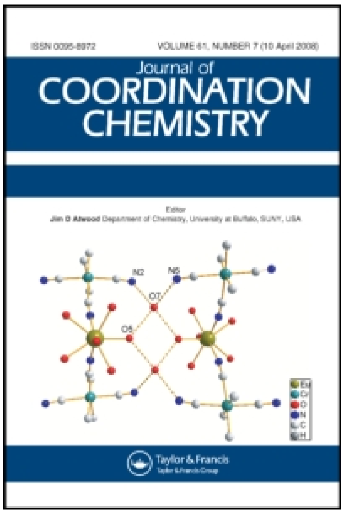

**Journal of Coordination Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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First published on: 06 December 2010

**To cite this Article** Mikhailov, O. V. and Chachkov, D. V.(2010) 'Self-assembly of supramolecular Ni(II) and Cu(II) metalmacrocyclic compounds with tetraazamacrocyclic ligand into a gelatin-immobilized matrix', Journal of Coordination Chemistry, 63: 24, 4309 — 4318, First published on: 06 December 2010 (iFirst)

**To link to this Article: DOI:** 10.1080/00958972.2010.536536

**URL:** http://dx.doi.org/10.1080/00958972.2010.536536

*Journal of Coordination Chemistry*
Vol. 63, No. 24, 20 December 2010, 4309–4318

# Self-assembly of supramolecular Ni(II) and Cu(II) metalmacrocyclic compounds with tetraazamacrocyclic ligand into a gelatin-immobilized matrix

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(*Received 14 May 2010; in final form 6 October 2010*)

Self-assembly in M(II)-ethanedithioamide [$H_2N$–C(=S)–C(=S)–$NH_2$]-propanone triple systems (M=Ni, Cu) into corresponding metal(II) hexacyanoferrate(II) gelatin-immobilized matrix systems under contact with aqueous-alkaline (pH ~ 12) solutions containing ethanedithioamide and propanone have been studied. Formation of supramolecular macrotetracyclic compounds of Ni(II) and Cu(II) with 2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2, 9-tetrathione-4,5,11,12 containing original "kernel" (metal complex) and "shell" surrounding this "kernel", of polypeptide chains of the gelatin molecules, occurs under such specific conditions.

*Keywords*: Self-assembly; Template synthesis; Supramolecular macrocyclic compound; Gelatin-immobilized matrix

## 1. Introduction

Ethanedithioamide-1,2 and dithiooxamide [$H_2N$–C(=S)–C(=S)–$NH_2$] are known to be good (N,S)-donor polydentate ligands forming stable chelate coordination compounds with a number of d-element ions, for example Ni(II) and Cu(II) [1]. Previously [2–9], we analyzed complexing processes proceeding in the M(II)-dithiooxamide system (M=Ni, Cu), when nickel(II)- and copper(II)-hexacyanoferrate(II) gelatin-immobilized matrix (**GIM**) is in contact with water-alkaline solutions of dithiooxamide. A series of gelatin-immobilized coordination compounds, which had not been observed before in solution or in the solid phase, could be obtained under these non-traditional conditions for coordination chemistry. Ethanedithioamide-1,2 is capable of participating in

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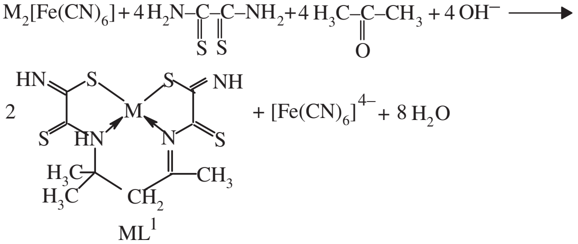
*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.536536

complexing as a ligand as well as acting as a ligand synthon in self-assembly processes of macrocyclic coordination compounds (known usually as template synthesis); organic compounds containing C=O groups may be other ligand synthons. One such compound is propanone $H_3C–C(=O)CH_3$.

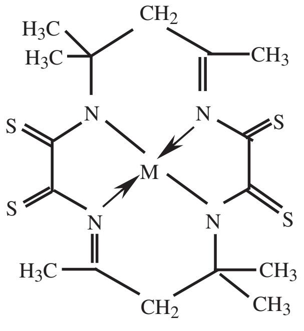
Gelatin is a high-molecular weight polypeptide containing intermolecular nano-sized cavities. These cavities may be considered as molecular nano-reactors and in them template syntheses may be realized that do not occur in solution or in the solid phase. Owing to the availability of intermolecular interactions, metal macrocyclic complexes formed in such cavities are bound rather strongly together in gelatin molecules; as a result, peculiar supramolecular compounds arise. Each contains original "kernel" (metal complex) and "shell" surrounding this "kernel" of polypeptide chains of gelatin molecules. In addition, within the "kernel" covalent bonds are realized; between "kernel" and "shell", intermolecular bonds occur [10]. Self-assembly processes in the M(II)-ethanedithioamide-1,2-propanone triple systems (M = Co, Ni, or Cu) proceed into corresponding metal(II) hexacyanoferrate(II) **GIMs** ($M_2[Fe(CN)_6]$-**GIM**) [11–19]. Formation of **ML¹** macrotricyclic complexes according to reaction (1), in the course of which, template "stitching" with the formation of one additional six-membered metal cycle, takes place in the given systems:



ML¹

(1)

Theoretically macrotetracyclic complexes, **ML²**, containing two additional six-membered metal cycles may be formed in the triple systems:



**ML²**

This article is devoted to establishing whether such macrotetracyclic complexes occur in $M_2[Fe(CN)_6]$-**GIM** in the M(II)-ethanedithioamide-1,2-propanone triple systems, where M = Ni or Cu, as a result of self-assembly processes proceeding at room temperature.

## 2. Experimental

$Ni_2[Fe(CN)_6]$- and $Cu_2[Fe(CN)_6]$-**GIM** were prepared according to the procedure described [2, 6, 7, 20]. As initial material for this purpose, commercial X-ray film "Structurix D-10" was used. The examples of given film were exposed with X-ray radiation with doses in 0.01–1.0 Röntgen range. Then, they were subjected to standard processing used in silver-halide photography [21] with water solution containing ($g\,L^{-1}$): methol (2.2), hydroquinone (8.8), $Na_2SO_3$ (96.0), $Na_2CO_3$ (48.0), and KBr (2.5) (known in silver-halide photography as developer **D-19**) during 6 min at 20°C. Afterwards, they were washed 5 min with running water, processed with 25% water solution of $Na_2S_2O_3$ for 15 min at 20°C and, again, washed with running water for 15 min. The objects obtained as a result (which are nothing but Ag **GIM**) were processed with water solution containing ($g\,L^{-1}$): $K_3[Fe(CN)_6]$ (50.0), $K_4[Fe(CN)_6]$ (20.0), KOH (10.0), and $Na_2CO_3$ (5.0) during 30 min at 20°C. As a result, the formation of $Ag_4[Fe(CN)_6]$-**GIM** takes place according to the reaction described by equation (2) (here and subsequently, substances immobilized into **GIM** have been marked with **bold type**).

$$4\mathbf{Ag} + 4[Fe(CN)_6]^{3-} \rightarrow \mathbf{Ag_4[Fe(CN)_6]} + 3[Fe(CN)_6]^{4-} \qquad (2)$$

Next, these matrices were contacted with $0.1\,mol\,L^{-1}$ water solutions of $NiCl_2$ or $CuCl_2$. As a result of such contact, the formation of nickel(II)hexacyanoferrate(II) and copper(II)hexacyanoferrate(II) occurs according to reactions (3) and (4), respectively.

$$\mathbf{Ag_4[Fe(CN)_6]} + 2NiCl_2 \rightarrow \mathbf{Ni_2[Fe(CN)_6]} + 4\mathbf{AgCl}, \qquad (3)$$

$$\mathbf{Ag_4[Fe(CN)_6]} + 2CuCl_2 \rightarrow \mathbf{Cu_2[Fe(CN)_6]} + 4\mathbf{AgCl}. \qquad (4)$$

Finally, samples were processed with 25% water solution of $Na_2S_2O_3$ during 5 min at 20°C and washed with running water for 15 min. The resulting matrices having a metal(II)hexacyanoferrate(II) concentration ($C_F$) in the $0.1–2.0\,mol\,dm^{-3}$ range were then treated with an aqueous solution containing ethanedithioamide-1,2 + propanone; the concentration of ethanedithioamide-1,2 in such solutions was $1.0 \times 10^{-3}–5.0 \times 10^{-2}\,mol\,dm^{-3}$. It may be expected that macrotetracyclic complexes of type $\mathbf{ML^2}$ will be formed at higher ethanedithioamide-1,2 : propanone molar ratio than macrotricyclic complexes of type $\mathbf{ML^1}$, which is formed at ethanedithioamide-1,2 : propanone molar ratio in 0.5–1.5 range [11–19]. In this work the molar ethanedithioamide-1,2 : propanone ratio varied from 0.2 to 0.5 at a fixed pH $12.0 \pm 0.1$. As previously [11–13, 15], this pH was chosen because at this pH essentially complete transformation of ethanedithioamide-1,2 into its singly deprotonated form occurs which then participates with propanone and $M_2[Fe(CN)_6]$ in self-assembly, and no deformation of polymer binder of the immobilized matrix occurs. The contact time for $M_2[Fe(CN)_6]$-**GIM** with ethanedithioamide-1,2 + propanone was 1–10 min at $20.0 \pm 0.5$°C. After completing the complexing process, the gelatin layers containing the M(II) chelate complexes were washed with running $H_2O$ for 15 min and then dried at room temperature.

In order to determine the empirical formulae for coordination compounds formed in the **GIM**, these compounds were isolated from the corresponding matrices by treating them with the solutions of proteolytic enzyme (i.e. trypsine) as described [5]. The precipitates isolated from **GIM** were subjected to chemical analysis by conventional procedures. Specially performed experiments for studying complexing M(II)-ethanedithioamide-1,2-propanone, with the samples of $M_2[Fe(CN)_6]$-**GIM** prepared using different types of gelatin, indicated that the complexing process in each system under examination is independent of the gelatin type. Thus, we can state that gelatin does not act as a ligand in the complexing process in the triple systems considered here; nevertheless, the polypeptide chains of gelatin create a "shell" around the molecules of corresponding macrocyclic chelate complexes formed from self-assembly into **GIM**.

To determine molecular masses of complexes obtained, Matrix-Assisted Laser Desorption/Ionization Time of Flight mass spectra (MALDI TOF) was used. MALDI TOF mass spectra of substances isolated from **GIM** were obtained using a Dynamo (Finnigan) and 4-nitroaniline matrix at 500 MHz frequency and 55.25 units of laser power. Electron absorption spectra of the **GIM** were recorded using Specord UV-VIS (Karl Zeiss, Germany) and PU-8710 (Philips, The Netherlands) spectrophotometers from 400 to 800 nm. To record IR spectra, a UR-20 spectrometer (Karl Zeiss, Germany) was employed.

## 3. Results and discussion

In the **Ni(II)-ethanedithioamide-1,2-propanone system**, at $C_F = 0.1–2.0\,\mathrm{mol\,dm^{-3}}$, $C_L{}^o = 5.0 \times 10^{-3}–5.0 \times 10^{-1}\,\mathrm{mol\,dm^{-3}}$, ethanedithioamide-1,2 : propanone molar ratio of 0.2–0.3 and $t = 2–10$ min, Ni**L**$^{\mathbf{2}}$ is formed into the **GIM**, coloring the gelatin mass greenish-brown. This color is retained upon treatment with both acid and alkali. There is the tail of an intensive absorption where maximum is in the UV region in the spectrum of this compound. Coloring **GIM** greenish brown is obtained into the polymer mass only on contact of $Ni_2[Fe(CN)_6]$-**GIM** with water-alkaline solutions containing ethanedithioamide-1,2 + propanone; in the absence of propanone, the formation of Ni(II)-ethanedithioamide-1,2 complex coloring the gelatin mass pinkish-violet occurs [11], showing that both ethanedithioamide-1,2 and propanone participate in the complexing process. Yield of Ni**L**$^{\mathbf{2}}$ is 40%–45% from theoretically expected value.

In the **Cu(II)-ethanedithioamide-1,2-propanone system**, at $C_F = 0.1–2.0\,\mathrm{mol\,dm^{-3}}$, $C_L{}^o = 3.0 \times 10^{-3}–2.0 \times 10^{-1}\,\mathrm{mol\,dm^{-3}}$, ethanedithioamide-1,2 : propanone molar ratio of 0.2–0.3 and $t = 2–10$ min, Cu**L**$^{\mathbf{2}}$ coloring the gelatin mass greenish-brown, is formed in the **GIM**. This color is retained upon treatment with acid or alkali. Compound coloring the **GIM** greenish-brown is formed in the polymer only when $Cu_2[Fe(CN)_6]$-**GIM** is in contact with aqueous-alkaline solutions containing ethanedithioamide-1,2 as well as propanone. Yield of Cu**L**$^{\mathbf{2}}$ is 45–50% from theoretically expected value.

The color of polymeric masses containing Ni**L**$^{\mathbf{2}}$ and Cu**L**$^{\mathbf{2}}$ may be connected either with the formation of heteroligand M(II) coordination compounds containing ethanedithioamide-1,2 and propanone or with intraspheric change of these organic compounds leading to the formation of M(II) chelates with some unknown ligands formed from ethanedithioamide-1,2 and propanone. However, there is no data in the literature about the complexing of Ni(II) or Cu(II) with propanone. Moreover, treating

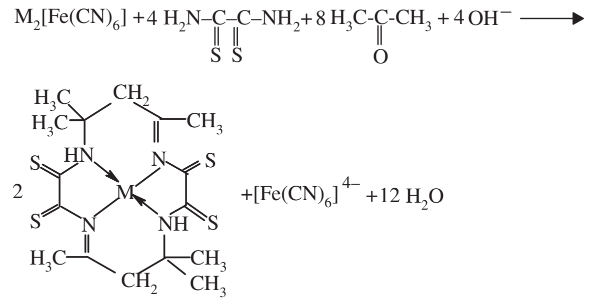
$Ni_2[Fe(CN)_6]$-**GIM** or $Cu_2[Fe(CN)_6]$-**GIM** with water-alkaline solutions of propanone, no changes of spectral characteristics of gelatin mass are observed. This shows that Ni(II) and Cu(II) complexes with propanone are formed neither by complexing in the **GIM**, nor in solution, perhaps because propanone is a hard base whereas Ni(II) and Cu(II) are rather soft acids [22].

Experiments indicated that no gelatin-immobilized M(II)-ethanedithioamide-1,2 chelates formed by complexing in the $Ni_2[Fe(CN)_6]$-**GIM** and $Cu_2[Fe(CN)_6]$-**GIM** [2–9] did not interact with water-alkaline solutions of propanone at any pH or concentration of reagent. Absorption spectra of water solutions containing only ethanedithioamide-1,2 and water solutions containing ethanedithioamide-1,2 + propanone at $pH > 9.0$ are identical. We assume that the formation of some unknown ligand from ethanedithioamide-1,2 and propanone takes place in both M(II)-ethanedithioamide-1,2-propanone triple systems under examination. Formation of such a ligand occurs only if there is a Ni(II) or Cu(II) in the system. The circumstance noted allow to maintain that in the M(II)-ethanedithioamide-1,2- propanone systems at the complexing in the corresponding $M_2[Fe(CN)]_6$-GIM, the template synthesis which is well known in coordination chemistry (see, for example, [23]), occurs.

When the **GIM** containing Ni**L**$^2$ and Cu**L**$^2$ are destroyed [5], the greenish-brown substances having empirical formula $C_{16}H_{22}MN_4S_4$ (M=Ni, Cu) may be isolated. In the case of M=Ni, calculated for this formula are (%): C 41.84, H 5.26, Ni 12.78, N 12.20, S 27.92; found (%): C 42.1, H 5.1, Ni 12.7, N 12.0, S 28.2. In the case of M=Cu, calculated for this formula are (%): C 41.40, H 5.21, Cu 13.69, N 12.07, S 27.63; found (%): C 41.3, H 5.3, Cu 13.4, N 11.9, S 28.1. According to X-ray diffraction analysis, each substance is only one phase and, hence, is an individual chemical compound. MALDI TOF mass-spectra of substances isolated from **GIM** containing Ni**L**$^2$ and Cu**L**$^2$ showed that they had molecular mass equal to 458.9 c.u. and 464.7 c.u., respectively, in full agreement with the $C_{16}H_{22}NiN_4S_4$ and $C_{16}H_{24}CuN_4S_4$ formulae (the molecular mass calculated are 459.32 c.u. and 464.16 c.u., respectively). Both these coordination compounds are practically insoluble in ethanol, acetone, chloroform, benzene, and tetrachloromethane but are weakly soluble in DMF, DMSO, and HMPT. UV-Vis spectra of DMF and DMSO solutions of these compounds practically coincide with those of a polymer mass from which they were isolated. The DTA data show that these compounds are very stable and are not destroyed even at 600°C.

There are not many characteristic bands in IR spectra of these complexes. A $\nu$(NH) band at 3400–3500 cm$^{-1}$ is characteristic for NH uncoordinated to central metal ion and is present in the prepared complexes (at 3420 and 3435 cm$^{-1}$, respectively). In addition, IR spectra exhibit a $\nu$(C=N) band at 1630 cm$^{-1}$ (Ni) and 1620 cm$^{-1}$ (Cu) (usually observed at 1625–1690 cm$^{-1}$) [24], indicating the presence of C=N groups in Ni**L**$^2$ and Cu**L**$^2$. Also, in the spectra of these compounds, bands at 3000–3050 cm$^{-1}$ related [17] to $\nu(CH_2)$ and at 3050–3070 cm$^{-1}$ related to $\delta(CH_3)$ are observed. These bands are absent in IR spectra of ethanedithioamide-1,2 and in IR spectra of coordination compounds of M(II) with this ligand [7, 9]. Hence, there are $CH_2$ and $CH_3$ in Ni**L**$^2$ and Cu**L**$^2$.

It may be concluded that Ni**L**$^2$ and Cu**L**$^2$ are macrocyclic coordination compounds with 2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2,9-tetrathione-4,5,11,12, namely (2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2,9-tetrathione-4,5,11,12)nickel(II) and (2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradeca-dien-2,9-tetrathione-4,5,11,12)copper(II), respectively, and the processes of their formation are described in scheme 1 (M = Ni, Cu).



Scheme 1. The general equation of formation of Ni$L^2$ and Cu$L^2$ complexes into **GIM**.

Formation of complexes is possible because in our case surplus propanone over ethanedithioamide-1,2 allows "stitching" (and, correspondingly, the formation of six-membered metal chelate) with the participation of all four nitrogen donors with M(II). In previous works [11–20], synthesis was carried out under the deficiency of oxygen-containing ligand (propanone), and that is why "stitching" with participation of only two nitrogen donors of four occurs there.

Processes according to scheme 1 are observed *only* in **GIM**. All our attempts to realize *such processes* with solid $Ni_2[Fe(CN)_6]$ and $Cu_2[Fe(CN)_6]$ with aqueous solutions of ethanedithioamide-1,2 + propanone at room temperature were unsuccessful. Our attempts to realize such processes in homogeneous medium were unsuccessful, from the interaction of water solutions of M(II) salts (i.e. $NiCl_2$ and $CuCl_2$) with mixtures indicated above. Under such conditions, only Ni(II) and Cu(II) coordination compounds with ethanedithioamide-1,2 are formed in the ($C_F$, $C_L{}^o$, $t$) range studied.

We failed to carry out XRD analysis of single crystals prepared in the $M_2[Fe(CN)_6]$-**GIM** because, by this method of isolation from the gelatin mass, they were obtained either as amorphous or as extremely small crystals unsuitable for diffraction. For this reason, exact structures of Ni(II) and Cu(II) compounds remain an open question, but it is possible to make reliable forecast concerning these structures by quantum-chemical calculation methods. Quantum-chemical calculation of molecular structures of metal macrotetracyclic coordination compounds formed in the M(II)-ethanedithioamide-1,2-propanone triple systems is possible. One of the most suitable and reliable methods for such calculation is hybrid method of the density functional theory DFT B3LYP. DFT B3LYP level of theory with the 6-31G(d) basis set [25, 26] in Gaussian 98 [27] was used to calculate basic geometric parameters of their structures; some results are discussed below. Such quantum-chemical calculation of metal complexes was made by us for the first time in the chemistry of template synthesis.

Some details of these structures are presented in table 1. Minimum energy corresponds to the complexes of M(II) with strong plane (NNNN) chelation (sum of (N1)(N2)(N3), (N2)(N3)(N4), (N3)(N4)(N1), and (N4)(N1)(N2) valence angles in the case of Ni(II) is 359.47°, in the case of Cu(II), 356.79°) showing $MN_4$ chelate is planar, too (sum of (N1)(M)(N2), (N2)(M)(N3), (N3)(M)(N4), and (N1)(M)(N4) valence angles for Ni(II) and Cu(II) is very near to 360°; table 2). The lengths of M–N bonds in both complexes differ among themselves (table 1). The lengths of carbon–nitrogen and carbon–sulfur bonds are practically equal. In each complex, bond lengths and valence angles in six-membered metal cycles are not equal; for example, in Cu$\mathbf{L^2}$, in the cycle

Table 1. Some parameters of molecular structure of supramolecular Ni(II) and Cu(II) complexes with 2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2,9-tetrathione-4,5,11,12.

| | $C_{16}H_{22}NiN_4S_4$ (Ni$\mathbf{L}^2$) | $C_{16}H_{24}CuN_4S_4$ (Cu$\mathbf{L}^2$) |
|---|---|---|
| *Selected bond lengths (pm)* | | |
| Bond | | |
| M–N1 | 189.9 | 195.1 |
| M–N2 | 194.7 | 202.2 |
| M–N3 | 186.1 | 193.9 |
| M–N4 | 192.6 | 198.2 |
| C4–N3 | 143.3 | 141.6 |
| C2–N1 | 144.1 | 143.0 |
| C2–S1 | 167.9 | 169.0 |
| N1–C5 | 130.3 | 130.6 |
| N2–C6 | 153.3 | 151.6 |
| N3–C8 | 129.9 | 130.1 |
| N4–C7 | 155.3 | 154.1 |
| *Selected valence angles (grad)* | | |
| Angle | | |
| (N1)(M)(N2) | 99.1 | 104.8 |
| (N2)(M)(N3) | 84.7 | 80.3 |
| (N3)(M)(N4) | 90.0 | 91.1 |
| (N4)(M)(N1) | 6.1 | 85.7 |
| Sum of valence angles at M atom | 359.8 | 361.8 |
| (M)(N1)(C2) | 111.3 | 113.0 |
| (M)(N4)(C1) | 109.4 | 110.8 |
| (N1)(C2)(C1) | 109.6 | 113.1 |
| (N4)(C1)(C2) | 111.1 | 114.3 |
| (N1)(C5)(C11) | 119.8 | 117.3 |
| (N2)(C6)(C11) | 106.0 | 104.7 |
| (N3)(C8)(C15) | 116.0 | 114.5 |
| (N4)(C7)(C15) | 108.8 | 108.6 |
| *Selected torsion angles (grad)* | | |
| Angle | | |
| (M)(N1)(C5)(C11) | 14.7 | 19.5 |
| (M)(N2)(C6)(C11) | 68.0 | 43.7 |
| (M)(N3)(C8)(C15) | 1.4 | 2.3 |
| (M)(N4)(C7)(C15) | 18.3 | 17.0 |
| (N1)(C5)(C11)(C6) | 37.9 | 68.0 |
| (N2)(C6)(C11)(C5) | 67.6 | 79.8 |
| (N3)(C8)(C15)(C7) | 57.6 | 65.6 |
| (N4)(C7)(C15)(C8) | 44.1 | 50.4 |
| (N1)(C2)(C1)(N4) | 38.7 | 25.4 |

formed by Cu, N1, C5, C11, C6, and N2, the lengths of N1–C5 and N2–C6 bonds is 130.6 and 151.6 pm whereas in the cycle formed by Cu, N3, C8, C15, C7, and N4, the analogous lengths of N3–C8 and N4–C7 bonds is 130.0 and 154.1 pm; similar situation occurs for valence and torsion angles. For example, (N1)(C5)(C11) angle is 117.3°, (N2)(C6)(C11), 104.8°, analogous angles (N3)(C8)(C15) and (N4)(C7)(C15) are 114.5° and 108.6°, respectively (table 1). However, the angles (C5)(C11)(C6) and (C7)(C15)(C8) are equal to each other (117.4° and 117.3°). In the Ni(II) complex, valence angles indicated some differences (119.3° and 117.5°, respectively). Torsion angles (N1)(C5)(C11)(C6) and (N2)(C6)(C11)(C5) in the first additional cycles are 68.0° and 79.8°, whereas analogous angles (N3)(C8)(C15)(C7) and (N4)(C7)(C15)(C8) in the second cycle are 65.6° and 50.4°, respectively. Also, there are no reasons to consider

Table 2. Calculated and observed IR frequencies.

| Frequency | | Value of given frequency in $C_{16}H_{22}NiN_4S_4$ ($Ni\mathbf{L}^2$) | | Value of given frequency in $C_{16}H_{24}CuN_4S_4$ ($Cu\mathbf{L}^2$) | |
|---|---|---|---|---|---|
| | | Calculated | Experimental | Calculated | Experimental |
| $\nu$(C=N) | (N5)(C1) | 1620 | 1630 | 1599 | 1620 |
| | (N3)(C8) | 1635 | | 1619 | |
| $\nu(CH_2)$ | (C11)(H8)(H9) | 2998 | 3000 | 3026 | 3020 |
| | (C15)(H19)(H20) | 3028 | | 3015 | |
| $N(CH_3)$ | (C9)(H2)(H3)(H4) | 3062, 3069 | 3050 | 3065 | 3060 |
| | (C10)(H5)(H6)(H7) | 3062, 3069 | | 3043 | |
| | (C12)(H10)(H11)(H12) | 3064 | | 3057 | |
| | (C13)(H13)(H14)(H15) | 3069 | | 3068 | |
| | (C14)(H16)(H17)(H18) | 3046 | | 3047 | |
| | (C16)(H21)(H22)(H23) | 3060 | | 3055 | |
| N(NH) | (N2)(H1) | 3415 | 3420 | 3415 | 3430 |
| | (N4)(H24) | 3425 | | 3456 | |
| N(C=S) | (C1)(S4) | 1109 | 1100 | 1139 | 1150 |
| | (C2)(S1) | 1109 | | 1139 | |
| $\nu$(C=S) | (C3)(S2) | 1139 | 1140 | 1142 | 1150 |
| | (C4)(S3) | 1139 | | 1142 | |

that two five-membered cycles are identical, valence angles (M)(N1)(C2), (M)(N4)(C1), (N4)(C1)(C2), and (N4)(C1)(C2) in the metal chelate cycle formed by Cu, N1, C2, C1, and N4, are 113.1°, 107.8°, 114.3° and 113.1°, whereas analogous angles (M)(N3)(C4), (M)(N2)(C3), (N2)(C3)(C4), and (N3)(C4)(C3) in the metal chelate cycle formed by Cu, N2, C3, C4, and N3, are 110.4°°, 103.7°, 112.1°, and 112.4°. The molecular structure of macrotetracyclic $Cu\mathbf{L}^2$ under examination with numbering of atoms is shown in figure 1. Each six-membered cycle formed as a result of template reaction was not of the same flatness with $MN_4$ alignment. The similar situation occurs in the $Ni\mathbf{L}^2$ complex also.

Torsion angle between the flatness of additional cycle and flatness of $N_4$, namely (N3)(N1)(N4)(C7), (N1)(N3)(N2)(C6), (N2)(N4)(N1)(C5), and (N4)(N1)(N3)(C8), are 88.1°, 70.3°, 74.9°, and 47.4° (Ni) and 85.9°, 14.9°, 25.1° and 53.5° (Cu). None of these six-membered cycles is itself planar – carbon of $CH_2$ is deflected from N–$CH_2$–$CH_2$–N plane on some angle; for example, torsion angles (N1)(N2)(C5)(C11) and (N3)(N4)(C8)(C15) are 176.8°, 146.8° ($Ni\mathbf{L}^2$) and 152.7°, 142.0° ($Cu\mathbf{L}^2$), respectively. M–N bond lengths calculated (186.1–194.7 pm for $Ni\mathbf{L}^2$ and 193.9–202.2 pm for $Cu\mathbf{L}^2$) are in the range of M–N bond lengths found experimentally in macrocyclic complexes having $MN_4$ coordination (176–211 pm and 188–216 pm, respectively).

According to the calculations, $Ni\mathbf{L}^2$ and $Cu\mathbf{L}^2$ have rather considerable electric dipole moments, 2.62 and 7.76 Debye units, respectively. Both are asymmetric, however a high value of electric dipole moment for Cu(II) complex shows that its asymmetry is bigger than in the Ni(II) complex.

Calculation of $\nu$(C=N), $\nu(CH_2)$, $\nu(CH_3)$, $\nu$(C=S), and $\nu$(NH) in IR spectra of macrotetracyclic Ni(II) and Cu(II) complexes with 2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2,9-tetrathione-4,5,11,12 are presented in table 2. The calculated values of characteristic frequencies are in good agreement with experimental data. Calculation of $\Delta G^0_{298}$ for reactions in scheme 1 with variant DFT B3LYP method

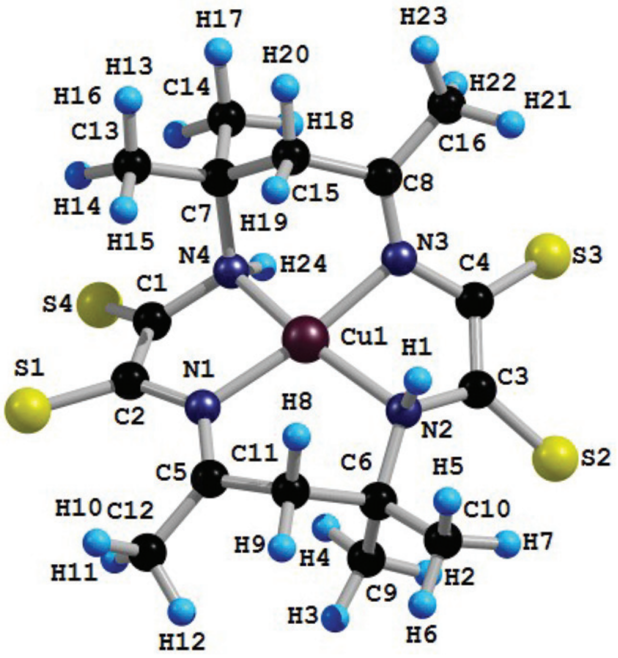


Figure 1 The molecular structure of (2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclo-tetradecadien-2, 9-tetrathione-4,5,11,12)copper(II).

gives values 796.8 kJ for the Ni**L**$^2$ complex and 706.5 kJ for the Cu**L**$^2$ complex, both positive and, hence, the reactions in *in solution* and in the *gas phase* at room temperature are *thermodynamically forbidden*. On the other hand, it may be easily shown that for these reactions *in solution* and in the *gas phase* $\Delta S^0_{298} < 0$; hence, they are thermodynamically forbidden at higher temperatures, too. Such reactions, however, may be realized in a number of cases in gelatin-immobilized matrices where [19], preliminary ‘‘regulation’’ of reaction system and ‘‘compulsory’’ decrease of entropy take place and the reactions were observed.

## 4. Conclusion

Under conditions of self-assembly in Ni(II)-ethanedithioamide-1,2-propanone and in Cu(II)-ethanedithioamide-1,2-propanone triple systems in **GIM**, formation of macrotetracyclic coordination compounds of nickel(II) and copper(II) with 14-membered tetraazacyclic ligand – 2,7,7,9,14,14-hexamethyl-3,6,10,13-tetraazacyclotetradecadien-2,9-tetrathione-4,5,11,12 is observed with metal ion : ligand ratio of 1 : 1. Both complexes have pronounced non-coplanar structures. The formation of these complexes occurs only in **GIM** but not in solution or in the solid phase. Reviews [14, 17] and original articles [28, 29] showed similar circumstance for a number of other (metal ion – (N,O,S)-ligand – carbonyl-containing ligand) triple systems; the system studied in this article is a good evidence in favor of specification of complexing into **GIM** systems.

## Acknowledgments

The financial support from Russian Foundation of Basic Researches (RFBR), grant no. 09-03-97001 is acknowledged. The authors are also grateful to the Supercomputer Center of RAS where all quantum-chemical calculations were carried out.

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