



SELF-ASSEMBLY OF COPPER(II) MACROTRICYCLIC CHELATE COMPLEX WITH 2,8-DITHIO-3,5,7-TRIAZANONANDITHIOAMIDE-1,9 WITH BIOPOLYMER-POLYPEPTIDE MATRIX

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A template synthesis of copper(II) chelate coordination compound with 2,8-dithio-3,5,7-triazanonandithioamide-1,9 ligand has been achieved under soft conditions at room temperature. Reaction of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ biopolymer-polypeptide matrix with aqueous-alkaline solutions containing dithiooxamide, formaldehyde and ammonia yielded the aforesaid chelate. It has been noted that the chelate is formed only under the given conditions and not in solution or solid phase. The molecular structure of the complex has been calculated using DFT B3LYP technique.

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Introduction

It is known that the template synthesis of metaheterocyclic compounds of *d*-elements occurs from simpler fragments (the so-called ligsons) in solutions and solid phase mostly under rather drastic conditions. However, it is possible, that under special conditions like complexing in 3*d*-metal-containing biopolymer-polypeptide (gelatin) immobilized matrix (BPIM), for example in some metal(II)hexacyanoferrate(II),¹⁻⁴ at least certain template processes to occur under soft conditions, primarily at room temperature. Indeed, such processes have been observed to take place^{5,6} with triple systems like the M(II)-dithiooxamide ($\text{H}_2\text{N}-\text{C}(\text{S})-\text{C}(\text{S})-\text{NH}_2$)-formaldehyde complexes where M = Co, Ni or Cu and with the M(II)-dithiooxamide-propanone, where M = Ni or Cu, in the corresponding $\text{M}_2[\text{Fe}(\text{CN})_6]$ -BPIM matrix. One more possible ligand synthon for template synthesis in the M(II)-dithiooxamide- formaldehyde system, is ammonia. We report in this communication that we have been able to perform such synthesis in the Cu(II)- dithiooxamide-formaldehyde- ammonia quaternary system in the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ -BPIM matrix and, as a result, to observe a formation of macrocyclic coordination compound of copper(II) with (N,N,S,S)-tetradentate ligand – 2,8-dithio-3,5,7-triazanonandithioamide-1,9.

Experimental

$\text{Cu}_2[\text{Fe}(\text{CN})_6]$ -BPIM was synthesized as described in the literature.¹⁻⁴ The synthesis of $\text{CuC}_6\text{S}_4\text{N}_5\text{H}_9$ occurs on contact of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ -BPIM with alkaline solutions (pH=11-12) containing dithiooxamide, formaldehyde and ammonia. The concentration of copper(II) hexacyanoferrate(II) in the matrix was 0.1-2.0 mol/dm³, the concentration of

dithiooxamide, formaldehyde and ammonia the solution was ($3.0 \cdot 10^{-3}$ - $5.0 \cdot 10^{-2}$) mol L⁻¹, ($1.5 \cdot 10^{-3}$ - $1.0 \cdot 10^{-1}$) mol L⁻¹ and ($3.0 \cdot 10^{-3}$ - $5.0 \cdot 10^{-2}$) mol L⁻¹, respectively. The duration of the process was 10-12 min at 18-20 °C. The matrix obtained was treated with the solution of proteolytic enzyme, *Bacillus mesentericus*, according to already described process,⁷ and as a result gelatin binding of matrix was split into soluble low molecular weight compounds whereas the synthesized coordination compound precipitated and was then isolated from the mother liquor. Finally, the coordination compound was washed with distilled water, ethanol and dried at room temperature. Found (%): Cu, 18.6; C, 21.1; S, 37.2; N, 20.5; H, 2.7; O was not found. $\text{CuC}_6\text{S}_4\text{N}_5\text{H}_9$, calc. (%): Cu, 18.53; C, 21.01; S, 37.40; N, 20.42; H, 2.64. Characteristic bands in the IR-spectra (cm⁻¹): 680 (ν(C=S)); 1640 (ν(C=N)); 2865, 2940 (ν(CH₂)); 3460 (ν(NH)). MALDI TOF mass spectrometry data: the molecular mass of the synthesized compound is 343.0.

Electron absorption spectra of the BPIM 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, a UR-20 spectrometer (Karl Zeiss, Germany) was employed. Matrix-Assisted Laser Desorption/Ionization Time of Flight mass spectra (MALDI TOF) of substances isolated from BPIM were received using a Dynamo (Fimigan) and 4-nitroaniline matrix at 500MHz and 55.25 units of laser power.

Results and Discussion

The resulting compound colours the polymeric masses of the BPIM, which becomes red-brown. The UV-VIS-spectra of this compound contains only a shoulder due to the intense charge transfer band, whose maximum is in the UV region. It should be noted that in the absence of formaldehyde a dark-green compound with spectral characteristics similar to those of the Cu(II)-dithiooxamide complex is formed,^{1,2,4} and in absence of ammonia, a brown compound having $\text{CuC}_6\text{S}_4\text{N}_4\text{OH}_8$ composition, is formed as it was shown in

our earlier work.⁵ Thus there is no doubt that formaldehyde, ammonia, together with dithiooxamide and Cu(II) participate in the complexation process that occurs under these specific conditions. Decomposition of the polymeric binder of BPIM by enzymes by the known procedure⁷ allowed us to isolate dark-brown compound CuC₆S₄N₅H₉. According to the data of MALDI TOF mass spectrometry, the molecular mass of compound synthesized is 343.0 which accords well with calculated value of 342.93.

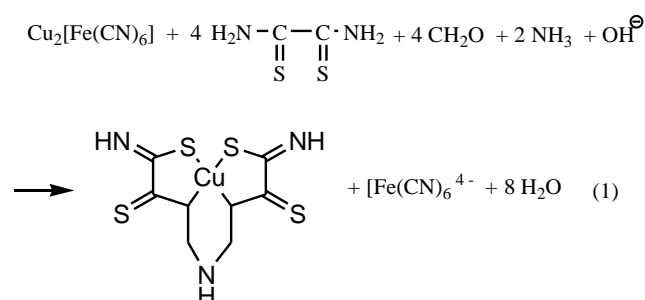
This compound is almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane, and poorly soluble in dimethylformamide, dimethylsulfoxide and hexamethylenephosphotriamide. The DTA data indicates that it is very stable and does not undergo pyrolysis up to 600°C. The compound is found to be paramagnetic ($\mu_{\text{eff.}} = 1.94 \mu_{\text{B}}$); it gives ESR signals at low (77 K, liquid nitrogen) as well as at room temperatures ($g_{\parallel} = 2.23$, $g_{\perp} = 2.06$). This allows us to assume that copper in the complex is in an oxidation state of +2 with planar D_{2h} - or C_{2h} -coordination of donor centers around metal atom. The UV-VIS spectra of DMF solution of this compound are almost identical to those of their source BPIM.⁸ This indicates that the immobilized compound is the same as that was isolated from BPIM.

The IR spectra of the complex have a band in the 3400-3500 cm^{-1} region, typical of NH or NH₂ groups uncoordinated to metal ion. Hence, at least a portion of the N atoms in these compounds are not bound to copper. In addition, the IR spectra of the compound under study contains $\nu(\text{C}=\text{S})$ at 680 cm^{-1} (usually observed at 705-570 cm^{-1}) and $\nu(\text{C}=\text{N})$ band at 1640 cm^{-1} (usually observed at 1690-1625 cm^{-1}) indicating the presence of (C=S) and (C=N) groups,⁹ respectively. Unfortunately, the IR spectra obtained in the region $<1000 \text{ cm}^{-1}$, where $\nu(\text{Cu}-\text{S})$ and $\nu(\text{Cu}-\text{N})$ frequencies should be observed,⁹ did not allow us to reliably assign the bands they contain to the stretching vibrations indicated above. Two medium-intensity peaks belonging to $\nu(\text{CH}_2)$ at 2940 and 2865 cm^{-1} (according to the literature,⁹ these bands lie within the 2945-2915 and 2870-2845 cm^{-1} ranges, respectively) was specially noted. These $\nu(\text{CH}_2)$ bands are absent in the IR spectra of dithiooxamide and in any of the coordination compounds of Cu(II) with this ligand known to date.³ Thus, one may conclude that compound under examination contain at least one new CH₂-structural group and it is quite evident that the formation of a Cu(II) coordination compound with some novel ligand has taken place. However, a band due to the stretching vibrations of the bridging C-O-C group at 1120-1100 cm^{-1} which is observed⁵ in a product of template synthesis in the Cu(II)- dithiooxamide- formaldehyde system, is absent in the IR spectra of compound studied. ¹³C NMR spectrum of this complex showed three signals.

Since compositions of compounds formed by the complexation in the Cu(II)- dithiooxamide- formaldehyde system⁵ (CuC₆S₄N₄OH₈) and in the Cu(II)- dithiooxamide-formaldehyde -ammonia one (CuC₆S₄N₅H₉) are different, it is obvious that in formation of this novel ligand, dithiooxamide and formaldehyde as well as ammonia participated. It should be noted especially in this connection that the UV-VIS absorption spectra of aqueous solutions of dithiooxamide of any concentrations in the range of 400-700 nm at pH>10 did not change even on addition of significant amounts of formaldehyde and ammonia and keeping for 2

days, and no indication of a chemical process between dithiooxamide, formaldehyde and ammonia was observed. Therefore, we have no doubt that the reaction between the reagents indicated above does not occur at all in absence of a metal ion. Such a phenomenon is possible only in template synthesis.^{10,11} Moreover, it seems that dithiooxamide, formaldehyde and ammonia act as ligand synthons.

By taking into consideration the all foregoing facts, the following scheme of template synthesis proceeding by an interaction between Cu(II), dithiooxamide, formaldehyde and ammonia in the Cu₂[Fe(CN)₆]-BPIM matrix and leading to formation of a metal heterocyclic compound, (2,8-dithio-3,5,7-triazanonandithioamide-1,9)copper(II), may be written:



X-ray diffraction analysis of the coordination compound prepared in the Cu₂[Fe(CN)₆]-BPIM matrix could not be performed as the experimental procedure of its isolation yielded the compound in the form of extremely small crystals, unsuitable for diffraction analysis. For this reason, the exact space structure of the synthesized Cu(II) complex remains an open question. However, presently it is possible to assign possible structure to this complex by means of modern quantum-chemical calculations. Therefore, quantum-chemical calculation of molecular structure of macrotricyclic Cu(II) coordination compound formed in the triple system under examination, was attempted. One of most suitable and reliable methods for such calculation is hybrid method of the density functional theory DFT B3LYP. In this work, DFT B3LYP level of theory with the 6-31G(d) basis set^{12,13} in Gaussian09 program¹⁴ was used. The preliminary appraisal of the above calculation method on various chelate complexes of 3d-elements showed that it is possible to calculate basic geometric parameters of their structures (the Cartesian coordinates of atoms, the lengths of bonds between atoms, the angles between bonds etc.). Therefore, we have carried out a quantum-chemical calculation of the molecular structure of the macrocyclic compound under examination. Major results of the calculation are discussed below.

The molecular structure of the complex indicated has been shown in Figure 1, the important parameters of this structure, in the Table 1. As may be seen from these data, that contrary to expectations, the complex has pronounced non-coplanar configuration.

It should be noted that in this complex, quadrangle of (NSSN) donor atoms is planar (the sum of inner angles is equal to 360°). CuN₂S₂ chelate grouping may be considered as practically planar because the sum of valence angles in the given metalchelate grouping, namely $\angle \text{N}_2\text{Cu}_1\text{N}_3$,

$\angle N3Cu1S4$, $\angle S4Cu1S1$ and $\angle S1Cu1N2$, is 357.2° , and, hence, Copper atoms are only slightly raised above (NSSN) plane. However, as it may be easily noted, both 5-numbered chelate rings as well as additional 6-numbered ring, formed as a result of template stitching, are not planar because the sums of their inner angles, 522.5° and 632.0° , respectively are considerably lesser than sums of inner angles in plane pentagon and plane hexagon (540° and 720° , respectively).

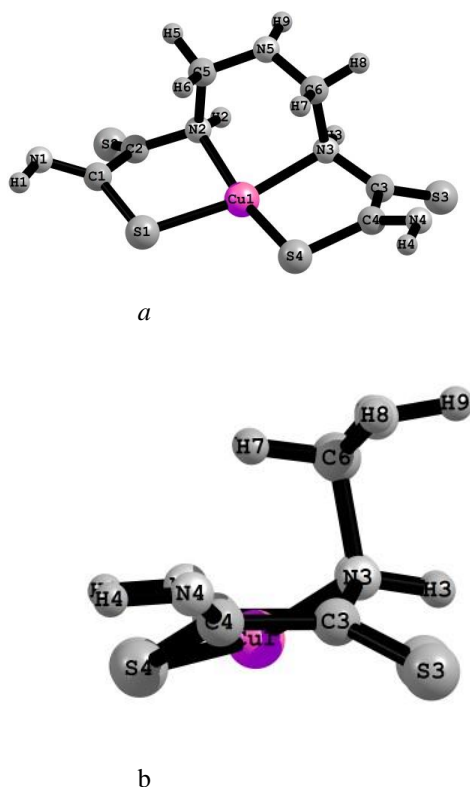


Figure 1. Molecular structure of (2,8-dithio-3,5,7-triazanonandithioamide-1,9)copper(II) with numbering of atoms: front view (a) and view from the side (b)

Besides, 6-numbered ring is not in one plane with metalchelate MN_2S_2 grouping but is inclined to it at 70.4° . It should be noted in this connection that the calculated Cu–N and Cu–S bond lengths (206.9 and 227.0 pm, respectively) are in the range of Cu–N and Cu–S bond lengths found experimentally in the macrocyclic complexes having MN_2S_2 chelate grouping (188–216 pm and 215–247 pm, respectively). Dipole moment of this complex is extremely high value (6.86 Debye units).

It is worth mentioning that processes of template synthesis between Cu(II), dithioamide, formaldehyde and ammonia occurs only in BPIM matrix; we failed to obtain this coordination compound in the reaction of $Cu_2[Fe(CN)_6]$ in solution or in the solid phase at room temperature. This fact indicates a specific role of gelatin-immobilized matrix system in the template synthesis in our case. It is interesting that compound under examination is not formed at interaction between NH_3 and $CuC_6S_4N_4OH_8$ synthesized by reported methods⁵ either in solution or BPIM matrix.

Table 1. Selected parameters of molecular structure of (2,8-dithio-3,5,7-triazanonandithioamide-1,9)copper(II).

Bond lengths, pm			
Cu1–N2	206.9	Cu1–N3	206.9
Cu1–S1	227.0	Cu1–S4	227.0
N2–C2	143.4	N3–C3	143.4
C1–C2	149.8	C3–C4	149.8
C1–S1	177.8	C4–S4	177.8
C2–S2	163.1	C3–S3	163.1
C1–N1	127.7	C4–N4	127.7
N2–C5	153.2	N3–C6	153.2
N1–H1	102.5	N2–H2	102.5
C5–N5	142.9	C6–N5	142.9
Valence angles, grad			
Valence angles in 5-numbered cycle 1		Valence angles in 5-numbered cycle 2	
$\angle Cu1S4C4$	98.3	$\angle Cu1S1C1$	98.3
$\angle S4C4C3$	113.1	$\angle S1C1C2$	113.1
$\angle C4C3N3$	113.2	$\angle C1C2N2$	113.2
$\angle C3N3Cu1$	110.6	$\angle C2N2Cu1$	110.6
$\angle N3Cu1S4$	87.3	$\angle N2Cu1S1$	87.3
Angles sum (VAS ⁵¹)	522.5	Angles sum (VAS ⁵²)	522.5
Torsion angles, grad			
$\angle N2Cu1N3C6$	70.4	$\angle Cu1N2C2S2$	131.0
$\angle N3Cu1N2C5$	70.4	$\angle Cu1N3C3S3$	130.9
$\angle N2C5C6N3$	0.0	$\angle N2C2C1S1$	45.0
$\angle N3C6C5N2$	0.0	$\angle N3C3C4S4$	44.9
$\angle S1Cu1N3C6$	7.9	$\angle S1C1C2S2$	131.1
$\angle S4Cu1N2C5$	7.6	$\angle S4C4C3S3$	131.0
$\angle Cu1S4C4N4$	161.1	$\angle N1C1C2S2$	47.0
$\angle Cu1S1C1N1$	160.9	$\angle N4C4C3S3$	46.9
$\angle Cu1N2C5N5$	70.1	$\angle Cu1N3C6N5$	70.1
$\angle N2C5N5C6$	62.6	$\angle N3C6N5C5$	62.6

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