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Research paper

Hexanuclear [Cu$_4^{II}$Ln$_2^{III}$] compounds incorporating N,O-donor ligands – Synthesis, crystal structures and physicochemical properties

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ABSTRACT

The reaction between N_2O_4-donor ligand *N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane ($H_4L = C_{17}H_{18}N_2O_4$) and different salts leads to the formation of novel hexanuclear clusters $[Cu_4Sm_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}9H_2O$ (**1**) and $[Cu_4Eu_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}3H_2O{\cdot}CH_3COOH{\cdot}CH_3OH$ (**2**) that crystallize in the triclinic system, space group *P*-1. The structures of **1** and **2** show two heterotrinuclear [Cu_2Ln] moieties that are linked by a nitrato bridge between two copper(II) ions. The [CuH_2L] fragments coordinated to the lanthanide(III) ion are not coplanar. Results of thermal analysis show that compounds **1** and **2** are stable at room temperature. The FTIR spectra of the gas phase products indicate that the decomposition of the title complexes is mainly connected with the release molecules of water, carbon dioxide, carbon monoxide, nitric oxides and ammonia. The solid residues obtained during the thermal decomposition of **1** and **2** in air atmosphere are the mixture of CuO and $CuLn_2O_4$.

1. Introduction

The heteronuclear 3*d*–4*f* complexes are of great interest in the coordination chemistry for their interesting structures and functional properties as magnetic, catalytic, optical and electronic materials [1–24]. As indicated by many examples N_2O_4-donor ligands tend to form heteronuclear Ln^{III}–M^{II} compounds which is the result of the fact that their inner, smaller pocket N_2O_2 indicates the preference for transition metal ions whereas the outer one O_4 shows preference for lanthanide ions [1–24]. Recently, several 3*d*–4*f* compounds, obtained by connecting heterodi- or heterotrinuclear cationic complexes with nitrato or polycarboxylato ions as linkers were reported [1,3,22]. Im et al. synthesized tetranucelar complex $[NiNd(L)(NO_3)_2(\mu\text{-}NO_3)(H_2O)(CH_3CN)]_2(H_2O)_2$ (where H_2L = 1,3-bis((3-methoxysalicylidene)aminopropane)) and its crystal structure can be described as being constructed from dinuclear [Ni^{II}–Nd^{III}] entities which are connected by two nitrato bridges μ-NO_3^- between Nd^{3+} and Ni^{2+} metal ions [1]. Two 3*d*–4*f* hexanuclear salen type compounds $[\{(LCu(ONO_2))(LCu(H_2O))Nd\}_2\text{-}(\mu\text{-}C_2O_4)](NO_3)_2{\cdot}6H_2O$ and $[\{(LNi(H_2O))(N(CN)_2)\}_2Pr\}_2(ONO_2)](OH){\cdot}2H_2O{\cdot}3CH_3CN$ (where L is the dianion of *N,N′*-bis(2-hydroxy-3-methoxybenzylidene)-1,3-diaminopropane) obtained by Gheorghe et al. are constructed from trinuclear [M^{II}–Ln^{III}–M^{II}] units which are linked by a bis-chelating oxalate bridge between the Nd^{3+} ions (the first complex) and by a nitrato group bridging two Pr^{3+} ions (the second complex), respectively [3]. Gheorghe et al. reported also $[\{(LCu^{II})_2Sm^{III}\}_2fum_2](OH)_2$ complex (where fum = fumarate dianion). The X-ray diffraction studies of this compound revealed its structure to be [Cu^{II}–Sm^{III}–Cu^{II}] moieties linked through carboxylato groups of two fum^{2-} ions acting as bridges between the Cu^{2+} and Sm^{3+} ions [22]. The hexadentate Schiff base *N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane, $H_4L = C_{17}H_{18}N_2O_4$ (Scheme 1) as a bicompartmental ligand possesses an inner smaller compartment with two N- and two O-donor chelating centers suitable for the coordination of metal ions, radii 0.60–0.75 Å *e.g.* copper, nickel or zinc ions and an outer bigger coordination site with four O-donor atoms being able to incorporate larger metal ions, radii 0.85–1.06 Å *e.g.* rare earth ions. In comparison to other N,O-donor ligands the unique feature of this compound is presence in its structure the additional OH groups that remain protonated upon complex formation.

We report herein novel heterohexanuclear cationic complexes $[Cu_4Sm_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}9H_2O$ (**1**) and $[Cu_4Eu_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}3H_2O{\cdot}CH_3COOH{\cdot}CH_3OH$ (**2**) which were obtained in the reaction of H_4L with the respective salts of Ln^{3+} and Cu^{2+}, their syntheses, unique structural features, spectroscopic and thermal characterization. These compounds are the example of 3d-4f complexes in which the hexanuclear compartment species

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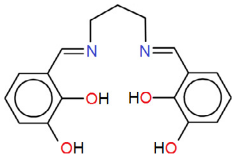

Scheme 1. Schematic diagram of the Schiff base ligand.

have been formed without the addition of an external linking ligand.

2. Experimental

2.1. Materials

The chemicals: 2,3-dihydroxybenzaldehyde, 1,3-diaminopropane, $Cu(CH_3COO)_2{\cdot}H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$, $Eu(NO_3)_3{\cdot}5H_2O$, as well as the solvent (methanol) were of analytical reagent grade. They were purchased from commercial sources and used as received without further purification.

2.2. Synthesis of *N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane H_4L

The H_4L ligand ($C_{17}H_{18}N_2O_4$) was synthesized by a condensation reaction between 2,3-dihydroxybenzaldehyde (1.38 g, 10 mmol) and 1,3-diaminopropane (0.37 g, 5 mmol) in methanol (50 ml) according to the reported procedure [25]. The compound was separated as yellow needles and recrystallized twice from methanol.

2.3. Synthesis of complexes $[Cu_4Sm_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}9H_2O$ (**1**) and $[Cu_4Eu_2(H_2L)_4(NO_3)_4(H_2O)_3]\ (NO_3)_2{\cdot}3H_2O{\cdot}CH_3COOH{\cdot}CH_3OH$ (**2**)

The hexanuclear complexes **1** and **2** were prepared as follows: the solution of $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol, 0.0799 g) in methanol (10 mL) was added dropwise to the stirred solution of *N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane, H_4L (0.4 mmol, 0.1248 g) in methanol (30 mL) to produce a green coloured mixture. The reaction mixture was stirred for 30 min at 45 °C. Next, the freshly prepared methanol solution (5 mL) of $Sm(NO_3)_3{\cdot}6H_2O$ (0.2 mmol, 0.0889 g) or $Eu(NO_3)_3{\cdot}5H_2O$ (0.2 mmol, 0.0856 g) was added slowly to the solution with constant stirring and the resulting deep green mixture 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 three weeks.

Yield 21% **1**. Anal. $C_{68}H_{88}N_{14}O_{46}Cu_4Sm_2$ 2393.38 (%): C, 34.11; H, 2.68; N, 8.19; Cu, 10.63; Sm, 12.57. Found: C, 34.40; H, 2.90; N, 7.80; Cu, 10.20; Sm, 12.20.

Yield 23% **2**. Anal. $C_{71}H_{86}N_{14}O_{43}Cu_4Eu_2$ 2381.62 (%): C, 35.77; H, 3.61; N, 8.23; Cu, 10.67; Eu, 12.76. Found: C, 35.80; H, 3.15; N, 8.00; Cu, 10.10; Eu, 12.40.

2.4. Methods

The contents of carbon, hydrogen and nitrogen in the compounds 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). Sample for FTIR spectra measurements was prepared as KBr discs (Table 1). Thermal analyses of complexes **1** and **2** and the Schiff base ligand (H_4L) 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 (ligand) at a heating rate of 10 °C·min^{-1}. The samples (7.27 mg (**1**), 7.80 mg (**2**) and 7.10 mg (ligand)) 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 700/1000 °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 transferline, 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 ($\lambda = 1.54187$ Å) over the scattering angular range $2\theta = 20–120°$.

2.5. X-ray crystal structure determination

The X-ray diffraction intensities for **1** and **2** were collected at 100 K on Oxford Diffraction Xcalibur CCD diffractometer with the graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ 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 [26,27] were used for data collection, cell refinement and data reduction. The structures were solved with the olex2.solve structure solution program using Charge Flipping and refined with the olex2.refine refinement package using Gauss-Newton

Table 1
Selected spectroscopic data of the Schiff ligand (*N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane), $Cu^{II}_2Sm^{III}_4$ (**1**), $Cu^{II}_2Eu^{III}_4$ (**2**).

Ligand	$Cu^{II}_2Sm^{III}_4$	$Cu^{II}_2Eu^{III}_4$	Proposed assignments
–	3456 m	3432 m	ν(O—H) + ν(C—H)
–	–	2920 w	$\nu(CH_3)_{as}$
–	–	2860 w	$\nu(CH_3)_s$
3200 m, *br*	–	–	ν(O—H) ↔ ν(N—H)
1640 *vs*	1620 *vs*	1620 *vs*	ν(C=N)
1544 m	1568 m	1568 m	ν(C=C)
1460 s	1468 s	1468 s	ν(C=C) + $\nu(N—O)_{comp.}$
1396 m	1384 w	1384 w	sc(C—H) + ν(CCC))
1356 m	–	–	δ(O—H)
–	1308 s	1300 s	ν(C—N) + ω(C—H) + ν(N—O)
–	1252 s	1256 s	ν(C—O)
1236 *vs*	1220 s	12120 s	$\nu\nu$(C—O) + δ(O—H)
1164 w	1172 w	1168 w	ν (C—C) + tw(C—H)
–	1088 w	1088 w	δ (C—H) + ν(N—O)
1064 m	1072 w	1072 w	skeletal
–	972 w	972 w	ρ(C—H) + CH_2 + δ(CCC)
900 w	–	–	γ(O—H)
868 w	864 m	864 m	δ(C–N=C)
788 w	784 w	784 w	γ(C—H) + ν(N—O)
748 *vs*	740 s	740 s	γ(C—H)
–	640 w	640 w	δ(C=C) + ring deform.
–	612 w	616 w	ring deform.
–	560 w	556 w	ν(M—O)
	524 w	524 w	γ(C—H)
504 w	500 w	500 w	γ(C—H)
–	412 w	412 w	ν(M—N)

vs – very strong, *s* – strong, *m* – medium, *w* – weak, *br* – broad, ν – stretching, δ – deformation in plane, sc – scissoring, ω – waggining, tw – twisting, ρ – rocking, γ – deformation out of plane, *as* – asymmetric, *sym* – symmetric, minimization [28]. Compound **1** crystallizes as a non merohedral twin. Although the model of crystal structure was found without difficulties, the refinement was not satisfactory. Finally the structure was refined as a two-component twin with the ratio of the twin components being of 0.46:0.54. The BASF parameter was 0.267(3). The R_1 value decreased from 0.160 to 0.070 for the twin refinement. One of the nitrate groups in **2** is disordered over two positions with occupancy of 0.58(2) for the major part. Due to low quality of crystals some of the C, N and O atoms were refined isotropically. The H atoms of water molecules were not found in the difference Fourier maps and were omitted from the model. The C-bonded H atoms were positioned geometrically and the 'riding' model for the C—H bonds was used in the refinement with $U_{iso}(H) = 1.5\ U_{eq}(C/O)$ for methyl groups and $U_{iso}(H) = 1.2\ U_{eq}(C)$ for the rest. The O-bonded H atoms of the Schiff base ligand were located in the difference Fourier maps and refined isotropically with restraints. The summary of experimental details and the crystal structure refinement parameters are given in Table 2. The molecular plots were drawn with Mercury CSD [29].

3. Result and discussion

3.1. Infrared spectra

The infrared spectra of compounds **1** and **2** have some common features as expected for their structural similarities. In order to get some information about binding mode of the N_2O_4-donor ligand (H_4L) to 3d and 4f metal ions the FTIR spectra of the obtained complexes were compared with the spectrum of the free Schiff base (Table 1). N,O-donor ligands are able to form coordinate bonds with various metal ions through azomethine as well as phenolic groups. The band characteristic of the azomethine group $\nu(C{=}N)$ of the free ligand H_4L appeared at 1640 cm^{-1} while in the analyzed complexes **1** and **2** this band is shifted to lower frequency and is observed at around 1620 cm^{-1} indicating 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 organic ligand [30–34]. The metal-nitrogen coordination bond is also confirmed by the new band presented at *ca.* 416 cm^{-1} that may be assigned to the ν(Cu–N) vibration [35,36]. The strong peak characteristic of phenolic ν(C—O) stretching vibration band observed at 1236 cm^{-1} for the free N,O-donor ligand is shifted to lower wavenumber in the FTIR spectra of complexes **1** and **2** and occurs at 1220 cm^{-1}, indicating the involvement of the phenolic oxygen atoms in the metal-ligand bonding [33,37]. The metal-oxygen coordination bond is confirmed by the new band presented at *ca.* 560 cm^{-1} that can be attributed to ν(M—O) vibration [35,36]. In the FTIR spectra of the analyzed compounds the characteristic frequencies of nitrate groups acting as mono- and bidentate ligands overlap and occur at about 1468 cm^{-1}, 1308 cm^{-1}, 1088 cm^{-1} and 784 cm^{-1} [38]. The weak bands at around 2920 cm^{-1} and 2860 cm^{-1} presented only in the spectrum of **2** may be attributed to asymmetric and symmetric stretching vibrations of the methyl group, $\nu(CH_3)$ [39]. A medium band characteristic of ν(O—H) stretching vibrations has its maximum at around 3430 cm^{-1} (caused by methanol and crystal water as well as the protonated hydroxyl groups of the Schiff base) [34,35,39,40].

Table 2
Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{68}H_{88}N_{14}O_{46}Cu_4Sm_2$	$C_{71}H_{86}N_{14}O_{43}Cu_4Eu_2$
Formula weight	2392.38	2381.62
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	13.2934(12)	13.2178(9)
b/Å	17.5990(10)	17.3653(13)
c/Å	19.9453(10)	20.1010(14)
α/°	85.892(5)	93.004(6)
β/°	89.181(5)	90.324(5)
γ/°	68.016(7)	110.313(7)
Volume/$Å^3$	4315.4(5)	4319.5(5)
Z	2	2
$\rho_{calc}g/cm^3$	1.841	1.831
$\mathbf{\mu}/mm^{-1}$	2.416	2.503
F(000)	2404.0	2392.0
Crystal size/mm^3	0.4 × 0.2 × 0.1	0.2 × 0.15 × 0.05
Reflections collected	29476	21206
Independent reflections	15551 [$R_{int} = 0.0629$, $R_{sigma} = 0.1588$]	21206 [$R_{sigma} = 0.1613$]
BASF	–	0.267(3)
Data/restraints/ parameters	15551/37/1047	21206/31/1087
Goodness-of-fit on F^2	0.955	0.973
Final R indexes [I > = 2σ (I)]	$R_1 = 0.0699$, $wR_2 = 0.1536$	$R_1 = 0.0880$, $wR_2 = 0.2188$
Largest diff. peak/hole / e $Å^{-3}$	1.71/-1.15	2.87/-3.67
CCDC No.	1517282	1517281

3.2. Crystal and molecular structure

Single-crystal X-ray studies revealed that $[Cu_4Sm_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}9H_2O$ (**1**) and $[Cu_4Eu_2(H_2L)_4(NO_3)_4(H_2O)_3](NO_3)_2{\cdot}3H_2O{\cdot}CH_3COOH{\cdot}CH_3OH$ (**2**) (where $H_2L = C_{17}H_{16}N_2O_4$ is a dianion of *N,N′*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane) crystallize in the triclinic space group *P*-1. The **1** and **2** consist of a hexanuclear complex cation $[Cu_4Ln_2(H_2L)_4(NO_3)_4(H_2O)_3]^{2+}$, two nitrate ions, crystal water and in the case of **2** methanol as well as acetic acid molecules. Details for the structure solution and refinement are summarized in Table 2, and selected bond distances and angles are listed in Table 3. A perspective view of the molecular structures of **1** and **2** is presented in Figs. 1 and 2 and the schematic diagram of the coordination unit is given in Fig. S1. In the molecules **1** and **2** one μ_2-NO_3 anion plays the role of connecting two Cu^{II} ions to generate a structure coupling two Cu^{II}-Ln^{III}-Cu^{II} units. The separation between two copper ions linked by the nitrate bridge is *ca.* 6.15 Å. In each heterotrinuclear unit Cu^{II} and Ln^{III} ions are located in the inner, smaller N_2O_2 pocket and outer, bigger O_4 one of H_2L^{2-} ligand, respectively and linked by two phenol oxygen atoms from the Schiff base ligand. The intramolecular Cu···Ln and Cu···Cu separations are *ca.* 3.5 and 7.0 Å, respectively. In the crystals **1** and **2** the Cu^{II} ions are five- (Cu2 and Cu3) and six-coordinate (Cu1 and Cu4) with distorted square pyramidal and distorted octahedral geometry, respectively (Fig. S2). The average Cu—N_{imine} and Cu—$O_{phenoxo}$ distances are in the typical ranges 1.97–2.01 Å and 1.93–1.97 Å, respectively [41,42,3,43,44].

The nine-coordinate sphere of Ln^{III} is formed by eight oxygen atoms from the two N_2O_4-donor ligands and one oxygen atom from the water molecule giving a tricapped trigonal prismatic geometry (Fig. S2). The distances Ln—O vary in the range 2.36–2.55 Å, the shortest ones being Ln—$O_{phenoxo}$ and the longest Ln—$O_{hydroxyl}$ bonds (Table 2). In the crystals **1** and **2** the three metallic centers of a trinuclear subunit $[Cu_2Ln]$ are almost collinear with the value of the Cu^{II}-Ln^{III}-Cu^{II} angle being *ca.* 170°. It should be noted that two $[CuH_2L]$ fragments coordinated to the lanthanide(III) ion are not coplanar. In the complexes **1** and **2** one CuO_2Ln fragment of the trinuclear unit is nearly planar with α values being of 3–8°, whereas the second half of the molecule is significantly twisted (α values are 15–20°). The separation between two Ln(III) ions is *ca.* 8.96 Å. In the crystals **1** and **2** there are many intra- as well as intermolecular hydrogen bonds. The adjacent molecules are bridged by hydrogen bonds through protonated hydroxyl group, nitrate ions, acetic acid (2), methanol (2) and water

Table 3
Intramolecular geometry for **1** and **2** [Å].

Distance	1	2	Distance	1	2
Cu1–N1	1.98(1)	1.976(8)	O1–Ln1	2.381(8)	2.370(7)
Cu1–N2	1.982(9)	1.971(9)	O2–Ln1	2.436(6)	2.395(7)
Cu1–O1	1.959(6)	1.932(7)	O3–Ln1	2.509(7)	2.466(7)
Cu1–O2	1.936(8)	1.960(7)	O4–Ln1	2.554(7)	2.512(7)
Cu1–O19	2.570(2)	2.470(1)	O5–Ln1	2.402(7)	2.414(7)
Cu1–O22	2.504(9)	2.520(7)	O6–Ln1	2.363(7)	2.357(7)
Cu2–N3	1.970(1)	1.980(1)	O7–Ln1	2.470(7)	2.476(7)
Cu2–N4	1.990(1)	1.972(9)	O8–Ln1	2.526(7)	2.498(7)
Cu2–O5	1.941(8)	1.935(7)	O17–Ln1	2.462(9)	2.440(8)
Cu2–O6	1.955(7)	1.948(7)	O9–Ln2	2.402(7)	2.395(7)
Cu2–O35	2.500(1)	3.310(1)	O10–Ln2	2.387(8)	2.370(8)
Cu2–O40	2.455(9)	2.455(9)	O11–Ln2	2.470(6)	2.455(7)
Cu3–N5	1.980(1)	1.960(1)	O12–Ln2	2.516(7)	2.496(8)
Cu3–N6	1.990(1)	2.010(1)	O13–Ln2	2.407(7)	2.404(7)
Cu3–O9	1.936(8)	1.938(7)	O14–Ln2	2.350(1)	2.338(7)
Cu3–O10	1.934(8)	1.953(8)	O15–Ln2	2.486(7)	2.465(7)
Cu3–O23	2.543(8)	2.550(7)	O16–Ln2	2.521(8)	2.486(7)
Cu4–N7	1.982(9)	1.982(9)	O18–Ln2	2.470(9)	2.479(8)
Cu4–N8	1.960(1)	1.968(9)	Cu1–Ln1	3.527(1)	3.513(1)
Cu4–O13	1.942(9)	1.947(7)	Cu2–Ln1	3.528(1)	3.521(1)
Cu4–O14	1.969(8)	1.966(7)	Cu3–Ln2	3.543(2)	3.514(2)
Cu4–O28	2.610(1)	2.430(1)	Cu4–Ln2	3.497(2)	3.483(1)
Cu4–O34/O25*	2.400(2)	2.430(1)	Ln1…Ln2^i	8.731(1)	8.960(1)

* bonds Cu4–O34 for **1** and Cu4–O25 for **2**, Ln = Sm for **1** and Eu for **2**. Symmetry code ^{i} *x*–1, *y*–1, *z*.

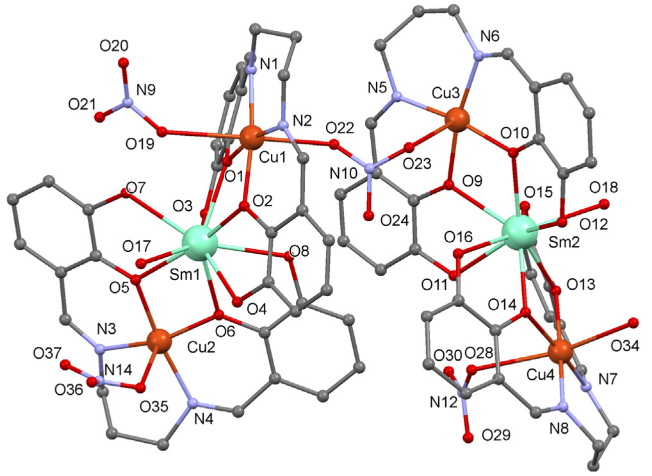

Fig. 1. Molecular structure with atom numbering scheme of Cu_4^{II}–Sm_2^{III} (**1**). The outer coordination sphere solvent molecules were omitted for clarity.

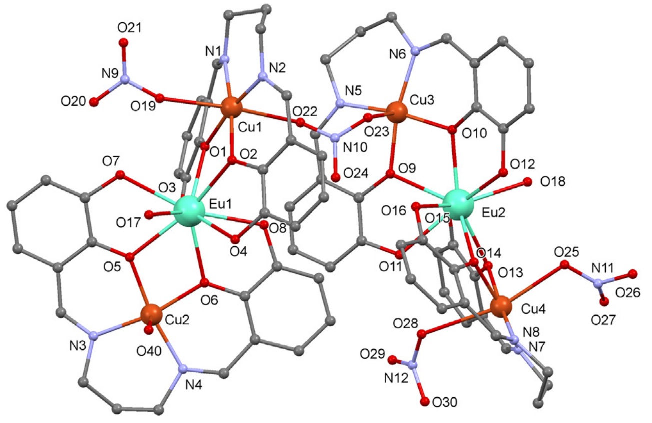

Fig. 2. Molecular structure with atom numbering scheme of Cu_4^{II}–Eu_2^{III} (**2**). The outer coordination sphere solvent molecules were omitted for clarity.

molecules. The hydroxyl groups of the ligand molecules remain protonated in the complex. This conclusion was drawn basing on the analysis of the intra- and intermolecular environment of each hydroxyl groups in the crystal (Fig. S3). The observed interatomic distances and the directional nature of the interactions correspond well with the expected hydrogen bond network. In both crystals the hydroxyl O8 and O16 atoms form hydrogen bonds with the central bridging NO_3^- anion, stabilizing the hexanuclear coordination unit. Atoms O3, O4, O7 and O11 link through hydrogen bonds to O-nitro atoms, whereas atoms O12 and O15 act as hydrogen bond donors to solvent molecules (to water in **1** and to methanol and acetic acid molecules in **2**). The geometry of chosen hydrogen bonds has been listed in the Table S1.

In the Table S2 there is comparison of some structural parameters (Cu–N (Å), Cu—O_{phen} (Å), Ln—O_{phen} (Å), Ln—$O_{methoxy}$ (Å), Cu···Ln (Å)) of chosen Cu^{II}-Ln^{III} compounds prepared with *o*-vanillin (or its derivatives). As shown in this table all compounds consist of diphenoxo-bridged heterometallic cores in which Cu^{II} metal ion is placed in N_2O_2 compartment of the Schiff-base ligand, while the Ln^{III} ion is present in the larger and open O_2O_2 [$O(_{phenoxo})_2O(_{methoxy})_2$] one. The Cu–N and Cu–O bond distances are similar and range from 1.9 to 2.0 Å. The Ln—O distances from the phenolato oxygen atoms are much shorter than those from the methoxy oxygens. The intramolecular separation Cu···Ln is about 3.4–3.5 Å. Three types of lanthanide counterions NO_3^-, Cl^- and different carboxylic acid ions (e.g. acetate, fumarate, oxalate, hexafluoroacetylacetonato) are mainly used in the synthesis of salen type 3*d*-4*f* compounds. It is worth mentioning that the structure of Cu^{II}-Ln^{III} complexes depends on several factors: the nature of the donor atoms of the linkers, the oxophilicity of the lanthanides, the preference of the Cu(II) ion for nitrogen atoms, the degree of deprotonation of the ligands, the stoichiometry of the used reagents and kind of used solvents. According to the literature (Table S2) in complexes nitrato anions contributing to the electroneutrality and also to the completion of the coordination sphere of the 4f ions (as chelating nitrato group) whereas the organic counterions act also as linkers i.e. carboxylato group works as a bridge between the lanthanide(III)/copper(II) and lanthanide(III) ions. In contrast to compounds presented in the Table S2, in the structures of complexes **1** and **2** two heterotrinuclear [Cu_2Ln] moieties are linked by a nitrato group acting as a bridge between two copper(II) ions.

3.3. Thermal properties

In order to examine the thermal behaviour and the stability of the Schiff base ligand and analyzed complexes **1** and **2** the TG, DTG and DSC curves were recorded. During heating in air the Schiff base ligand is stable up to 167 °C (Fig. S4) and next at the beginning of its thermal decomposition on the DSC curve an endothermic effect is observed. This effect is connected with the negligible mass loss, which is characteristic of the melting process. It should be noticed that DSC peak is sharp which indicates that the ligand is a crystalline, pure substance. The melting point observed on the DSC curve is about 170 °C and the enthalpy of fusion equals 25.93 $kJmol^{-1}$. As shown in Figs. S5 and S6 the compounds **1** and **2** are stable at room temperature. The TG curves of **1** and **2** display practically the same weight-loss patterns. Heating the samples up to *ca.* 130 °C in air atmosphere leads to the weight loss of 6.00% (calculated 6.77%) (**1**) and 4.70% (calculated 4.03%) (**2**) consistent with the lose solvent molecules (water (**1**), methanol and water (**2**)). This process is accompanied with small endothermic effect seen on the DSC curves with the maximum at ~90 °C. The values of the enthalpy of the desolvation processes are 149.86 $kJ\ mol^{-1}$ (**1**) and 371.49 $kJmol^{-1}$ (**2**), respectively. These results are also confirmed by the TG-FTIR analysis (Figs. S7–S12). The recorded FTIR spectra of evolved gas phase for the analyzed compound**s** 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 H_2O molecules [39], whereas the bands associated with the presence of CH_3OH are observed at 3368 cm^{-1}, 1307 cm^{-1} and 1095 cm^{-1}, respectively [33]. The second mass weight in the temperature range of 140–275 °C (**1**) and 145–280 °C (**2**) may be due to the lose nitrate and coordinated water molecules in the case of the compound **1** (calculated 17.81%, found 18.10%) and nitrate, acetic acid and coordinated water molecules in the case of the complex **2** (calculated 20.41%, found 20.20%), respectively. The FTIR spectra recorded during this stage show the presence of bands characteristic of the N_2O (double peaks at 2250–2150 cm^{-1} and 1250–1000 cm^{-1}), H_2O (4000–3400 cm^{-1} and 2060–1260 cm^{-1}) and CH_3COOH (3600 cm^{-1}, double peaks at 1900–1750 cm^{-1} and some peaks at 1400 cm^{-1}, 1275 cm^{-1}, 1075 cm^{-1}, 1000 cm^{-1} and 650 cm^{-1}, Fig. S13). During further heating of the samples **1** and **2** the destruction and combustion of the Schiff base ligand is observed. It is mainly connected with the release molecules of H_2O, NH_3, CO_2, CO, CH_3OH. The bands characteristic for NH_3 are principally observed in the range of 750–1200 cm^{-1} with the specific double peak bands with the maximum at 965 and 931 cm^1, respectively [33,39,45] and additionally in the spectral region of 3100–3800 cm^{-1} some bands due to N—H stretching are also recorded. The bands characteristic for molecules of CH_3OH are observed at 3368 cm^{-1}, 1307 cm^{-1} and 1095 cm^{-1}, respectively [33]. Double peak at 2275–2050 cm^{-1} confirms the presence of CO in the gaseous products. The absorption bands in the range of 2450–2300 cm^{-1} and 760–600 cm^{-1} can be attributed to the formation of CO_2 [33].

The decomposition process of heteronuclear complexes **1** and **2** is intricate and was not possible to distinguish intermediate solid products. The final products (mixtures of metal oxides CuO and $CuSm_2O_4$ (**1**) and CuO and $CuEu_2O_4$ (**2**)) obtained during thermal decomposition of complexes were calculated from TG curves and experimentally verified by X-ray diffraction powder patterns (Fig. S14). The percentages calculated from TG curves (27.80% (**1**), 27.70% (**2**)) were coincided fairly with the theoretical values (27.88% (**1**), 28.14% (**2**)). These results are in accordance with those presented by other researches [46].

4. Conclusion

The $Cu^{II}_4Ln^{III}_2$ complexes can be considered as resulting from the assembly of two [$Cu^{II}_2Ln^{III}$] building blocks. In the each heterotrinuclear unit, Cu^{II} and Ln^{III} ions are located in the inner N_2O_2 and outer O_4 pockets of the Schiff base ligand, respectively. The 3d and 4f metal ions are bridged by two phenoxo oxygen atoms belonging to the N, O-donor ligand. The coordination number of lanthanide(III) ion is equal to nine whereas the copper(II) ions are five- and six-coordinated. The destruction and combustion of the Schiff base ligand is mainly connected with the release molecules of NH_3, CO_2, CO, N_2O, NO. The compounds are stable at room temperature and their decomposition processes proceed in the similar way. Heating of complexes leads at first to the desolvation and next to decomposition processes. The final solid products of the complex decomposition are CuO and Ln_2CuO_4.

Appendix A. Supplementary data

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre: CCDC 1517282 and 1517281, respectively. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2017.06.002.

References

[1] H.J. Im, S.W. Lee, Polyhedron 101 (2015) 48–55.
[2] H.J. Im, S.W. Lee, Polyhedron 110 (2016) 24–30.
[3] R. Gheorghe, M. Andruh, J.-P. Costes, B. Donnadieu, M. Schmidtmann, A. Müller, Inorg. Chim. Acta 360 (2007) 4044–4050.
[4] T. Ishida, R. Watanabe, K. Fujiwara, A. Okazawa, N. Kojima, G. Tanaka, S. Yoshii, H. Nojiri, Dalton Trans. 41 (2012) 13609–13619.
[5] T. Kajiwara, M. Nakano, K. Takahashi, S. Takaishi, M. Yamashita, Chem.-Eur. J. 17 (2011) 196–205.
[6] T.D. Pasatoiu, A. Ghirri, A.M. Madalan, M. Affronte, M. Andruh, Dalton Trans. 43 (2014) 9136–9142.
[7] X.-Y. Lu, Y.-Q. Liu, X.-W. Deng, Z.-X. Zhu, M.-X. Yao, S. Jing, New J. Chem. 39 (2015) 3467–3473.
[8] F. Cimpoesu, F. Dahan, S. Ladeira, M. Ferbinteanu, J.-P. Costes, Inorg. Chem. 51 (2012) 11279–11293.
[9] T.D. Pasatoiu, A.M. Madalan, M.U. Kumke, C. Tiseanu, M. Andruh, Inorg. Chem. 49 (2010) 2310–2315.
[10] X. Yang, R.A. Jones, V. Lynch, M.M. Oye, A.L. Holmes, Dalton Trans. (2005) 849–851.
[11] S. Sakamoto, T. Fujinami, K. Nishi, N. Matsumoto, N. Mochida, T. Ishida, Y. Sunatsuki, N. Re, Inorg. Chem. 52 (2013) 7218–7229.
[12] T.D. Pasatoiu, C. Tiseanu, A.M. Madalan, B. Jurca, C. Duhayon, J.P. Sutter, M. Andruh, Inorg. Chem. 50 (2011) 5879–5889.
[13] O.V. Amirkhanov, O.V. Moroz, K.O. Znovjyak, T.Yu. Sliva, L.V. Penkova, T. Yushchenko, L. Szyrwiel, I.S. Konovalova, V.V. Dyakonenko, O.V. Shishkin, V.M. Amirkhanov, Eur. J. Inorg. Chem. (2014) 3720–3730.
[14] J.S. Elias, M. Risch, L. Giordano, A.N. Mansour, Y. Shao-Horn, J. Am. Chem. Soc. 136 (2014) 17193–17200.
[15] T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Brefuel, J.-P. Tuchagues, L. Vendier, W. Wernsdorfer, Inorg. Chem. 49 (2010) 9125–9135.
[16] H.L.C. Feltham, R. Clerac, A.K. Powell, S. Brooker, Inorg. Chem. 50 (2011) 4232–4234.
[17] K. Ehama, Y. Ohmichi, S. Sakamoto, T. Fujinami, N. Matsumoto, N. Mochida, T. Ishida, Y. Sunatsuki, M. Tsuchimoto, N. Re, Inorg. Chem. 52 (2013) 12828–12841.
[18] T.D. Pasatoiu, M. Etienne, A.M. Madalan, M. Andruh, R. Sessoli, Dalton Trans. 39 (2010) 4802–4808.
[19] M. Dolai, T. Mistri, A. Panja, M. Ali, Inorg. Chim. Acta 399 (2013) 95–104.
[20] X.-C. Huang, C. Zhou, H.-Y. Wei, X.-Y. Wang, Inorg. Chem. 52 (2013) 7314–7316.
[21] M. Ren, Z.-L. Xu, S.-S. Bao, T.-T. Wang, Z.-H. Zheng, R.A.S. Ferreira, L.-M. Zheng, L.D. Carlos, Dalton Trans. 45 (2016) 2974–2982.

[22] R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu, S. Shova, Chem. Eur. J. 12 (2006) (2006) 187–203.
[23] A.S. Dinca, S. Shova, A.E. Ion, C. Maxim, F. Lloret, M. Julve, M. Andruh, Dalton Trans. 44 (2015) 7148–7151.
[24] L. Xu, Q. Zhang, G. Hou, P. Chen, G. Li, D.L.M. Pajerowski, C.L. Dennis, Polyhedron 52 (2013) 91–95.
[25] C.T. Zeyrek, A. Elmali, Y. Elerman, J. Mol. Struct. 740 (2005) 47–52.
[26] Oxford Diffraction, Xcalibur CCD System, CRYSALIS Software System, Version 1.171, Oxford Diffraction Ltd. 2009.
[27] CrysAlisPro, Agilent Technologies, Version 1.171.37.34 (release 22–05-2014 CrysAlis171.NET).
[28] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H.J. Puschmann, Appl. Cryst. 42 (2009) 339–341.
[29] Mercury CSD 2.0 - C.F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P.A. Wood, J. Appl. Cryst., 41 (2008) 466–470.
[30] 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) 177–183.
[31] A.-N.M.A. Alaghaz, B.A. El-Sayed, A.A. El-Henawy, R.A.A. Ammarb, J. Mol. Struct. 1035 (2013) 83–93.
[32] R.K. Dubey, P. Baranwal, A.K. Jha, J. Coord. Chem. 65 (2012) 2645–2656.
[33] A. Bartyzel, J. Coord. Chem. 66 (2013) 4292–4303.
[34] A. Gutiérrez, M.F. Perpiñán, A.E. Sánchez, M.C. Torralba, V. González, Inorg. Chim. Acta 453 (2016) 169–178.
[35] S.O. Bahaffi, A.A.A. Aziz, M.M. El-Naggar, J. Mol. Struct. 1020 (2012) 188–196.
[36] S. Yadav, M. Ahmad, K.S. Siddiqi, Spectrochim Acta A 98 (2012) 240–246.
[37] R. Takjoo, A. Hashemzadeh, H.A. Rudbari, F. Nicolò, J. Coord. Chem. 66 (2013) 345–357.
[38] B. Cristóvão, J. Kłak, B. Miroslaw, J. Coord. Chem. 67 (2014) 2728–2746.
[39] B. Cristóvão, B. Miroslaw, Inorg. Chim. Acta 401 (2013) 50–57.
[40] Aziz, A.N.M. Salem, M.A. Sayed, M.M. Aboaly, J. Mol. Struct. 1010 (2012) 130–138.
[41] L. Xu, Q. Zhang, G. Hou, P. Chen, G. Li, D.l.M. Pajerowski, C.L. Dennis, Polyhedron 52 (2013) 91–95.
[42] P. Zhang, L. Zhang, S.-Y. Lin, J. Tang, Inorg. Chem. 52 (2000) 6595–6602.
[43] J.P. Costes, B. Donnadieu, R. Gheorghe, G. Novitchi, J.P. Tuchagues, L. Vendier, Eur. J. Inorg. Chem. (2008) 5235–5244.
[44] J.P. Costes, F. Dahan, A. Dupuis, Inorg. Chem. 39 (2000) 5994–6000.
[45] G. Li, C.A. Jones, V.H. Grassian, S.C. Larsen, J. Catal. 234 (2005) 401–413.
[46] 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) 2719–2727.