu1	02	La1	108.1(1)	Cu1	02	Pr1	108.8(1)	Cu1	02	Nd1	109.1(2)
Cu2	05	La1	109.1(1)	Cu2	06	Pr1	108.2(1)	Cu2	05	Nd1	107.5(2)
Cu2	06	La1	109.0(1)	Cu2	05	Pr1	110.4(1)	Cu2	06	Nd1	110.9(2)



Fig. 2. Molecular structure with atom numbering scheme of Cu^{II}-La^{III}-Cu^{II} (1). The outer coordination sphere solvent molecules were omitted for clarity.

differentiated by the presence in benzene ring the various substituent at the *meta* position (–OH or –OCH₃/–OC₂H₅). As shown in the Scheme 1 and in the Table S4 all compared complexes consist of diphenoxo-bridged heterometallic cores in which 3d metal ion is situated in the smaller N₂O₂ compartment of the Schiff base ligand, while the 4f ion is present in the larger and open O₂O₂ [O(phenoxo)2 O(methoxy/ethoxy/hydroxy)2] one. The Cu–N and Cu–Ophen bond distances are similar and range from 1.92 to 1.99 Å (complexes 1–3) and from 1.95 to 2.00 Å (compounds placed in the Table S4). The Ln—O_{phen} bond distances from the phenolato oxygen atoms range from 2.47 to 2.55 Å (complexes **1–3**) and from 2.33 to 2.43 Å (compounds placed in the Table S4) are shorter than those from the hydroxy/meth-oxy/ethoxy oxygens Ln—O_{hydroxy/methoxy/ethoxy} range from 2.49 to 2.60 Å (complexes **1–3**) and 2.43 to 2.65 Å (compounds placed in the Table S4), respectively. The intramolecular separation Cu…Ln is ~3.62–3.68 Å (complexes **1–3**) and ~3.44–3.52 Å (compounds placed



Fig. 3. Molecular structure with atom numbering scheme of Cu^{II}-Pr^{III}-Cu^{II} (2). The outer coordination sphere solvent molecules were omitted for clarity.



Fig. 4. Molecular structure with atom numbering scheme of Cu^{II}–Nd^{III}–Cu^{II} (3). The outer coordination sphere solvent molecules were omitted for clarity.

in the Table S4). In the benzene ring the hydroxy as well as aloxy groups are electron donating substituents so they have similar influence on the structural parameters of the compared complexes. The structure of Cu^{II}–Ln^{III} coordination compounds depends also on the oxophilicity of the lanthanides(III), the preference of the copper(II) ion for nitrogen atoms, the degree of deprotonation of the ligands, the stoichiometry of the used reagents, kind of used solvents etc. In the analysed complexes nitrato anions contributing to the electroneutrality and also to the completion of the coordination sphere of the 4f and 3d metal ions as a monodentate or a bidentate chelating ligand [28–35].

3.3. Thermal properties

In order to examine the thermal behaviour and the stability of the **H**₄**hamp** and Cu^{II}–Ln^{III}–Cu^{II} coordination compounds **1–3** the TG, DTG and DSC curves were recorded in air atmosphere. The N₂O₄-donor ligand is stable up to 170 °C (Fig. S3). During further heating of the sample an endothermic effect is observed on the DSC curve. This effect is connected with the negligible mass loss,

which is characteristic of the melting process. The melting point observed on the DSC curve is about 175 °C and the enthalpy of fusion equals 27.75 kJ mol⁻¹. The DSC peak is sharp which indicates that the ligand is a crystalline, pure substance. As shown in Fig. 5 and Figs. S4–S6 the complexes 1–3 are stable at room temperature. The recorded TG curves of 1-3 display very similar mass loss patterns. The samples of compounds 1-3 during heating up to ca. 190 °C undergo desolvation process. The complex 1 in the first step loses one methanol and water molecules (mass loss found 3.20%, calculated 3.70%) while the second one is mainly related to the further partial release of methanol molecules (ca. two molecules). The remaining solvents are removed together with nitrate ions above 200 °C. In the case of the compound **2** the first mass loss 9.40% corresponds to the loss of four methanol molecules per formula unit (calculated 9.40%). Similarly to the complex 1, the two methanol molecules are removed at higher temperature (above 200 °C) together with nitrate ions. Overall found mass loss for six methanol molecules and three nitrate ions is 29.00% whereas the calculated one is equal to 28.50%. During the heating of 3 the two-step desolvation process connected with loss molecules of



Scheme 1. Schematic representation of the synthesis and structural units of the diphenoxo bridged Cu^{II}-Ln^{III}-Cu^{II} complexes.



Fig. 5. TG curves of thermal decomposition of complexes 1-3 in air.

methanol and water is observed (overall mass loss found 8.50%, calculated 8.20%). These results are also confirmed by the TG-FTIR analysis. The recorded FTIR spectra of evolved gas phase for the complexes **1–3** (Figs. 6 and S7, S8) show that water and methanol are the main products released during this stage. The characteristic vibration bands in the wavenumber ranges 4000–3400 cm⁻¹ and 2060–1260 cm⁻¹ correspond to stretching and deforming vibrations of H₂O molecules, whereas the bands associated with the presence of CH₃OH are observed at 3368 cm⁻¹, 1307 cm⁻¹ and 1095 cm⁻¹, respectively [19]. The desolvation process of the compounds **1–3** is accompanied with small endothermic effect seen on

the DSC curves with the maximum at ~98 °C (1), ~112 °C (2), ~106 °C and ~136 °C (3). The values of the enthalpy of the above processes are 58.79 kJ mol⁻¹ (1), 105.08 kJ mol⁻¹ (2) and 76.85 kJ mol⁻¹ (3), respectively. The decomposition process of the Cu^{II}– Ln^{III}–Cu^{II} complexes 1–3 is intricate and it was not possible to distinguish intermediate solid products. The final products (mixtures of metal oxides CuO and CuLn₂O₄ Ln = La, Pr, Nd) obtained during thermal decomposition of 1–3 in air were calculated from TG curves and experimentally verified by X-ray diffraction powder patterns. The percentages 24.50% (1), 25.50% (2), 25.90% (3) calculated from TG curves at about 700 °C are coincide fairly with the theoretical values 25.42% (1), 24.82% (2), 26.82% (3).

3.4. Magnetic properties

The magnetic properties of heteronuclear $Cu^{II}-Ln^{III}$ compounds are governed by three factors: the thermal population of the Stark components of Ln^{III} , the $Cu^{II}\cdots Cu^{II}$ interactions (including intermolecular interaction) and the $Cu^{II}\cdots Ln^{III}$ interactions. Temperature-dependent molar susceptibility measurements of randomly oriented crystalline samples of $Cu^{II}-La^{III}-Cu^{II}$ (1), $Cu^{II}-Nd^{III}-Cu^{II}$ (2) and $Cu^{II}-Pr^{III}-Cu^{II}$ (3) were carried out in an applied magnetic field of 0.1 T over the temperature range 1.8–300 K. The Fig. 7 shows the $\chi_M T$ and χ_M^{-1} versus T plots (χ_M is the molar magnetic susceptibility and T is the absolute temperature). At a high temperature region, the $\chi_M T$ value approached the theoretical values.

For Cu^{II}–La^{III}–Cu^{II} (1) the experimental $\chi_M T$ is equal to 0.730 cm³ mol⁻¹ K at 300 K. This value is close to the theoretically calculated one 0.750 cm³ mol⁻¹ K by the Eq. (1) for two uncorrelated Cu^{II} (3 d^9 , $S = \frac{1}{2}$) ions, since no contribution is expected from the nonmagnetic La^{III} ion (4 f^0 , S = 0).



Fig. 6. FTIR spectra of gaseous products evolved during the desolvation process of 1 recorded at 83, 163 and 196 °C.

)

$$\chi_{M}T = (N\beta^{2}/3k)2g_{Cu}^{2}S_{Cu}(S_{Cu}+1)$$
(1)

where N is Avogadro constant, β is the Bohr magneton and k is Boltzman's constant.

As the temperature decreases the $\chi_M T$ product remains almost unchanged in magnitude until 1.8 K. In **1** the intramolecular Cu1...Cu2 distance of 7,1813(8) Å is relatively large and may preclude any significant magnetic interactions between the copper centers in the heterotrinuclear unit. The magnetization versus field curve of **1** at 2 K is depicted in Fig. 8. The measurement shows a saturation value of *ca.* 1.9 μ_B , which is the expected value for two independent *S* = 1/2 system with *g* = 2.

In the case of **2** the experimental value of $\chi_M T$ at room temperature equal to 2.23 cm³ mol⁻¹ K corresponds to the value 2.35 cm³ mol⁻¹ K theoretically calculated (Eq. (2)) for one Pr^{III} (4 f^2 , J = 4, S = 1, L = 5, ³H₄) and two Cu^{II} (3 d^9 , $S = \frac{1}{2}$) isolated paramagnetic metal ions.



Fig. 7. Temperature dependence of experimental $\chi_M T$ and χ_M^{-1} versus T for $Cu^{II}-La^{III}-Cu^{II}$ (1) $Cu^{II}-Pr^{III}-Cu^{II}$ (2) and $Cu^{II}-Nd^{III}-Cu^{II}$ (3).

$$\chi_{\rm M} T = ((N\beta^2/3k)[2g_{\rm Cu}^2S_{\rm Cu}(S_{\rm Cu}+1) + g_{\rm Ln}^2J_{\rm Ln}(J_{\rm Ln}+1)]) \tag{2}$$

where *N* is Avogadro constant, β is the Bohr magneton and *k* is Boltzman's constant. In this equation g_{Ln} is the *g* factor of the ground *J* terms of Ln^{III} and is expressed as:

$$g_{Ln} = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$
(3)

Similarly for **3** the experimental value 2.02 cm³ mol⁻¹ K at 300 K is close to the calculated value equal to 2.39 cm³ mol⁻¹ K (the equation (1)) for one Nd^{III} (4*f*³, *J* = 9/2, *S* = 3/2, *L* = 6, ⁴I_{9/2}) and two Cu^{II} (3*d*⁹, *S* = ½) noninteracting metal ions.



Fig. 8. Field dependence of the magnetization for complexes 1, 2 and 3 at 2 K.

As depicted in Fig. 7 the values of $\gamma_{\rm M}T$ decrease by lowering of temperature to $0.52 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **2** and $0.22 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **3**, respectively in 1.8 K. This decrease could be caused by crystal field effect, as well as the antiferromagnetic interactions between neighboring 3d and 4f metal ions. Unfortunately, the quantitative description of the magnetic properties of heterometallic complexes containing lanthanide(III) ions is not an easy task because of the ligand-field effect and spin-orbit coupling of the Ln^{III} ion [36,37]. To confirm the nature of the ground state of **2** and **3**, we investigated the variation of the magnetization, M, with respect to the field, at 2 K (Fig. 8). The compounds do not reach the saturation in the applied field range and magnetization in 5 T is equal to 1.90 μ_B for **2** and 1.00 μ_B for **3**. This further indicates that studied Cu¹¹₂Ln¹¹¹ systems display an antiferromagnetic coupling. In fact, this results are in good agreement with a theoretical model of Kahn [37] according to the Ln^{III} ions with $f^1 - f^6$ configurations should exhibit antiferromagnetic coupling.

4. Conclusion

The X-ray crystal structure analysis of **1–3** revealed that the coordination modes of the Schiff base ligands toward the lanthanide(III) and copper(II) ions are the same. In the Cu^{II}–Ln^{III}–Cu^{II} core the Ln(III) ion is ten-coordinated whereas the coordination number of copper(II) ions is equal to five. The main differences between **1**, **2** and **3** originate in the nature of the polynuclear species (cationic (**1**, **3**) versus neutral (**2**)), the kind and amount of solvent molecules in the outer coordination sphere and the type of ligands coordinated to copper(II). The desolvation process of **1–3** is consistent with the lose molecules of methanol and water (**1**, **3**) and only methanol (**2**). The interaction between neighboring Cu^{II} and Pr^{III}/Nd^{III} ions is antiferromagnetic.

Acknowledgements

The X-ray crystal structure determination of complexes 1–3 was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Operational Program Development of Eastern Poland 2007–2013 (Contract No. POPW.01.03.00-06-009/11-00, equipping the laboratories of the Faculties of Biology and Biotechnology, Mathematics, Physics and Informatics, and Chemistry for studies of biologically active substances and environmental samples).

Appendix A. Supplementary data

CCDC 1584666–1584669 contains the supplementary crystallographic data for **H**₄**hamp** and its complexes **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, 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. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.poly.2018.01.023.

References

- [1] A.F.H. Allen, Acta Crystallogr. Sect. B 58 (2002) 380.
- [2] L. Salmon, P. Thuéry, M. Ephritikhine, Polyhedron 25 (2006) 1537.
- [3] L. Salmon, P. Thuéry, M. Ephritikhine, Polyhedron 26 (2007) 645.
- [4] T. Le Borgne, E. Riviére, J. Marrot, J.-J. Girerd, M. Ephritikhine, Angew. Chem., Int. Ed. 39 (9) (2000) 1647.
- [5] T. Le Borgne, E. Riviére, J. Marrot, P. Thuéry, J.-J. Girerd, M. Ephritikhine, Chem. Eur. J. 8 (4) (2002) 773.
- [6] K. Bhattacharya, M. Maity, S.M.T. Abtab, M.C. Majee, M. Chaudhury, Inorg. Chem. 52 (2013) 9597.
- [7] A. Aguiari, E. Bulita, U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato, Inorg. Chim. Acta 202 (1982) 157.
- [8] M.R. Bermejo, M.I. Fernandez, E. Gomez-Forneas, A. Gonzalez-Noya, M. Maneiro, R. Pedrido, M.J. Rodriguez, Eur. J. Inorg. Chem. (2007) 3789.
- [9] O. Kahn, Molecular Magnetism, VCH Publishers Inc, New York, 1993.
- [10] G.A. Bain, J.F. Berr, J. Chem. Educ. 85 (2008) 532.
- [11] Oxford Diffraction Xcalibur CCD System, CRYSALIS Software System Version 1.171, Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK, 2009.
- [12] CrysAlisPro Software System, Version 1.171.37.34, Agilent Technologies, Oxford, UK, 2014.
- [13] M. Sheldrick, Acta Cryst. A 64 (2008) 112.
- [14] L.J. Faruggia, J. Appl. Crystallogr. 32 (1999) 837.
- [15] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H.J. Puschmann, Appl. Cryst. 42 (2009) 339.
- [16] G.-B. Li, X.-J. Hong, Z.-G. Gu, Z.-P. Zheng, Y.-Y. Wu, H.-Y. Jia, J. Liu, Y.-P. Cai, Inorg. Chim. Acta 392 (2012) 177.
- [17] A.-N.M.A. Alaghaz, B.A. El-Sayed, A.A. El-Henawy, R.A.A. Ammarb, J. Mol. Struct. 1035 (2013) 83.
- [18] R.K. Dubey, P. Baranwal, A.K. Jha, J. Coord. Chem. 65 (2012) 2645.
- [19] A. Bartyzel, J. Coord. Chem. 66 (2013) 4292.
- [20] A. Gutiérrez, M.F. Perpiñán, A.E. Sánchez, M.C. Torralba, V. González, Inorg. Chim. Acta 453 (2016) 169.
- [21] R. Takjoo, A. Hashemzadeh, H.A. Rudbari, F. Nicolò, J. Coord. Chem. 66 (2013) 345.
- [22] B. Cristóvão, J. Kłak, B. Miroslaw, J. Coord. Chem. 67 (2014) 2728.
- [23] F.H. Allen, O. Kennard, D.G. Watson, L.A. Brammer, G. Orpen, J. Chem. Soc. Perkin Trans., 2 (1987) S1.
- [24] A.A.B.C. Júnior, G.S.G. De Carvalho, L.F. Marques, C.C. Corrêa, A.D. Da Silva, F.C. Machado, Acta Cryst. C 69 (2013) 934–936.
- [25] K. Ouari, M. Merzouguia, L. Karmazin, Acta Cryst., E 71 (2015) 1010.
- [26] G. Alpaslan, M. Macit, A. Erdönmez, O. Büyükgüngör, J. Mol. Struct. 997 (2011) 70
- [27] A. Bartyzel, Polyhedron 134 (2017) 30.
- [28] T. Kajiwara, M. Nakano, K. Takahashi, S. Takaishi, M. Yamashita, Chem. Eur. J. 17 (2011) 196.
- [29] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, New J. Chem. 22 (1998) 1525.
- [30] J.P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 165.
- [31] J.P. Costes, F. Dahan, A. Dupuis, J.P. Laurent, Inorg. Chem. 36 (1997) 3429.
- [32] G. Novitchi, J.P. Costes, B. Donnadieu, Eur. J. Inorg. Chem. (2004) 1808.
- [33] T. Ishida, R. Watanabe, K. Fujiwara, A. Okazawa, N. Kojima, G. Tanaka, S. Yoshii, H. Nojiri, Dalton Trans. 41 (2012) 13609.
- [34] T. Kajiwara, K. Takahashi, T. Hiraizumi, S. Takaishi, M. Yamashita, Polyhedron 28 (2009) 1860.
- [35] J.P. Costes, F. Dahan, W. Wernsdorfer, Inorg. Chem. 45 (2006) 5.
- [36] G. Li, C.A. Jones, V.H. Grassian, S.C. Larsen, J. Catal. 234 (2005) 401.
- [37] A.J. Blake, V.A. Cherepanov, A.A. Dunlop, C.M. Grant, P.E.Y. Milne, J.M. Rawson, R.E.P. Winpenny, J. Chem. Soc. Dalton Trans. (1994) 2719.