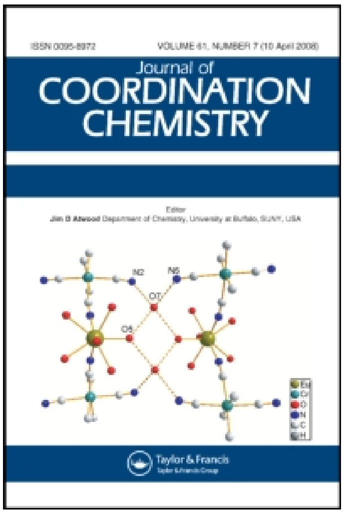

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Mild template synthesis in the iron(III)-ethanedithioamide-1,2-formaldehyde triple system on a K[Fe$_2$(CN)$_6$] gelatin-immobilized matrix

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Mild template synthesis in the iron(III)-ethanedithioamide-1,2-formaldehyde triple system on a $K[Fe_2(CN)_6]$ gelatin-immobilized matrix

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Complexation of Fe^{III}, in the form of $K[Fe_2(CN)_6]$ gelatin-immobilized matrix, in contact with aqueous-alkaline solutions ($pH \sim 12$) containing ethanedithioamide-1,2 and formaldehyde, has been studied. Template synthesis leading to a chelate Fe^{III} coordination compound with a tetradentate N,N,S,S-donor ligand identified as 4,4,6-trimethyl-1,9-diamino-1,9-dimercapto-3,7-diazanon-3-en-2,8-dithione and hydroxy co-ligand occurs under these specific conditions. Ethanedithioamide-1,2 and formaldehyde are the ligand synthons in the process studied.

Keywords: Template synthesis; Immobilized matrix; Macrocyclic complex; Hexacyanoferrate(II)

1. Introduction

The majority of coordination compounds have been prepared in solution, with most of the remainder having been prepared by solid phase methods such as direct reaction of the metal ion with a liquid ligand. We have been exploring an alternative synthetic method based on gelatin-immobilized matrices (GIM). In our previous article [1], we described and analyzed processes for soft template synthesis in cobalt(III)-dithiooxamide-formaldehyde and cobalt(III)-dithiooxamide-glyoxal triple systems in contact with potassium-cobalt(III)hexacyanoferrate(II) gelatin-immobilized matrix ($K[CoFe(CN)_6]$GIM) with aqueous alkaline solutions containing dithiooxamide (ethanedithioamide-1,2) $H_2N–C(=S)–C(=S)–NH_2$ and formaldehyde (methanol) $H_2C(=O)$ or glyoxal (ethanediol) $HC(=O)–HC(=O)$. This article is devoted to establishing whether such a template synthesis occurs in the iron(III)-ethanedithioamide-1,2-formaldehyde system in the presence of iron(III) hexacyanoferrate(II) gelatin-immobilized matrix ($K[Fe_2(CN)_6]$GIM). Such a complexation process in the triple system has not been studied.

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2. Experimental

$K[Fe_2(CN)_6]$GIM, prepared according to a literature procedure [2, 3] and having a potassium-iron(III)hexacyanoferrate(II) concentration (C_F) in the 0.1–2.0 mol dm^{-3} range, was then treated with an aqueous solution containing a mixture of ethanedithioamide-1,2 plus formaldehyde. The ethanedithioamide-1,2 concentrations in these solutions were $(1.0 \times 10^{-3} - 2.0 \times 10^{-1})$ mol dm^{-3}. The molar ethanedithioamide-1,2: formaldehyde ratio was varied from 0.5 to 2.0 at a fixed pH (12.0 ± 0.1) which was adjusted by addition of KOH (established experimentally) in the solution contacting GIM. The choice of pH was substantiated in our work [4]. The contact time for the $K[Fe_2(CN)_6]$GIM with given solutions was 1–10 min at 20.0 ± 0.5°C. After completing the template process, the gelatin layers containing iron(III) chelate complexes were washed with running water for 15 min and then dried at room temperature. The kinetics of the complexing reaction was described by the equation $D^{\blacktriangledown} = f(C_F, C^{\circ}_L, t)$ where $D^{\blacktriangledown}$ is the absorbance of the metal chelate GIM and is a function of the initial concentration of $K[Fe_2(CN)_6]$ in the matrix (C_F, mol dm^{-3}), the concentration of ethanedithioamide-1,2 in the solution in contact with this matrix (C°_L, mol dm^{-3}) and the complexation process time (t, min). To determine the stoichiometric coefficients in equations relating to the elementary steps of the complexing process, we used the coordinate sections [C_F = constant, varied C°_L, argument t) and [C°_L = constant, varied t, argument C_F] which were analyzed by a procedure developed previously [5]. In order to determine the empirical formula of coordination compounds formed in the GIM, these compounds were isolated from the corresponding GIM by treating them with solutions of proteolytic enzymes (e.g., *Bacillus mesentericus*) as described elsewhere [6]. After washing and drying, the isolated precipitates were chemically analyzed by conventional procedures. The yield of product in the system under examination was 80–85% of the value expected.

A series of experiments was undertaken to study the complexation reaction in the triple system with samples of $K[Fe_2(CN)_6]$GIM prepared using different types of gelatin. These experiments indicated that the complexing process in the system is independent of the gelatin type and, hence, the gelatin is not acting as a ligand synthon in the template process.

The transmitted light absorbance of the GIM ($D^{\blacktriangledown}$) was measured with a Macbeth TD504 photometer (Kodak Co., USA) in the 0.1–5.0 absorbance unit range with an accuracy of ±2%. Electronic absorption spectra of the GIMs 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 (MALDI TOF) mass spectra of substances isolated from GIMs were recorded using a Dynamo instrument (Finigan) and 4-nitroaniline matrix at 500 MHz and 55.25 units of laser power.

3. Results and discussion

The triple systems under examination, at very low concentration of ethanedithioamide-1,2 in the solution in contact with the $K[Fe_2(CN)_6]$GIM ($C^{\circ}_L < 10^{-3}$ mol dm^{-3}), any C_F, molar ethanedithioamide-1,2 : formaldehyde ratios in the range 0.5–2.0 and a sufficiently long (more than 5 min), give **1**. When the gelatin masses containing **1** are destroyed by the proteolytic enzymes [6], brown-yellow substance may be isolated. A chemical analysis showed that it had the empirical $HFeO_2$ in agreement with polymeric iron(III) oxohydroxide $[FeO(OH)]_n$. [Found: Fe, 62.4; O, 36.5; H, 1.3. $[FeO(OH)]_n$ Calcd: Fe, 62.9; O, 36.0; H, 1.1%]. According to analysis of the $D^{\blacktriangledown} = f(C_F, C_L^{\circ}, t)$ kinetic curves in the (C_F, C_L°, t) ranges corresponding to formation of **1** [5], addition of neither ethanedithioamide-1,2 nor formaldehyde is observed under these conditions. There is only the shoulder of an intense electronic absorption within the range of our spectrophotometer, *i.e.* a maximum in the UV region for this compound. $K[Fe_2(CN)_6]$ is easily destroyed by alkaline solutions [7] with formation of oxo-hydroxocomplexes of iron according to general equation (1):

$$nK[Fe_2(CN)_6] + 3nOH^- \rightarrow [FeO(OH)]_n + n[Fe(CN)_6]4^- + nK^+ + nH_2O \qquad (1)$$

According to data presented [3], the process of equation (2) proceeds parallel

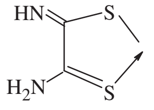
$$nK[Fe_2(CN)_6] + 2nOH^- \rightarrow [Fe(OH)2]_n + n[Fe(CN)_6]^{3-} + nK^+ \qquad (2)$$

Indirect evidence on existence of process (2) in our case are the chemical analysis of **1** (with content of hydrogen slightly more than expected for $[FeO(OH)]_n$).

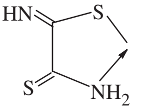
However, at $C_F = 0.1$–$2.0\,mol\,dm^{-3}$, $C_L^{\circ} = 4.0 \times 10^{-3} - 2.0 \times 10^{-1}\,mol\,dm^{-3}$, ethanedithioamide-1,2 : formaldehyde molar ratio of 0.5–1.5 and $t > 6$ min, complex **2** coloring the gelatin mass blue-green, was formed in the GIM. The color of the gelatin layer was retained upon treatment with acid as well as alkali. There is a rather intense band having maximum in the UV region at $\lambda = 630$ nm, in the electronic absorption spectra of GIMs containing this compound. When the GIMs containing **2** were destroyed [7], a blue-green substance having empirical formula $C_6H_{11}FeN_4O_3S_4$ may be isolated from the gelatin layer [Found: C, 19.1; H, 3.2; N, 15.3; Fe, 14.9; S, 34.2. $C_6H_{11}FeN_4O_3S_4$ calcd: C, 19.4; H, 3.0; N, 15.1; Fe, 15.0; S, 34.5%]. The ratio of four N atoms and four S atoms to one Fe is evidence for the presence of two ethanedithioamide-1,2 fragments per iron ion in **2**. Blue-green coloration of the gelatin layer is only observed when $K[Fe_2(CN)_6]$GIM is in contact with aqueous-alkaline solutions containing ethanedithioamide-1,2 as well as formaldehyde; in the absence of CH_2O in the given solution, the gelatin layer is tinged brownish-yellow from alkaline destruction of potassium-iron(III)hexacyanoferrate(II). According to chemical analysis of substance isolated from corresponding GIMs, formation of polymeric iron(III) oxohydroxide $[FeO(OH)]_n$ occurs in the triple system studied.

Blue-green color of the polymeric mass may be associated with either the formation of heteroligand iron(III) coordination compounds containing ethanedithioamide-1,2 and formaldehyde, or with the formation of iron(III) chelates with a ligand for which the structural fragments are ethanedithio-amide-1,2 and CH_2O. There are no data available for complexes of iron(III) with methanol in solution in the literature, however. When $K[Fe_2(CN)_6]$GIM is in contact with aqueous-alkaline solution of formaldehyde, only alkaline destruction of potassium-iron(III)-hexacyanoferrate(II) occurs according to equations (1) and (2) and gelatin layer is tinged brownish-yellow, connected with formation of polymeric iron(III) oxohydroxide $[FeO(OH)]_n$. These observations indicate that no iron(III) complexes with formaldehyde are formed in the GIM or solution. By judging that in the absence of CH_2O in the solution contacting K[$Fe_2(CN)_6$]GIM, only alkaline destruction of potassium-iron(III) hexacyanoferrate(II) occurs, it can be asserted that ethanedithioamide-1,2 does not coordinate iron(III) in the conditions of our experiment. Thus, formation of heteroligand complex of iron(III) containing inner coordination ethanedithioamide-1,2 and formaldehyde, can be rejected. We therefore assume that formation of some ligand derived from ethanedithioamide-1,2 and formaldehyde occurs in the triple system. Absorption spectra of aqueous solutions containing only ethanedithioamide-1,2 and aqueous solutions containing mixture of ethanedithioamide-1,2 and formaldehyde at $pH > 9.0$ are identical, indicating that formation of such a ligand does not occur when iron(III) is absent from the system. The resulting iron coordination compound, having $C_6H_{11}FeN_4O_3S_4$ formula, is paramagnetic ($\mu_{eff} = 5.92\,\mu_B$) and exhibits e.s.r. signals at room temperature, typical for iron(III) chelates with pseudo-O_h-coordination of donor atoms [8]. Taking into consideration all the foregoing, we conclude that some transmutation of ethanedithioamide-1,2 and CH_2O into inner coordination sphere occurs in the conditions of our experiment.

Ethanedithioamide-1,2 is an ambidentate (N, S)-ligand with two S-donor and two N-donor atoms in its singly deprotonated form and is able to coordinate as a monoanionic ligand to metal ions through two S-donor atoms (**I**), one S- and one N-donor atoms (**II**) and two N-donor atoms (**III**)



I



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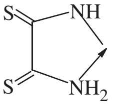


III

Four versions of inner coordination sphere may be assumed:

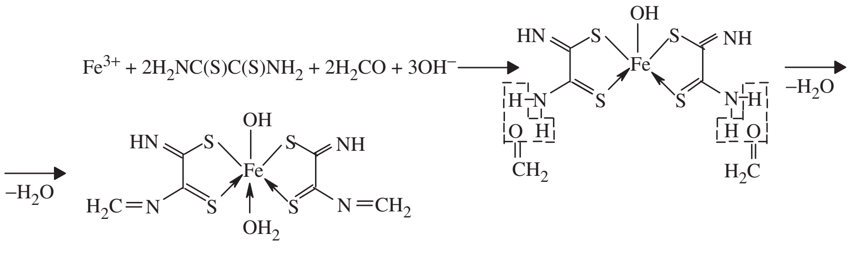
(a) Formation of iron(III) coordination compound (**A**) with a bidentate ligand coordinated to the metal ion through four S atoms. Such a ligand is formed from two molecules of ethanedithioamide-1,2 and two molecules of formaldehyde as a result of Schiff's condensation according to scheme 1.

(b) Formation of iron(III) coordination compound (**B**) with a tetradentate ligand coordinated to the metal ion through two sulfurs and two nitrogens. Such a ligand formed from two molecules of ethanedithioamide-1,2 and two molecules of formaldehyde as a result of template synthesis as shown in scheme 2.

(c) Formation of iron(III) coordination compound (**C**) with a tetradentate ligand coordinated to the iron(III) ion through four nitrogens. As in previous version, in the given case the ligand is formed from two molecules of ethanedithioamide-1,2 and two molecules of formaldehyde as a result of template synthesis (scheme 3).

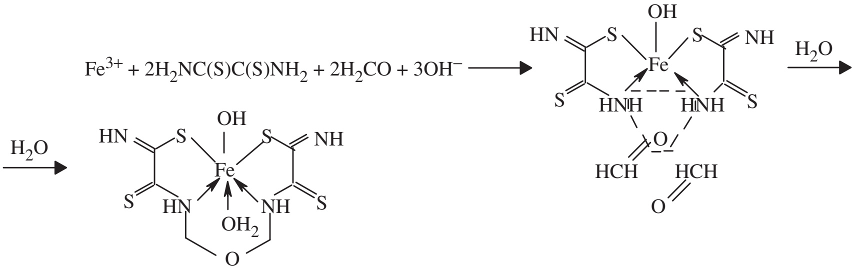
(d) Formation of iron(III) coordination compound (**D**) with a tetradentate ligand coordinated to iron(III) through four nitrogen atoms. Here the ligand is formed from two molecules of ethanedithioamide-1,2 and four molecules of formaldehyde, also as a result of template synthesis (scheme 4).

Mathematical processing of $D^{\blacktriangledown} = f(C_F, C_L^{\circ}, t)$ relationships according to our previous studies [5] in ranges corresponding to formation of **2** show that one equivalent of the ligand formed from two molecules of ethanedithioamide-1,2 and two molecules of



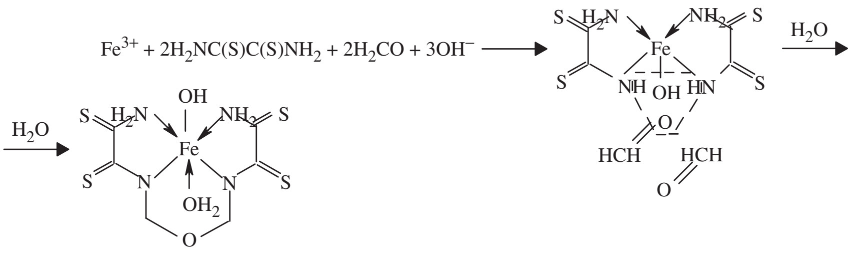
A

Scheme 1. Proposed method of formation of coordination compound **A**.



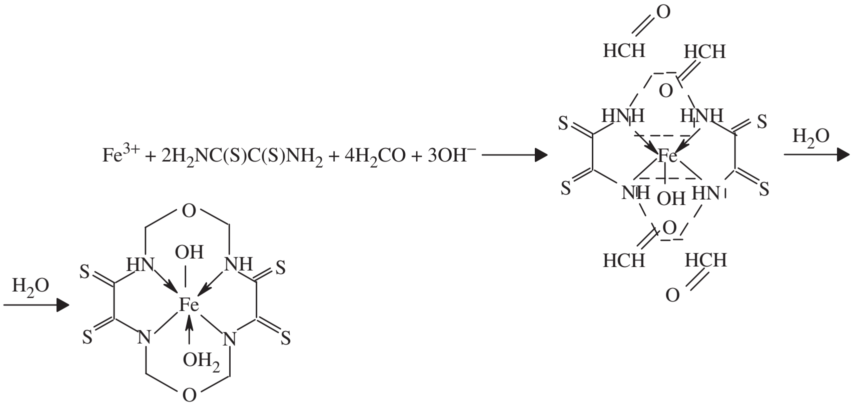
B

Scheme 2. Proposed method of formation of coordination compound **B**.



C

Scheme 3. Proposed method of formation of coordination compound **C**.



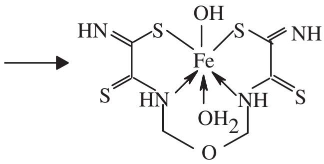
D

Scheme 4. Proposed method of formation of coordination compound **D**.

formaldehyde were added to each iron(III) [the calculated ratio of such pre-fabricated ligand to iron(III) ions is 1.2]. A very similar result was obtained in our previous study of Co(III)-ethanedithioamide-1,2-formaldehyde triple system where this ratio is also 1.2 [1]. These values are close to those expected (1.0) and in agreement with quantities of ethanedithioamide-1,2 and formaldehyde in schemes 1–3. Composition of **2** ($C_6H_{11}FeN_4O_3S_4$) is in agreement with compositions according to scheme 2 (**B**) and scheme 3 (**C**), but does not coincide with composition of final product expected according to scheme 1 (**A**) ($C_6H_9FeN_4O_2S_4$) and scheme 4 (**D**) ($C_8H_{13}FeN_4O_4S_4$). The MALDI TOF mass spectrum of **2** shows only one peak for the molecular ion having molecular mass $M = 371$ c.u, very near the molecular mass expected for $C_6H_{11}FeN_4O_3S_4$ (calculated value M for such a formula is 371.3 c.u.). Computer analysis of possible products in the iron(III)-ethanedithioamide-1,2-formaldehyde triple system provides evidence that the molecular mass may correspond ***only*** to $C_6H_{11}FeN_4O_3S_4$; no compounds which theoretically might be formed in the triple system, cannot have the molecular mass indicated. These data favor the indicated composition.

The IR spectrum of **2** exhibits a broad ν(NH) at 3400–3500 cm^{-1}, typical for noncoordinated NH or NH_2 groups, suggesting that not all nitrogens are coordinated to iron(III), consistent with **B**. Moreover, the IR spectra exhibit a ν(C=N) at 1645 cm^{-1} (usually observed at 1625–1690 cm^{-1} [9]), also consistent with structure **B**. In addition, the spectra of **2** exhibit a ν(C=S) band at 695 cm^{-1} (usually observed at 570–705 cm^{-1} [9]), two bands at 2855 cm^{-1} and 2920 cm^{-1} associated with $\nu(CH_2)$ and the band at 1115 cm^{-1} associated with ν(C–O–C) in agreement with literature ranges for these bands [9]. These three bands are absent in the IR spectra of ethanedithioamide-1,2. According to Pearson's classification [10], Fe(III) is a very hard acid and coordination through N donors with greater electronegativity than S donors, (N,N,N,N) coordination might be expected. In the analogous complex formed in the cobalt(III)-ethanedithioamide-1,2-formaldehyde [1], (N,N,S,S) coordination of tetradentate ligand occurs; Co(III) is a harder Pearson acid in comparison to Fe(III) [10]. The data indicated above allow us to conclude that in the triple system under examination the general process in equation (3) occurs

$$K[Fe_2(CN)_6] + 2H_2NC(S)C(S)NH_2 + 2H_2CO + 3OH^- \longrightarrow$$

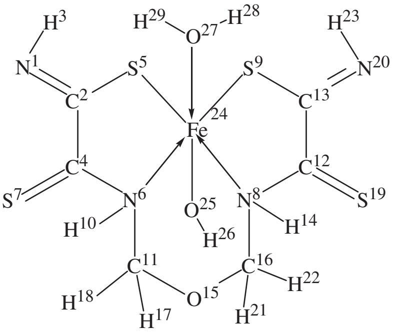


$$+ [Fe(CN)_6]^{4-} + K^+ + 2H_2O \qquad (3)$$

with **2** being (2,8-dithio-3,7-diaza-5-oxanonandithioamide-1,9)aquahydroxyiron(III).

The (2,8-dithio-3,7-diaza-5-oxanonandithioamide-1,9)aquahydroxyiron(III) is virtually insoluble in ethanol, acetone, chloroform, benzene and tetrachloromethane, but weakly soluble in dimethylformamide, dimethylsulfoxide and hexamethylenephosphortriamide. It is rather stable on heating and is not destroyed to 400°C. The electronic absorption spectra of this compound (in dimethylformamide and dimethylsulfoxide solutions) coincide perfectly with those of the GIMs from which it was isolated. Unfortunately, we were unable to obtain crystals of this compound large enough for X-ray crystallographic analysis.

Quantum-chemical calculations of **B**, **C** and **D** were carried out to corroborate our conclusions concerning the structure of **2** using hybrid **DFT B3LYP** density functional method with standard basis set 6-31G(d) [11, 12]. These calculations were made using Gaussian 98 program [12] and basis set indicated where each inner atomic orbital (AO) was described by six functions of Gauss's type (GTO), s-AO – by three GTO and p-AO – by one GTO. Besides, polarization d-GTO was added to each p-function. A harmony of stationary points found to energy minimums was argued by calculation of Hessian. The procedure allows calculation of basic geometric parameters (the Cartesian coordinates of all atoms, the lengths of bonds between atoms, angles between bonds and so forth). Such calculations of template reactions and metal complexes formed as a result of these reactions were carried out by us for the first time; a time of these calculations was from two (complex **B**) to seven (complex **D**) months. These calculations show that, indeed, **B** is more stable than **C** and **D**. The data for **B** are presented in table 1; numbering of the atoms is shown below



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According to these calculations, spin sextet $^6A_1$ has lowest energy; spin doublet nearest to spin sextet has higher energy ($\Delta E = 38.5$ kJ).

In the Cambridge Structural Database, there are structures known of 15 coordination compounds containing $FeO_2N_2S_2$ structural fragment. According to these data, the range of Fe–O bond lengths is 190–215 pm (average value 200 pm), the range of Fe–N bond lengths is 195–226 pm (average value 210 pm), and the range of Fe–S bond lengths is 223–256 pm (average value 239 pm). Comparison of data indicated with Fe–O, Fe–N and Fe–S bond lengths calculated by us, Fe–S bond lengths calculated (239.53 and 239.54 pm) coincide with average value of length for Fe–S bonds in $FeO_2N_2S_2$ complexes (239 pm), whereas Fe–N bond lengths calculated (229.84 and 229.96 pm) are a little more than maximal value of length for Fe–N bond in the complexes containing the same structural fragment (226 pm). Fe–O bond lengths calculated (183.83 pm for coordinated OH group and 230.99 pm for coordinated H_2O) are typical for the iron–oxygen bonds Fe(III)–OH_2 and Fe(III)–OH.

The structure of **B** [in two projections, namely (a) ("open," front view) and (b) ("shielded," view from the side)] has been shown on figure 1. The (N,N,S,S) chelate in this complex is practically planar, and iron only slightly raised above the plane. The flatness of N–CH_2–CH_2–N is almost perpendicular to the plane [figure 1(a)]. Oxygen of

Table 1. Selected bonds lengths and angles calculated in **B**.

Bond lengths d, pm					
d (1,2)	126.88	d (6,11)	151.12	d (15,16)	140.72
d (2,4)	150.05	d (6,24)	229.84	d (24,25)	183.83
d (2,5)	180.46	d (8,16)	151.12	d (24,27)	230.99
d (4,6)	144.22	d (8,24)	229.96	d (25,26)	96.92
d (4,7)	163.07	d (9,24)	239.53	d (27,28)	97.51
d (5,24)	239.54	d (11,15)	140.72	d (27,29)	97.51
Angles A, grad					
A(2,5,24)	91.70	A (16,8,24)	106.29	A (5,24,9)	110.65
A(4,6,24)	108.51	A (13,9,24)	91.71	A (6,24,8)	77.70
A(11,6,24)	106.34	A (11,15,16)	118.31	A (8,24,9)	84.29
A(12,8,24)	108.48	A (5,24,6)	84.30	A (25,24,27)	169.58
Torsion angles D, grad					
D(5,24,8,6)	191.2803	D (11,6,24,8)	−63.7072	D (6,11,15,16)	−76.3564
D(6,24,9,5)	164.5239	D (14,8,12,19)	18.6781	D (11,15,16,8)	76.4024
D(25,24,27,5)	171.2901	D (24,8,12,13)	−31.4531	D (26,25,27,28)	−55.6842
D(3,1,2,4)	178.4376	D (24,8,16,15)	−75.2780	D (26,25,27,29)	56.1325
D(3,1,2,5)	2.6475	D (24,8,16,21)	47.6526	D (5,24,27,28)	−110.5079
D(5,2,4,7)	111.0733	D (12,8,24,27)	−89.3916	D (5,24,27,29)	−0.6314
D(2,5,24,27)	−107.9824	D (16,8,24,6)	63.7172	D (6,24,27,28)	164.5578
D(10,6,11,15)	−46.8638	D (16,8,24,9)	−127.5112	D (6,24,27,29)	−85.5656
D(24,6,11,18)	−47.6850	D (16,8,24,25)	−27.5407	D (8,24,27,28)	85.5251

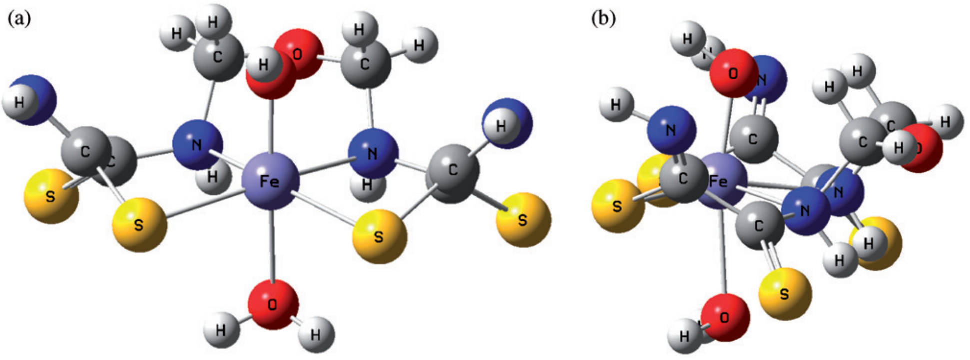

Figure 1. The structure of **B**. (a) "Open," front view. (b) "Shielded," view from the side.

N–CH_2–O–CH_2–N formed as a result of template stitching, figure 1(b), is not at the same plane with nitrogens and carbons and is inclined at 90°. The H_2O molecule, by calculations, is weakly connected with Fe(III).

In conclusion, we note that the template process observed in the GIM was not observed in the iron(III)-ethanedithioamide-1,2-formaldehyde triple system at room temperature when reaction was carried out in aqueous solution or in the solid phase. Processes analogous to equation (3) are not realized when $FeCl_3$, ethanedithioamide-1,2 and formaldehyde are in ethanol solution even upon heating to 80°C. In our opinion, which was voiced in a previous article, the cause of this phenomenon [13] can be attributed to a more favorable entropy for formation of **2** in the GIM compared to analogous reaction in solution.

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