

Synthesis and magnetic properties of heteronuclear 3d-4f compound

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Abstract: A novel heteronuclear 3d-4f compound having formula $\text{NdCu}_3\text{L}_3 \cdot 13\text{H}_2\text{O}$ (where H_3L = Schiff base derived from 5-bromosalicylaldehyde and glycylglycine and $\text{L}^{3-} = \text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$) was obtained. It was characterized by elemental and thermal analyses and magnetic measurements. The Cu(II)–Nd(III) compound is stable up to 323 K. During dehydration process the water molecules are lost in two stages. The magnetic susceptibility data for this complex change with temperature according to the Curie-Weiss law with $\Theta = -35$ K. The magnetic moment values decrease from $5.00\mu_{\text{B}}$ at 303 K to $4.38\mu_{\text{B}}$ at 76 K.

Keywords: heteronuclear compound, 3d-4f compound, magnetic moment; magnetic susceptibility

Introduction

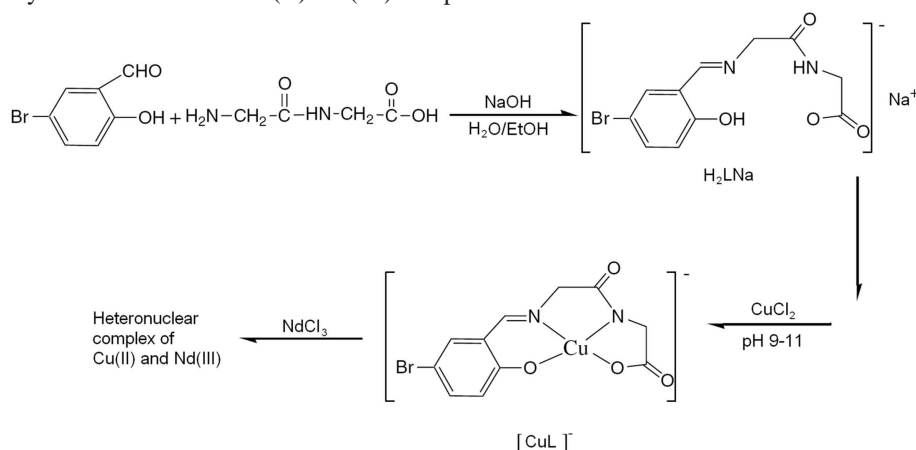
In recent years interest in heteronuclear complexes containing two different metal ions is fundamental, not only for gaining insight in the structural and electronic factors governing magnetic exchange interaction between paramagnetic centers, but also for obtaining information about designing and synthesizing molecule-based magnets and investigating the spin-exchange between paramagnetic metal ions. These compounds have potential applications in production of high temperature superconductors and magnetic materials. Compared with the studies dealing with heteronuclear system comprising *d*-transition metal ions, relatively few concern heterometal complexes containing *d*-transition metal and lanthanide(III) ions (so-called *d*-*f* heteronuclear complexes), due to the very weak interaction and the large anisotropic effect of lanthanide(III) ions. Literature survey shows also that heterometallic compounds ligated by carboxylate groups have not been well

documented; some examples of heteronuclear Cu-Ln compounds have recently been received and described. This may be attributed to the fact that Cu and Ln have different coordination capabilities. Therefore heteronuclear Cu-Ln compounds have commonly been synthesized with hetero-donor ligands, comprising two types of ligating atoms (such as N and O) coordinated each to Cu and Ln atoms, respectively [1-21]. Taking into account presented above facts and the necessity for a better understanding of the magnetic properties of this kind of compounds the present investigation was undertaken in order to prepare the 3d-4f complex and to study its magnetic and thermal properties.

Experimental details

The violet crystalline compound of $\text{NdCu}_3\text{L}_3 \cdot 13\text{H}_2\text{O}$ ($\text{L}^{3-} = \text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$) was synthesized from Schiff base (5-bromosalicylideneglycylglycine), copper(II) chloride and neodymium(III) chloride by using the adjusted procedure described in Ref. [1].

Figure 1. Synthetic route to the Cu(II)-Nd(III) compound.



The Schiff base was prepared by the reaction of the corresponding substituted salicylaldehyde with glycylglycine in the following way: 5-bromosalicylaldehyde (5 mmol) in hot aqueous-alcoholic medium with the volume ratio of 1 : 1 was added to the same volume also aqueous-alcoholic solution of glycylglycine (5mmol), and NaOH (10 mmol). The mixture was refluxed for several hours. CuCl₂·2H₂O (5mmol) was then added to the solution whose pH was finally adjusted to ~ 9. Next excess of NdCl₃ (8 mmol) was added. The solution was filtered off and the filtrate was allowed to evaporate slowly at room temperature. After a few weeks violet crystalline compound was obtained. In spite of our several efforts, single crystals suitable for X-ray crystallography measurements have not been obtained yet.

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

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

Anal. Calc. for C₃₃H₅₀O₂₅N₆Br₃Cu₃Nd: C, 26.6 %; H, 3.2 %; N, 5.7 %; Cu, 12.8 %; Nd, 9.7 %. Found: C, 27.8 %; H, 2.7 %; N, 5.5 %; Cu, 12.2 %; Nd, 10.3 %.

The dehydration process of Cu(II)-Nd(III) complex 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 K. The sample (4.86 mg) of compound was heated in Al₂O₃ crucibles with the heating rate of 10 K·min⁻¹.

The magnetic susceptibility values of the Cu(II)-Nd(III) complex were determined by Gouy method in the temperature range of 76 – 303 K. The calibrant employed was Hg[Co(SCN)₂] for which the magnetic susceptibility of 1.644·10⁻⁵ cm³g⁻¹ was taken. Correction for diamagnetism of the constituent atoms was calculated by the use of Pascal's constants [22].

Results and Discussion

The new heteronuclear compound of Cu(II)-Nd(III) with 5-bromosalicylideneglycylglycine was synthesized and its formula NdCu₃(C₁₁H₈N₂O₄Br)₃·13H₂O was established on the basis of elemental and thermal analyses and also with the use of literature data concerning these type compounds [1]. Its thermal stability was studied in air in the temperature range of 297–773 K with the heating rate of 10 K·min⁻¹. The TG, DTG and DTA curves of decomposition process were registered and are presented in Fig. 2.

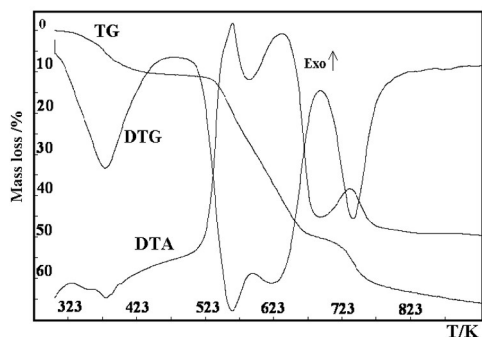


Figure. 2. TG, DTG and DTA curves for the Cu(II)-Nd(III) compound.

During heating the dehydration process of Cu(II)-Nd(III) compound occurs at first and it proceeds in two steps. In the first stage at 323–473 K, the loss of mass estimated from TG, being equal to 10.6%, corresponds to the loss of 8 water molecules (theoretical value is 9.7 %). Then DTA curve shows the endothermic peak connected with the dehydration process that was taken place. In the second step of decomposition at 535 K–673 K the mass loss corresponds 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.* [23] and Singh *et al.* [24] 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 curve difficult for interpretation. From the obtained results it appears that 8 water molecules being lost in one step in the range of 323–423 K are the lattice water bounded in the complex 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 compound 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 complex was confirmed by the data of elemental analysis, thermal and spectral results.

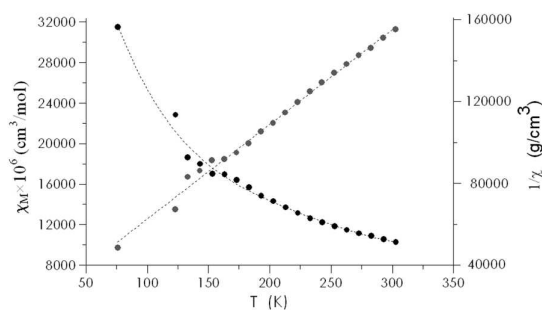


Figure. 3. Experimental magnetic data plotted as magnetic susceptibility χ_M (●) and $1/\chi$ (○) versus temperature.

In order to obtain further information on the properties of the heteronuclear complex, variable-temperature (76 ~ 303 K) magnetic susceptibility data were collected, and the results are presented in Table 1 and Fig. 3 as plots χ_M and $1/\chi$ versus T, where χ_M , χ , and T denote magnetic

susceptibility per molecule, magnetic susceptibility per gram, and absolute temperature, respectively.

Table 1. The magnetic data of $\text{NdCu}_3\text{L}_3 \cdot 13\text{H}_2\text{O}$

| Temperature (K) | $\chi_M \times 10^6$ (cm^3/mol) | $\mu_{\text{eff}} (\mu_B)$ |
|-----------------|--|----------------------------|
| | $\Theta = -$ 35.00 | |
| 76 | 31491 | 4.38 |
| 123 | 22824 | 4.74 |
| 133 | 18616 | 4.46 |
| 143 | 17985 | 4.54 |
| 153 | 17003 | 4.57 |
| 163 | 16933 | 4.70 |
| 173 | 16372 | 4.76 |
| 183 | 15657 | 4.79 |
| 193 | 14844 | 4.79 |
| 203 | 14311 | 4.83 |
| 213 | 13694 | 4.83 |
| 223 | 13147 | 4.85 |
| 233 | 12614 | 4.85 |
| 243 | 12207 | 4.88 |
| 253 | 11814 | 4.89 |
| 263 | 11464 | 4.92 |
| 273 | 11141 | 4.94 |
| 283 | 10889 | 4.97 |
| 293 | 10552 | 4.98 |
| 303 | 10286 | 5.00 |

The magnetic susceptibility changes with temperature according to the Curie-Weiss law with $\Theta = -35$ K indicating the weak antiferromagnetic interaction in this complex (Table 1, Fig. 3).

The effective magnetic moment values were calculated from the equations:

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

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

They decrease from $5.00\mu_B$ at 303 K to $4.38\mu_B$ at 76 K (Table 1, Fig. 3). This decrease could be also caused by the crystal-field effects as well as a cooperative antiferromagnetic interaction of metal ions [1, 2, 8, 9].

In order to describe the mechanism of the exchange interaction, several models have been proposed [25-27]. According to them, strict orbital orthogonality results in ferromagnetism, otherwise an antiferromagnetic coupling should be expected. The superexchange depends on

it that two or more paramagnetic atoms or ions through diamagnetic ligand may interact by coupling exchange electrons yielding the ferro- or antiferromagnetic character of substance. In principle these properties may directly result from metal-metal or ion-metal bond. However when the distance between magnetic centres is longer than 3 \AA then metal or ion orbital overlapping is not possible. At that time the molecular antiferromagnetism may occur when two transition metal ions (Cu-Nd) containing unpaired electrons interact through bridging ligand. Free electron of one metal ion (for example Cu^{2+}) forms bond with that of the opposite spin on ligand orbital. This way on the ligand orbital may be one electron having spin parallel to that on the second metal ion orbital (for example Nd^{3+}). It may create the Cu-Nd ions arrangement to be antiferromagnetically coupled.

The magnetic measurements of $\text{NdCu}_3\text{L}_3 \cdot 13\text{H}_2\text{O}$ in the temperature range of 1.7 – 76 K and the mechanism of the $d-f$ system interaction in this heteronuclear compound will be the subject of the future studies.

Conclusions

The heteronuclear Co(II)-Nd(III) compound having formula $\text{NdCu}_3\text{L}_3 \cdot 13\text{H}_2\text{O}$ was obtained by reacting $\text{Na}[\text{CuL}]$ (where $\text{L}^{3-} = \text{C}_{11}\text{H}_8\text{N}_2\text{O}_4\text{Br}$) with NdCl_3 . Its thermal stability was studied in air in the temperature range of 297–773 K. From the obtained results it appears that analysed complex contains 8 molecules of lattice water and 5 molecules that are coordination water. The various character of the water molecules confirms their different localization in the complex coordination sphere which causes its two stage dehydration process. Its magnetic moment and magnetic susceptibility values decrease with raising temperature which can be due

to crystal field effect and antiferromagnetic interactions of metal ion pairs. In the analysed Cu(II)–Nd(III) complex the free electron of Cu ion probably forms bond with that of the opposite spin on ligand orbital

and one electron on the ligand orbital with spin parallel to that on the Nd³⁺ orbital may create the Cu–Nd ion arrangement to be antiferromagnetically coupled.

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References

- [1] Y. Zou, W.-L. Liu, S. Gao, C.-S. Lu, D.-B. Dang, Q.-J. Meng, *Polyhedron*, 23 (2004) 2253.
- [2] B. Wu, W. Lu, X. Zheng, *Trans. Met. Chem.*, 28 (2003) 323.
- [3] M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, J. C. Trombe, *J. Am. Chem. Soc.*, 115 (1993) 1822.
- [4] Q. Y. Chen, Q. H. Luo, Z. L. Wang, J. T. Chen, *J. Chem. Soc. Chem. Commun.*, (2000) 1033.
- [5] X. M. Chen, M. S. J. Aubin, Y. L. Wu, Y. S. Yang, T. C. W. Mark, D. N. Hendrickson, *J. Am. Chem. Soc.*, 117 (1995) 9600.
- [6] S. Wang, Z. Pang, D. L. Smith, *Inorg. Chem.*, 32 (1993) 4992.
- [7] E. K. Brechin, S. G. Harris, S. Parson, R. E. Winpenny, *J. Chem. Soc., Dalton Trans.*, (1997) 1665.
- [8] E. Huskowska, J. Legendziewicz, *J. Alloys Comp.* 300-301 (2000) 303.
- [9] G. Oczko, J. Legendziewicz, J. Mroziński, G. Meyer, *J. Alloys Comp.* 275-277 (1998) 219.
- [10] O. Kahn, *Struct. Bond.* 68 (1987) 89.
- [11] O. Kahn, *Molecular Magnetism*, New York, Verlag-Chemie, 1993.
- [12] Y. T. Li, C. W. Yan, S. H. Miao, D. Z. Liao, *Polyhedron* 15 (1998) 2491.
- [13] N. Matsumoto, M. Ohba, M. Mitsumi, K. Inoue, Y. Hashimoto and H. Okawa, *Mol. Cryst. Liq. Cryst.* 233 (1993) 299.
- [14] K. Nakatani, J. Y. Carriat, O. Kahn, F. Lloret, J. P. Renard, P. Yu, J. Sletten, M. Verdguer, *J. Am. Chem. Soc.* 111 (1989) 5735.
- [15] A. Caneschi, D. Gatteschi, M. C. Malendri, P. Rey, R. Sessoli, *Inorg. Chem.* 29 (1990) 4228.
- [16] M. Ohba, H. Tamaki, N. Matsumoto, H. Okawa, *Inorg. Chem.* 32 (1993) 5383.
- [17] K. Nakatani, J. Sletten, S. Hault-Desporte, S. Jeannin, Y. Jeannin, O. Kahn, *Inorg. Chem.* 30 (1993) 164.
- [18] R. Cortes, M. K. Urriaga, L. Lezama, M. Isabel, T. Rajo, *Inorg. Chem.* 33 (1994) 829.
- [19] A. Chisari, A. Musmeci, M. Vidali, A. Seminara, *Inorg. Chem. Acta*, 81 (1984) 119.
- [20] K. K. Abid, D. E. Fenton, *Inorg. Chem. Acta*, 94 (1984) 73.
- [21] A. Bencini, C. Benelli, A. Caneschi, A. Dei, D. Gatteschi, *Inorg. Chem.* 25 (1993) 527.
- [22] E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer Verlag, Berlin 1966.
- [23] A. V. Nikolaev, V. A. Logvinienko, L. I. Myachina, *Thermal Analysis*, Academic Press, New York, 1969.
- [24] B. Singh, B. V. Agarwala, P. L. Mourya, A. K. Dey, *J. Indian. Chem. Soc.* 59 (1982) 1130.
- [25] P. J. Hay, J. C. Thibeault, R. Hoffman, *J. Am. Chem. Soc.* 97 (1975) 4884.
- [26] O. Kahn, M. F. Charlot, *Nouv. J. Chem.* 4 (1980) 567.
- [27] G.-M. Yang, J. Shi, S.-P. Yan, D.-Z. Liao, Z.-H. Jiang, G.-L. Wang, *Polyhedron* 17 (1998) 1587.