

## Synthesis and magnetic studies of copper(II)-lanthanide(III) 5-bromosalicylidene-glycylglycine

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**Abstract:** The physico-chemical properties of the new 3d-4f heteronuclear complexes with general formula  $\text{LnCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  (where Ln = Pr, Eu, Gd, Tb, Er, Yb and  $\text{H}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})$  – 5-bromosalicylidene-glycylglycine) were studied. The compounds were characterized by elemental, spectral and thermal analyses and magnetic measurements. The formation of Schiff base is evidenced by a strong band at *ca.* 1646–1650  $\text{cm}^{-1}$  attributable to C=N stretching mode. The presence of water molecules is confirmed by broad absorptions with maximum at 3360 – 3368  $\text{cm}^{-1}$ . The Cu(II)–Ln(III) complexes are stable up to *ca.* 318 K. During dehydration process the water molecules are lost probably in two stages. The magnetic susceptibility data for these complexes change with temperature according to the Curie-Weiss law.

**Keywords:** lanthanide; copper; Schiff base; magnetic moment; magnetic susceptibility.

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### Introduction

Magnetism of molecular complexes simultaneously comprising 3d and 4f metal ions has been the subject of investigation in the last few years. These compounds are important not only in preparative coordination chemistry but also to understand the mechanism of the magnetic interaction between 3d and 4f centres, which are potential magnetic materials. The magnetic interactions between rare-earth and d block metal ions have been found to be weak, as one can expect given the relatively low covalency of the lanthanide-to-ligand bonds, but their effects are by no means negligible, producing profound modifications on the nature of the magnetic materials, depending on the nature of the lanthanides and 3d metal ions involved. In particular the copper(II)–gadolinium(III) couple has been extensively studied both from a structural as well as

from magnetic point of view, in a number of binuclear Cu(II)–Gd(III) and polynuclear system with  $\text{Cu}_2\text{Gd}$ ,  $\text{Cu}_4\text{Gd}$ ,  $\text{Cu}_4\text{Gd}_2$  or  $(\text{CuGd})_n$  cores, bridged by phenoxo or multidentate ligand with hetero donating groups. The most frequently used ligands are polydentate Schiff base. The nature of the magnetic interaction between Cu(II) and Gd(III) ions within polynuclear species is, in most cases, ferromagnetic, as in dinuclear complexes. From a magnetic point of view, well isolated dinuclear complexes have a great advantage for they only contain the Cu–Gd interaction parameter. On the contrary, in complexes of higher nuclearity, as in trinuclear  $\text{Cu}_2\text{Gd}$  complexes for example, we have to take into account the desired Cu–Gd interaction but also a possible Cu–Cu interaction (antiferromagnetic, ferromagnetic or equal to zero) [1-14].

As a continuation of our earlier work here we reported the magnetic properties of original

polynuclear lanthanide(III) and copper(II) complexes containing 5-bromosalicylideneglycylglycine.

## Experimental details

The violet compounds of  $\text{LnCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Er}, \text{Yb}$ ) were synthesized from Schiff base –  $\text{H}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})$  (5-bromosalicylideneglycylglycine), copper(II) chloride and lanthanide(III) chlorides by using the procedure described in Ref. [15, 16].

The contents of carbon, hydrogen and nitrogen in the analysed compounds were determined by elemental analysis using a CHN 2400 Perkin Elmer analyser.

The contents of lanthanide and copper were established using ED XRF spectrophotometer (Canberra-Packard).

The IR spectra of complexes were recorded over the range of  $4000 - 400 \text{ cm}^{-1}$  using M – 80 spectrophotometer (Carl Zeiss Jena). Samples for IR spectra measurements were prepared as KBr discs.

The dehydration process of Cu(II)–Ln(III) complexes was studied in air using a Setsys 16/18 TG, DTA instrument. The experiment was carried out under air flow in the temperature range of  $297-773 \text{ K}$ . Samples ranging from 7.62 mg (Pr), 7.26 mg (Eu), 7.55 mg (Gd), 7.08 mg (Tb), 7.53 mg (Er) to 7.19 mg (Yb) were heated in

$\text{Al}_2\text{O}_3$  crucibles with the heating rate of  $10 \text{ K} \cdot \text{min}^{-1}$ .

The magnetic susceptibility values of the Cu(II)-Ln(III) compounds were determined by Gouy method in the temperature range of  $76 - 303 \text{ K}$ . The calibrant employed was  $\text{Hg}[\text{Co}(\text{SCN})_2]$  for which the magnetic susceptibility of  $1.644 \cdot 10^{-5} \text{ cm}^3 \text{g}^{-1}$  was taken. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [17].

## Results and Discussion

The heterometallic copper(II) and lanthanide(III) complexes of 5-bromosalicylideneglycylglycine –  $\text{H}_3\text{L}$  ( $\text{L} = \text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$ ) were synthesized. The formulation of these complexes as  $\text{PrCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{EuCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{GdCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{TbCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$ ,  $\text{ErCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  and  $\text{YbCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  follows from elemental and thermal analysis, spectroscopic data (IR), and literature data concerning these type of compounds [15].

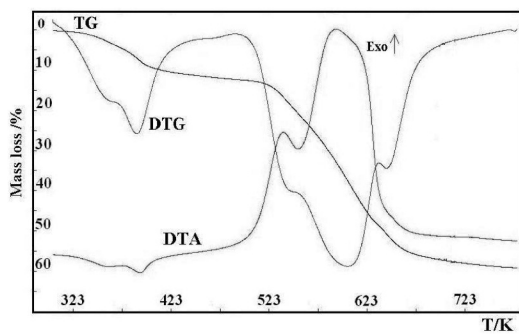
The formation of Schiff base is evidenced by an IR strong bands at *ca.*  $1646-1650 \text{ cm}^{-1}$  attributable to C=N stretching mode and the absence of bands characteristic of carbonyl and amine groups of the starting materials. The bands arising from asymmetric and symmetric vibra-

**Table 1.** Elemental analysis data of heteronuclear Cu(II)–Ln(III) (where Ln = Pr, Eu, Gd, Tb, Er and Yb, respectively) complexes with 5-bromosalicylideneglycylglycine.

Compound	H %		C %		N %		Ln %		Cu %	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found
$\text{PrCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.33	2.55	26.38	25.38	5.60	5.28	9.39	9.16	12.69	11.98
$\text{EuCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.31	2.96	26.18	26.10	5.59	5.31	10.05	10.20	12.61	12.10
$\text{GdCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.29	2.66	26.10	25.43	5.53	5.72	10.36	9.80	12.55	11.88
$\text{TbCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.29	2.62	26.01	25.15	5.21	5.53	10.46	9.98	12.55	12.30
$\text{ErCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.27	2.73	25.92	25.34	5.50	5.36	10.95	10.60	12.47	11.98
$\text{YbCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$	3.26	3.12	25.83	25.30	5.48	5.26	11.28	12.00	12.43	12.10

tions of COO<sup>-</sup> group occur at 1600–1599 cm<sup>-1</sup> and 1403–400 cm<sup>-1</sup>, respectively, which confirms that no COOH is present in the complexes. All the complexes show broad band with maximum at 3360 – 3368 cm<sup>-1</sup> due to the stretching and bending modes of water molecules. In the spectra of complexes, additional bands of medium intensity occur in the 556–560 cm<sup>-1</sup> region and may be assigned to the metal–oxygen vibration. Therefore, the metal ions in these complexes may be bridged by ligands coordinating through the oxygen atoms [18–24].

In order to verify the compositions of the 3d-4f heteronuclear compounds, to determine the temperature ranges of their thermal stability, and decomposition during heating in air and to evaluate the type of processes that occur during heating, the thermal stability of copper(II) and lanthanide(III) complexes of 5-bromosalicylidene-glycylglycine was studied in air in the temperature range of 297–773 K with the heating rate of 10 K min<sup>-1</sup>. The TG, DTG and DTA curves of decomposition process of all compounds were registered and for Cu–Gd complexes are presented in Fig. 1.



**Figure 1.** TG, DTG and DTA curves for the Cu(II)-Gd(III) complex.

During heating the dehydration process of Cu(II)-Ln(III) compounds occurs at first and it proceeds in two steps. In the first stage at *ca.* 318–453 K, the loss of mass estimated from TG curve, being equal to 10.20% (Cu-Pr), 10.40% (Cu-Eu), 9.80% (Cu-Gd), 10.10% (Cu-Tb), 10.20% (Cu-Er) and 9.90% (Cu-Yb), respectively corresponds to the loss of 8 water molecules. Theoretical values are 9.60 % (Cu-Pr), 9.50% (Cu-

Eu, Cu-Gd and Cu-Tb, ) and 9.40% (Cu-Er). The DTA curve shows the endothermic peak connected with the dehydration process that was taken place. In the second step of decomposition at 523 K–673 K the mass loss corresponds probably to the release of 5 water molecules and is connected simultaneously with the decomposition of organic ligand. Therefore the DTA curve presents mainly the exothermic peak due to the ligand decomposition. The anhydrous derivatives needed for identification could not be isolated. Considering the temperature at which the dehydration process takes place and the way by which it proceeds it may be assumed that the molecules of water are differently bounded in the complex. According to Nikolaev *et al.* [25] and Singh *et al.* [26] water eliminated below 413 – 423 K can be considered as lattice water while that eliminated above 423 K may be coordinated to the central ion. In the present investigation 8 molecules of water being eliminated below 413 K and 5 lost above 423 K reveal them to be the lattice and coordination water, respectively. The absence of clear plateau below 673 K makes the TG curves difficult for interpretation. From the obtained results it appears that 8 water molecules being lost in one step in the range of 318–453 K are the lattice water bounded in the complexes by hydrogen bonds while those of 5 molecules are coordinated to the metal ion through electron pairs on the oxygen atoms. Their presence as coordination water was confirmed by the elemental analysis done for the compounds dried at 423 K. Therefore they are supposed to be lost with the ligand thermal decomposition. However its destruction was not studied in details. The presence of 13 water molecules in analysed compounds was confirmed by the data of elemental analysis, thermal and spectral results. Until now, we have not been able to isolate crystals suitable for an X-ray structural determination. A survey of the literature shows that Y. Zou *et al.* [15] obtained and described the crystal structure complexes of Cu-La and Cu-Ce with 5-bromosalicylidene-glycylglycine as ligand. These complexes are isostructural and have general formula [Ln(H<sub>2</sub>O)<sub>5</sub>(CuL)<sub>2</sub>][CuL]·8H<sub>2</sub>O (where Ln = La, Ce and L = C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Br, respectively) Y. Zou *et al.* indicated that the crystal structure of the obtained compounds consists of a centrosymmetric hexa-

nuclear  $[\text{Ln}_2(\text{H}_2\text{O})_{10}(\text{CuL})_4]^{2+}$  ring-like cation, two  $[\text{CuL}]^-$  anions and lattice water molecules. The coordination environment of the copper(II) centres is approximately square-planar. The Schiff base ligand is deprotonated and acts as triple negatively charged quadridentate ONNO chelate, coordinated to the copper(II) via one phenolic oxygen, one deprotonated amide nitrogen atom, one imino nitrogen atom and one carboxylate oxygen atom. In the crystal there are three types of  $[\text{CuL}]^-$  sub-units. The first acts as a counter ion, the second coordinates to Ln(III) through one carboxylate oxygen and one carbonyl oxygen, and the third coordinates to Ln(III) through two carboxylate oxygens, respectively. It follows from the structure described by Y. Zou *et al.* that Ln(III) is 9-coordinated by five water molecules, three carboxylic oxygen atoms and one carbonyl oxygen. The  $[\text{CuL}]^-$  and lanthanide ions join together to form a ring structure. The hydrogen atoms of water are involved in both intra- and intermolecular hydro-

gen bonds, bonding with the carbonylic, carboxylic and phenolic oxygen of the Schiff base ligand.

The magnetic behaviour of the title compounds was studied in the temperature range 76 – 303 K and the results are presented in Table 2 and Fig. 2 as plots  $\chi_M$  and  $1/\chi_M$  versus T, where  $\chi_M$  and T denote magnetic susceptibility per molecule and absolute temperature, respectively.

The effective magnetic moment values ( $\mu_{\text{eff}}$ ) were calculated from the equations:

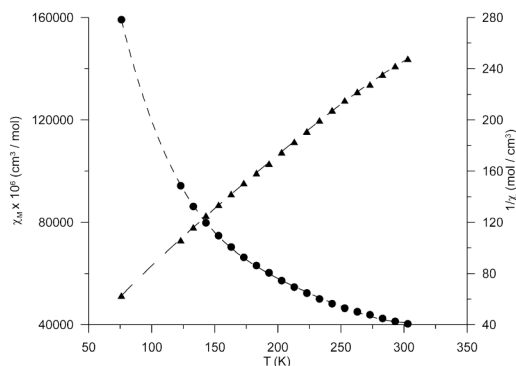
$$\mu_{\text{eff}} = 2.83 (\chi_M \cdot T)^{1/2} \quad (1)$$

$$\mu_{\text{eff}} = 2.83 [\chi_M (T - \Theta)]^{1/2} \quad (2)$$

For  $\text{GdCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  complex the magnetic susceptibility changes with temperature according to the Curie-Weiss law and the observed effective moment at 76 K is  $9.84\mu_B$ , while at room temperature it is  $9.90\mu_B$  (Table 2, Fig. 2). This value is higher than the spin only value calculated that the spin-spin interaction is

**Table 2.** The magnetic data of heteronuclear Cu(II)–Ln(III) (where Ln = Pr, Eu, Gd, Tb, Er and Yb, respectively complexes with 5-bromosalicylidene-glycine.

Temp. (K)	$\chi_M \times 10^6$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$\mu_{\text{eff}}$ ( $\mu_B$ )	Temp. (K)	$\chi_M \times 10^6$ ( $\text{cm}^3 \cdot \text{mol}^{-1}$ )	$\mu_{\text{eff}}$ ( $\mu_B$ )
<b>PrCu<sub>3</sub>(C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Br)<sub>3</sub>·13H<sub>2</sub>O</b>			<b>GdCu<sub>3</sub>(C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Br)<sub>3</sub>·13H<sub>2</sub>O</b>		
76	77236	6.86	76	159150	9.84
123	51418	7.12	123	94261	9.64
133	47699	7.13	133	86157	9.58
143	44872	7.17	143	79796	9.56
153	42413	7.21	153	74800	9.57
163	40446	7.27	163	70327	9.58
173	38663	7.32	173	66348	9.59
183	37157	7.38	183	63095	9.62
193	35682	7.43	193	60277	9.65
203	34391	7.48	203	57227	9.65
213	33131	7.52	213	54671	9.66
223	31932	7.55	223	52348	9.67
233	29504	7.42	233	50082	9.67
243	28428	7.44	243	48194	9.68
253	27598	7.48	253	46451	9.70
263	26769	7.51	263	45057	9.74
273	25969	7.54	273	43924	9.80
283	25263	7.57	283	42472	9.81
293	24463	7.58	293	41310	9.85
303	24033	7.64	303	40352	9.90



**Figure 2.** Experimental magnetic data plotted as magnetic susceptibility  $\chi_M$  (•) and  $1/\chi$  ( $\Delta$ ) versus temperature for the Cu(II)-Gd(III) complex.

absent between Cu(II) ( $S = 1/2$ ) and Gd(III) ( $S = 7/2$ ). A survey of the literature shows that for  $\text{Cu}_2\text{Gd}$  compound the spin-only value expected for isolated two Cu(II) and one Gd(III) ions is equal to  $8.30\mu_B$ . Here it should be noted that Gd(III) is a  $4f^7$  ion with a  $^8S_{7/2}$  ground state with the first excited states very high in energy. As the zero-field splittings of the ground states are fairly small, the spin-only formalism may be applied to the magnetic study of the (Cu-Gd) and (Cu-Gd-Cu) clusters [1, 5, 27-34]. According to Bencini *et al.* (in the case of compounds having one gadolinium(III) and two copper(II) ions) if the three spins  $S_{\text{Gd}} = 7/2$  and  $S_{\text{Cu1}} = S_{\text{Cu2}} = 1/2$  are allowed to interact, the resulting total spin states are one  $S = 9/2$ , one  $S = 5/2$ , and two  $S = 7/2$  [1, 29]. The calculated spin-only value for  $S = 9/2$  resulting from the ferromagnetic interaction between Cu(II) and Gd(III) ions is  $9.95\mu_B$  [33]. On the basis of literature and obtained values of effective magnetic moment which are in the range  $9.58 - 9.90\mu_B$  we can suppose that coupling between gadolinium(III) and copper(II) in analysed Cu-Gd compound is ferromagnetic.

One plausible mechanism that cause a ferromagnetic coupling between gadolinium(III) and copper(II) as proposed by C. Benelli *et al.* and O. Kahn *et al.* is the spin-polarization, that occurs when the magnetic orbital of copper(II) overlaps with the empty  $5d$  orbital of gadolinium through a filled bridging orbital. The fraction of unpaired electron, thus polarized from copper(II) to gadolinium(III) is parallel to the  $f$  electrons due to Hund's rule, affording a ferromagnetic coupling between

copper(II) and gadolinium(III). The fact that  $4f$  orbital is shielded by the outer filled  $5s$  and  $5p$  orbitals, and lanthanoid ions generally form complexes using  $6s$ , and/or  $5d$  orbitals, further supports the spin-polarization mechanism [12, 28]. Indeed, ferromagnetic coupling between gadolinium(III) and copper(II) is possible only through a superexchange interaction mediated by the bridging oxygen ligands. In other words, the magnetic orbitals centered on Gd(III) and Cu(II) must have a fairly large overlap density on the oxygen atom, which can be obtained only through a fairly substantial covalency of the Gd-O bond [1, 12, 28, 30-32]

Owing to the difficulties in analysing the magnetic properties of (Cu, Ln) pairs involving a Ln(III) ions, which possesses a first-order orbital moment [27], we restricted ourselves to consider only (Cu, Gd) complex. According to J.-P. Costes *et al.* [27] and O. Kahn *et al.* [12] for the  $4f^1-4f^6$  configurations of  $\text{Ln}^{3+}$ , angular and spin moment are antiparallel in  $^{2S+1}L_J$  free-ion ground state ( $J = L - S$ ) (where  $S$ ,  $L$  and  $J$ , are the spin, orbital and total quantum numbers, respectively). A parallel alignment of the  $\text{Cu}^{2+}$  and  $\text{Ln}^{3+}$  spin momenta would lead to an antiparallel alignment of the angular momenta, that is to an overall antiferromagnetic interaction. Conversely, for the  $4f^8-4f^{13}$  configurations ( $J = L + S$ ), a parallel alignment of the  $\text{Cu}^{2+}$  and  $\text{Ln}^{3+}$  spin momenta would result in an overall ferromagnetic interaction.

## Conclusions

The new heterometallic copper(II) and lanthanide(III) complexes of 5-bromosalicylidene-glycylglycine -  $\text{H}_3\text{L}$  ( $\text{L} = \text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$ ) having general formula  $\text{LnCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  (where Ln = Pr, Eu, Gd, Tb, Er, Yb) were synthesized. For  $\text{GdCu}_3(\text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br})_3 \cdot 13\text{H}_2\text{O}$  complex the magnetic susceptibility changes with temperature according to the Curie-Weiss law and the observed effective moment at 76 K is  $9.84\mu_B$ , while at room temperature it is  $9.90\mu_B$ . The coupling between  $\text{Gd}^{3+}$  and  $\text{Cu}^{2+}$  ions in analysed Cu-Gd compound is probably ferromagnetic.

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