

Research paper

Hexanuclear [Cu₄Ln₂^{III}] compounds incorporating N,O-donor ligands – Synthesis, crystal structures and physicochemical propertiesBeata Cristóvão^{a,*}, Barbara Miroslaw^b, Agata Bartyzel^a^a Department of General and Coordination Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska sq. 2, 20-031 Lublin, Poland^b Department of Crystallography, Maria Curie-Skłodowska University, Maria Curie-Skłodowska sq. 3, 20-031 Lublin, Poland

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ABSTRACT

The reaction between N₂O₄-donor ligand *N,N'*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane (H₄L = C₁₇H₁₈N₂O₄) and different salts leads to the formation of novel hexanuclear clusters [Cu₄Sm₂(H₂L)₄(NO₃)₄(H₂O)₃](NO₃)₂·9H₂O (**1**) and [Cu₄Eu₂(H₂L)₄(NO₃)₄(H₂O)₃](NO₃)₂·3H₂O·CH₃COOH·CH₃OH (**2**) that crystallize in the triclinic system, space group *P*-1. The structures of **1** and **2** show two heterotrinnuclear [Cu₂Ln] moieties that are linked by a nitrate bridge between two copper(II) ions. The [CuH₂L] 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 CuLn₂O₄.

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1. Introduction

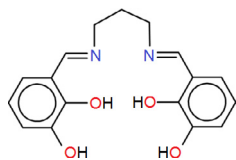
The heteronuclear 3d-4f complexes are of great interest in the coordination chemistry for their interesting structures and functional properties as magnetic, catalytic, optical and electronic materials [1–24]. As indicated by many examples N₂O₄-donor ligands tend to form heteronuclear Ln^{III}-M^{II} compounds which is the result of the fact that their inner, smaller pocket N₂O₂ indicates the preference for transition metal ions whereas the outer one O₄ shows preference for lanthanide ions [1–24]. Recently, several 3d-4f compounds, obtained by connecting heterodi- or heterotrinnuclear cationic complexes with nitrate or polycarboxylato ions as linkers were reported [1,3,22]. Im et al. synthesized tetranuclear complex [NiNd(L)(NO₃)₂(μ-NO₃)(H₂O)(CH₃CN)]₂(H₂O)₂ (where H₂L = 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 nitrate bridges μ-NO₃⁻ between Nd³⁺ and Ni²⁺ metal ions [1]. Two 3d-4f hexanuclear salen type compounds [Cu₄(ONO₂)₂(LCu(H₂O))₂Nd₂-(μ-C₂O₄)](NO₃)₂·6H₂O and [Cu₄(ONO₂)₂(LCu(H₂O))₂Pr₂-(ONO₂)](OH)·2H₂O·3CH₃CN (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 Nd³⁺ ions (the first complex) and by a nitrate group bridging two Pr³⁺ ions (the second complex), respectively [3]. Gheorghe et al. reported also [Cu^{II}-Sm^{III}-Cu^{II}](fumarate)₂(OH)₂ complex (where fumarate = 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 fumarate²⁻ ions acting as bridges between the Cu²⁺ and Sm³⁺ ions [22]. The hexadentate Schiff base *N,N'*-bis(2,3-dihydroxybenzylidene)-1,3-diaminopropane, H₄L = C₁₇H₁₈N₂O₄ (Scheme 1) as a bicompartamental 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 [Cu₄Sm₂(H₂L)₄(NO₃)₄(H₂O)₃](NO₃)₂·9H₂O (**1**) and [Cu₄Eu₂(H₂L)₄(NO₃)₄(H₂O)₃](NO₃)₂·3H₂O·CH₃COOH·CH₃OH (**2**) which were obtained in the reaction of H₄L with the respective salts of Ln³⁺ and Cu²⁺, 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, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 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 ($\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_4$) 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 $[\text{Cu}_4\text{Sm}_2(\text{H}_2\text{L})_4(\text{NO}_3)_4(\text{H}_2\text{O})_3](\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (**1**) and $[\text{Cu}_4\text{Eu}_2(\text{H}_2\text{L})_4(\text{NO}_3)_4(\text{H}_2\text{O})_3](\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{COOH} \cdot \text{CH}_3\text{OH}$ (**2**)

The hexanuclear complexes **1** and **2** were prepared as follows: the solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.4 mmol, 0.0799 g) in methanol (10 mL) was added dropwise to the stirred solution of *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 $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.2 mmol, 0.0889 g) or $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (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. $\text{C}_{68}\text{H}_{88}\text{N}_{14}\text{O}_{46}\text{Cu}_4\text{Sm}_2$ 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. $\text{C}_{71}\text{H}_{86}\text{N}_{14}\text{O}_{43}\text{Cu}_4\text{Eu}_2$ 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 (Cannberra–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 $\text{CuK}\alpha$ radiation ($\lambda = 1.54187 \text{ \AA}$) over the scattering angular range $2\theta = 20\text{--}120^\circ$.

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 $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). 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 [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), $\text{Cu}_2^{\text{II}}\text{Sm}_2^{\text{III}}$ (**1**), $\text{Cu}_2^{\text{II}}\text{Eu}_2^{\text{III}}$ (**2**).

Ligand	$\text{Cu}_2^{\text{II}}\text{Sm}_2^{\text{III}}$	$\text{Cu}_2^{\text{II}}\text{Eu}_2^{\text{III}}$	Proposed assignments
–	3456 m	3432 m	$\nu(\text{O–H}) + \nu(\text{C–H})$
–	–	2920 w	$\nu(\text{CH}_3)_{as}$
–	–	2860 w	$\nu(\text{CH}_3)_s$
3200 m, br	–	–	$\nu(\text{O–H}) \leftrightarrow \nu(\text{N–H})$
1640 vs	1620 vs	1620 vs	$\nu(\text{C=N})$
1544 m	1568 m	1568 m	$\nu(\text{C=C})$
1460 s	1468 s	1468 s	$\nu(\text{C=C}) + \nu(\text{N–O})_{comp.}$
1396 m	1384 w	1384 w	$\nu(\text{C–H}) + \nu(\text{CCC})$
1356 m	–	–	$\delta(\text{O–H})$
–	1308 s	1300 s	$\nu(\text{C–N}) + \omega(\text{C–H}) + \nu(\text{N–O})$
–	1252 s	1256 s	$\nu(\text{C–O})$
1236 vs	1220 s	12120 s	$\nu(\text{C–O}) + \delta(\text{O–H})$
1164 w	1172 w	1168 w	$\nu(\text{C–C}) + \text{tw}(\text{C–H})$
–	1088 w	1088 w	$\delta(\text{C–H}) + \nu(\text{N–O})$
1064 m	1072 w	1072 w	skeletal
–	972 w	972 w	$\rho(\text{C–H}) + \text{CH}_2 + \delta(\text{CCC})$
900 w	–	–	$\gamma(\text{O–H})$
868 w	864 m	864 m	$\delta(\text{C–N=C})$
788 w	784 w	784 w	$\gamma(\text{C–H}) + \nu(\text{N–O})$
748 vs	740 s	740 s	$\gamma(\text{C–H})$
–	640 w	640 w	$\delta(\text{C=C}) + \text{ring deform.}$
–	612 w	616 w	ring deform.
–	560 w	556 w	$\nu(\text{M–O})$
–	524 w	524 w	$\gamma(\text{C–H})$
504 w	500 w	500 w	$\gamma(\text{C–H})$
–	412 w	412 w	$\nu(\text{M–N})$

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

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