



SELF-ASSEMBLY OF SUPRAMOLECULAR COMPLEX OF Zn(II) AND 2,7-DITHIO-3,6-DIAZAOCTADIEN-3,5-DITHIOAMIDE-1,8 IN AN IMMOBILIZED Zn₂[Fe(CN)₆]-GELATIN MATRIX

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Keywords: template synthesis; gelatin-immobilized matrix; zinc(II) ethanedithioamide; DFT method; 2,7-dithio-3,6-diazaoctadien-3,5-dithioamide-1,8; self-assembly

A new complex formation process was occurred in the Zn(II)–ethanedithioamide–ethanedial three-components system when a nano-reactor consist of zinc(II) hexacyanoferrate(II)-gelatin immobilized matrix was contacted with an aq. alkaline (pH~12) solutions containing ethanedithioamide and ethanedial. It has been shown that self-assembly (template synthesis) of supramolecular (555)macrotricyclic Zn(II) coordination compound with chelating ligand 2,7-dithio-3,6-diazaoctadien-3,5-dithioamide-1,8 occurs under these conditions. Besides, ethanedithioamide and ethanedial act as ligand synthons in this process.

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Introduction

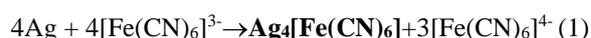
Complex formation processes proceeding in Co(II)–dithiooxamide–glyoxal, Ni(II)–dithiooxamide–glyoxal and Cu(II)–dithiooxamide–glyoxal systems under contact of corresponding metal(II) hexacyanoferrate(II)-gelatin-immobilized matrix (GIM) with aqueous-alkaline solutions containing dithiooxamide (ethanedithioamide) H₂N–C(=S)–C(=S)–NH₂ (EDTHA) and glyoxal (ethanedial) (EDA) HC(=O)–CH(=O), were described and analyzed.¹⁻⁴ The room-temperature self-assembly (template synthesis) of novel coordination compounds that was not formed in solution or the solid phase could be occurred in these specific conditions; besides, EDTHA and EDA were acted as ligand synthones in given process.

This paper is devoted to study similar self-assembly processes in the Zn(II)–EDTHA–EDA ternary system with using zinc(II) hexacyanoferrate(II)-gelatin-immobilized matrix (Zn₂[Fe(CN)₆]-GIM) at room temperature.

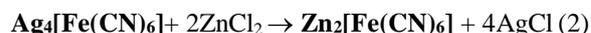
Experimentals

Zn₂[Fe(CN)₆]-GIM was prepared according to the original procedure.⁵ Commercial X-ray film “Structurix D-10” was used as starting material. The samples were exposed with X-ray radiation with exposing doses of 0.01–1.0 Röntgen. Then, they were subjected to standard processing used in silver-halide photography⁶ with treatment an aq. solution containing (g·L⁻¹) the following chemicals: methol 2.2,

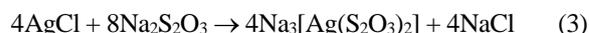
hydroquinone 8.8, Na₂SO₃ (96.0), Na₂CO₃ (48.0) and KBr (2.5) (this solution is known in silver-halide photography as developer D-19) for 6 min at 20 °C. After washing with running water for 5 min, the samples were treated with a 25 % aq. solution of Na₂S₂O₃ for 15 min at 20 °C and a running water washing was done for 15 min. The samples obtained as a result of given procedure (**Ag-GIM**) were treated with an aq. solution containing (g·L⁻¹): K₃[Fe(CN)₆] (50.0), K₄[Fe(CN)₆] (20.0), KOH or NaOH (10.0) and Na₂CO₃ (5.0) for 30 min at 20 °C. This treatment results formation of **Ag₄[Fe(CN)₆]-GIM** according to the reaction described by equation (1) (here and subsequently, substances immobilized into GIM, have been marked with bold type)



These matrixes were contacted with 0.1 M aq. solutions of zinc(II) chloride. The formation of zinc(II) hexacyanoferrate(II) and silver(I) chloride are occurred according to reaction (2):



Finally, the samples obtained were contacted with a 25 % aq. solution of Na₂S₂O₃ at 20 °C for 5 min in order to remove AgCl from the matrix which results a zinc(II)hexacyanoferrate(II) containing GIM matrix according to the reaction (3)



The Zn₂[Fe(CN)₆]-GIM samples obtained in this way were washed with running water for 15 min. The resulting matrixes having 0.1-2.0 mol·dm⁻³ zinc(II) hexacyanoferrate(II) concentration (C_F).

The samples were treated with an aqueous solutions containing the mixture (EDTHA + EDA). The concentration of EDTHA in the solutions (C_L^0) was $(1.0 \cdot 10^{-3} - 5.0 \cdot 10^{-1} \text{ mol} \cdot \text{dm}^{-3})$. The molar EDTHA: EDA ratio was varied between 0.5 to 2.0, pH of the solutions were 12.0 ± 0.1 . The contact time of GIM with the EDTHA + EDA mixture solutions was 1-10 min at $20.0 \pm 0.5^\circ\text{C}$. The gelatin layers containing the Zn(II) chelate complexes were washed with running H_2O for 15 min and then dried at room temperature. In order to determine the empirical formulas of coordination compounds formed in the GIM, these compounds were isolated from the corresponding matrixes by treating them with solutions of proteolytic enzyme (e.g. trypsin) as described in literature.⁷ The Zn-complex containing GIM samples were placed in a 3 % aq. solution of trypsin or proteolytic enzyme of *Bacillus mesentericus*, then the solution was heated to $35-40^\circ\text{C}$ and hold at this temperature until the gelatinous layer of GIM was completely disappeared (typically it takes 15-20 min). The precipitate formed was filtered off from the mother liquor, washed with water and dried at room temperature. The yield of Zn(II) chelate complex was in range 80-85 %. The precipitates isolated from GIM phase in the abovementioned way were subjected to chemical analysis. In order to determine the molecular masses of complexes obtained a Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass spectroscopy (MALDI TOF) method was used with registration positively charged molecular ions (positive mode) signals. MALDI TOF mass spectra of substances isolated from GIM were obtained using a Dynamo (Finnigan) instrument in 4-nitroaniline matrix at 500 MHz frequency and 55.25 units of laser power.

Electron absorption spectra of the GIM substances were recorded using Specord UV-VIS (Karl Zeiss, Germany) and PU-8710 (Philips, The Netherlands) spectrophotometers in the 400-800 nm range. In order to record IR spectra in the 400-4000 cm^{-1} range, UR-20 and Specord M-80 spectrometers (Karl Zeiss, Germany) were used. The samples for IR measurements were suspended in vaseline oil. Thermal studies were made with using a Derivatograph 1000D (MOM, Hungary) instrument. Quantum-chemical calculations were carried out in the Kazan Branch of Joint Super-Computer Center of RAS (<http://kbjscc.knc.ru>).

Results and Discussion

A brownish-yellow colouring of the GIM phase was observed when the values of C_F and C_L^0 were varied between 0.1 and 2.0 $\text{mol} \cdot \text{dm}^{-3}$, or $5.0 \cdot 10^{-3}$ and $5.0 \cdot 10^{-1} \text{ mol} \cdot \text{dm}^{-3}$, respectively, at 0.5-1.5 EDTHA:EDA molar ratio and $t = 2-10$ min reaction time. This colour does not change even upon treatment of the GIM phase formed with acids and alkalis. However, the coloured substance can be obtained only if $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM phase is contacted with aqueous-alkaline solutions of both EDTHA and EDA, in the absence of EDA the formation of the brownish substance could not be occurred at all.

There is an intensive absorption band maximum in UV region of the electron absorption spectrum of this compound. It proves evidence that both EDTHA and EDA have to be participated in the formation of the brownish coloured compound.

The brownish-yellow color of GIM samples may be arisen from formation of a coordination compound can contain EDTHA and EDA ligands or a new ligand formed from EDA and EDTHA.

There are no data about existence Zn(II)-glyoxal (ethanedial) in the chemical literature. When $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM was treated with an aqueous-alkaline solutions of EDA, no any changes in the spectral characteristics of gelatin mass could be detected. This fact unambiguously shows that Zn(II) does not form any complex with EDA either in the GIM or in aq. Phase, since EDA is a «hard» Pearson's base whereas Zn(II) is rather «soft» Pearson's acid.⁸

Supposing a mixed ligand complex formation of Zn(II) with EDTHA and EDA in the GIM-phase, it might be expected that the color of this mixed ligand-containing compound will differ from the color of homoligand Zn(II) complexes of EDTHA and EDA. Both $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM contains EDA and $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM contains EDTHA are yellow. The color changes of the GIM phase from slight yellow to brownish-yellow could only be observed, however, when EDTHA: EDA ratio is higher than 1:2.

Experiments with gelatin-immobilized Zn(II)-EDTHA chelate formed in the $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM phase did not interact with aq. alkaline solutions of EDA at any pH and EDA concentration. Thus, the formation of a mixed ligand complex of Zn(II) with EDTHA and EDA seemed to be improbable based on the observed experimental data.

Since the absorption spectra of aqueous solutions containing only EDTHA and the aqueous solutions containing compositions of EDTHA + EDA at $\text{pH} > 9.0$ were quite identical, if a new ligand was formed, then there was no doubt that the $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM system had to play role in the formation of this new ligand.

Taking into consideration the all conditions and results, this possibility proved to be reality, namely, a new ligand formed in the Zn(II)- EDTHA-EDA system with self-assembling template synthesis of the new ligand in the $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM "reactor".

When the polymeric GIM phase contains the Zn-complex (compound **1**) were destroyed according to the known method,⁷ a brown substance having empirical formula $\text{C}_6\text{H}_4\text{N}_4\text{S}_4\text{Zn}$ (**1**) could be isolated [calcd. for this formula, %: C, 22.12; H, 1.24; N, 17.20; S, 39.37; Zn, 20.07; Found, %: C, 22.0; H, 1.3; N, 17.5; S, 40.0; Zn, 19.7]. The compound **1** proved to be practically insoluble in ethanol, acetone, chloroform, benzene and tetrachloromethane, and weakly soluble in coordinating solvents like DMFA, DMSO and HMPTA.

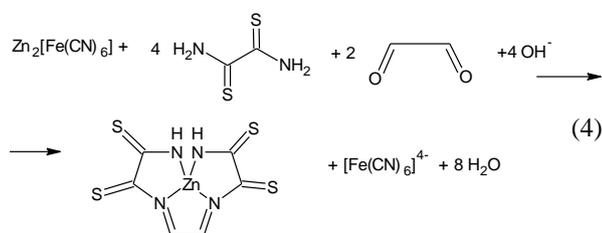
The band positions in the electron absorption spectra of the compound **1** measured in DMFA and DMSO solutions were completely coincided with bands observed in the UV spectrum of the reaction product of $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM with EDTHA and EDA. This indicates that substance immobilized in the GIM is identical with the compound **1**.

The DTA data showed that this compound was extremely stable on heating and was not destroyed even at 400°C .

The mass-spectrum of compound **1** showed the peak of positive charged molecular ions having $M/z^+ = 326.0$ ($C_6H_4N_4S_4Zn$, calculated value of $M = 325.7$) and a fragment peak with $M/z^+ = 262$ ($C_6H_6N_4S_4^+$, $M = 262.4$, the free ligand arises from the destruction of complex).

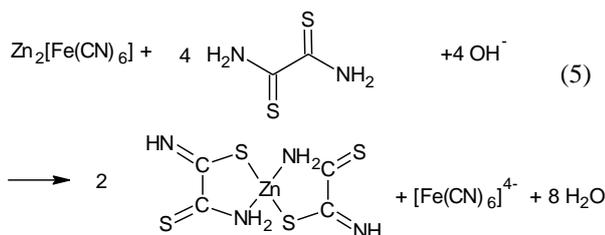
There is a band at 3544 cm^{-1} in the IR spectrum of **1** which is characteristic for $\nu(\text{NH})$ groups coordinated to metal ions, thus at least a part of NH groups in the compound **1** has to be connected to the zinc(II)-ion. Besides, IR spectrum of **1** exhibits intensive $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ bands at 1633 cm^{-1} and at 690 cm^{-1} as evidences the presence of C=S and C=N groups, respectively, in the complex **1**.⁹ Bands belong to the C-S or N=C-S groups could not be detected at all, consequently C-S bond are not present the structure of complex **1**.

The ^{13}C NMR spectrum of compound **1** showed three signals. Based on the spectroscopic results, it can be concluded that the complex **1** is the (2,7-dithio-3,6-diazaoctadien-3,5-dithioamide-1,8)zinc(II) formed in the reaction (4).



It should be noted that the reaction (4) cannot not be proceeded in the zinc(II)-EDTHA-EDA system at room temperature in aqueous solutions or in solid phase. Reacting $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ or other Zn(II) salt, e.g. ZnCl_2 with a mixture EDTHA+ EDA at pH 12.0, a brownish-yellow substance having empirical formula $\text{C}_4\text{H}_6\text{N}_4\text{S}_4\text{Zn}$ could be isolated from GIM (calcd. for this formula, %: C, 15.82; H, 1.99; N, 18.45; S, 42.22; Zn, 21.52; found, %: C, 16.1; H, 1.8; N, 18.3; S, 41.9; Zn, 21.7). The same product, $\text{C}_4\text{H}_6\text{N}_4\text{S}_4\text{Zn}$ was formed when $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ or ZnCl_2 reacted with aq. alkaline (pH 12.0) solution containing only EDTHA.

This substance was proved to be a Zn(II)-ethanedithioamide complex having metal ion: deprotonated EDTHA ratio was equal to 1:2 which formed according to a simple complex forming process (5)



The coordination compound of Zn(II) with 2,7-dithio-3,6-diazaoctadien-3,5-dithioamide-1,8 (**1**) synthesized had not been known previously. Unfortunately, all of our attempts to isolate single crystal and doing X-ray diffraction analysis

were failed, because the preparation method using $\text{Zn}_2[\text{Fe}(\text{CN})_6]$ -GIM always led to the amorphous form of the compound **1**. This amorphous form of compound **1** was unsuitable even for powder X-ray diffractometry as well. Due to this situation the exact spatial structure of the synthesized complex (**1**) is still open question which requires further studies.

The quantum-chemical calculations on the structural features of metal-macrocycle coordination mode in the compound **1** formed in the Zn(II)-EDTHA-EDA ternary system, however, obviously give some reliable structural information. One of the most suitable method for such kind of calculations was the hybrid method of the density functional theory, DFT B3LYP. In this work a DFT B3LYP level of theory with the 6-31G(d) basis set in Gaussian03 was used.¹⁰⁻¹² The preliminary results given by this method for various chelate complexes of 3d-elements showed that the method allows a good possibility to calculate the basic geometric parameters of these type of structures.

As it was expected from our experimental IR data, the ZnN_4 -coordinated isomer proved to be more stable comparing that with the isomer with ZnS_2N_2 coordination mode. According to our calculations, the total energy of Zn(II) chelate complex formed in the template reaction (4) and contains ZnN_4 chelating group was less with 92.8 kJ mol^{-1} than the total energy of the ZnN_2S_2 chelate isomer complex.

Some quantum-chemical calculations were also carried out to determine the molecular structure as well for the compound formed according to the Eqn. (4) and contained ZnN_4 coordination mode. The molecular structure of "template" Zn(II) complex considered can be seen in Fig. 1, and the important parameters of the structure are given in the Table 1.

As it can be seen from the parameters given in Table 1, the complex **1** has distorted square-planar configuration of ZnN_4 (sum of valence angles $\angle\text{N4Zn1N1}$, $\angle\text{N3Zn1N2}$, $\angle\text{N2Zn1N1}$ and $\angle\text{N4N1N2}$ is 336.9° , which shows an important distortion from the ideal ZnN_4 square-planar configuration. However, the atom located in the three 5-membered metal chelate rings as well as the four (NNNN)-coordinating donor atoms are located in a plane.

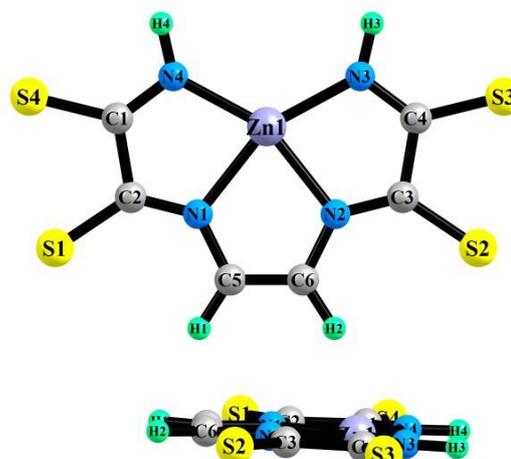


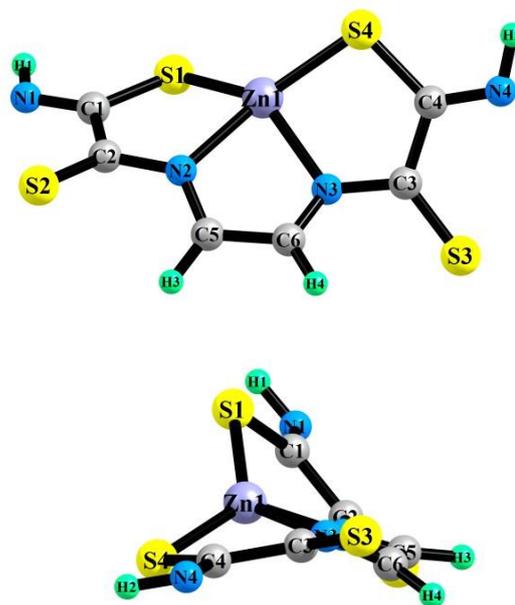
Figure 1. Molecular structure of Zn(II) complex with (2,7-dithio-3,6-diazaoctadien-3,5-dithioamide-1,8)zinc(II) with (NNNN)-coordination: front view (a) and view from the side (b)

Table 1. Selected parameters of molecular structure of complex with (NNNN)-coordination of donor centers formed in the Zn(II)–ethanedithioamide–ethanedial ternary system.

| Bond lengths, pm | | | |
|--------------------------------------|-------|--|-------|
| Zn1–N1 | 209.1 | Zn1–N2 | 209.1 |
| Zn1–N3 | 199.5 | Zn1–N4 | 199.5 |
| N1–C2 | 130.2 | N2–C3 | 130.2 |
| C1–C2 | 150.5 | C3–C4 | 150.5 |
| C1–N4 | 131.3 | C4–N3 | 131.3 |
| N1–C5 | 137.5 | N2–C6 | 137.5 |
| C2–S1 | 171.2 | C3–S2 | 171.2 |
| C1–S4 | 170.5 | C4–S3 | 170.5 |
| N3–H3 | 101.7 | N4–H4 | 101.7 |
| C5–C6 | 136.8 | | |
| Valence angles, ° | | | |
| Valence angles in 5-membered cycle 1 | | Valence angles in 5-membered cycle 2 | |
| ∠Zn1N1C2 | 114.0 | ∠Zn1N2C3 | 114.0 |
| ∠N1C2C1 | 113.8 | ∠N2C3C4 | 113.8 |
| ∠C2C1N4 | 117.3 | ∠C3C4N3 | 117.3 |
| ∠C1N4Zn1 | 114.7 | ∠C4N3Zn1 | 114.7 |
| ∠N4Zn1N1 | 80.2 | ∠N3Zn1N2 | 80.2 |
| Angles sum (VAS ⁵¹) | 540.0 | Angles sum (VAS ⁵²) | 540.0 |
| Valence angles in 5-membered cycle 3 | | Non-valence angles in NiN ₂ S ₂ grouping | |
| ∠Zn1N1C5 | 115.6 | ∠N1N2N3 | 100.2 |
| ∠N1C5C6 | 116.2 | ∠N2N3N4 | 79.8 |
| ∠C5C6N2 | 116.2 | ∠N3N4N1 | 79.8 |
| ∠C6N2Zn1 | 115.6 | ∠N4N1N2 | 100.2 |
| ∠N2Zn1N1 | 76.3 | Angles sum (NVAS) | 360.0 |
| Angles sum (VAS ⁵³) | 540.0 | | |
| Torsion angles, ° | | | |
| ∠N4Zn1N2C6 | 0.07 | ∠N1C2C1N4 | 0.06 |
| ∠N3Zn1N1C5 | 1.06 | ∠N2C3C4N3 | 0.06 |
| ∠Zn1N1C5C6 | 0.09 | ∠Zn1N1C2S1 | 180.0 |
| ∠Zn1N2C6C5 | 0.10 | ∠Zn1N2C3S2 | 180.0 |
| ∠N1C5C6N2 | 0.00 | ∠Zn1N4C1S4 | 180.0 |
| ∠N2C6C5N1 | 0.00 | ∠Zn1N3C4S3 | 180.0 |
| ∠Zn1N1C2C1 | 0.02 | ∠C2N1C5C6 | 180.0 |
| ∠Zn1N2C3C4 | 0.03 | ∠C3N2C6C5 | 180.0 |

The calculations performed on the structure of N₂S₂-coordinated Zn-complex of 2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8, the N₂S₂ coordination centers are not located in one plane, and the structure is extremely distorted (Fig. 2). This may be the main reason for its less stability comparing it with the ZnN₄ coordinated isomer.

The calculated dipole moment of the complex is 1.75 Debye units, and according to our calculated parameters the ground state of the complex **1** is a spin singlet, thus it must be diamagnetic nature.

**Figure 2.** Molecular structure of Zn(II) complex with (2,7-dithio-3,6-diazaoctadiene-3,5-dithioamide-1,8)zinc(II) with (N₂S₂)-coordination: front view (a) and view from the side (b)

Conclusion

A reaction of ethanedithioamide and ethanedial with a Zn₂[Fe(CN)₆]-GIM (gelatin-immobilized matrix) system in the presence of aq. alkalies resulted specific conditions to form a “self-assembled” macrotricyclic distorted square-planar Zn(II) chelate complex with metal ion:ligand ratio of 1:1. This complex can be formed only in the GIM system but does not form either in solution or in solid phase, as it was observed in the reaction of Cu(II), Co(II) and Ni(II) containing GIM phases with (N,S)-group and carbonyl-group containing ligands.¹³⁻¹⁵

It should be noted that the Zn(II) complex has ZnN₄-coordination mode, which is different from the similar Cu(II), Ni(II) and Co(II) complexes of this ligand.

Acknowledgements

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