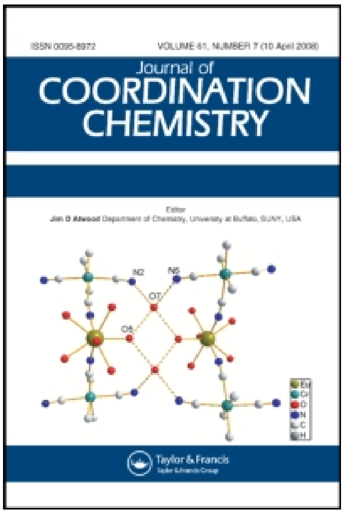

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Complexing reactions in the Ni(II)-5-methyl-4-amino-3-thiooxo-1,2,4-triazapentene-1-methanal and Ni(II)-5-methyl-4-amino-3-thiooxo-1,2,4-triazapentene-1-propanone triple systems

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Complexing processes in the Ni^{II}-**TTA**-methanal (**A**) and Ni^{II}-**TTA**-propanone (**B**) triple systems (**TTA** – 5-methyl-4-amino-3-thiooxo-1, 2, 4-triazapentene-1) in ethanol solution and nickel(II)hexacyanoferrate(II) gelatin-immobilized matrix have been studied. In the Ni^{II}-**TTA**-methanal system, formation of Ni^{II} oligomeric coordination compounds in which metal chelate cycles are connected by $–H_2C–O–CH_2–$ structural groups, takes place. In the Ni^{II}-**TTA**-propanone triple system, formation of only Ni^{II} complexes with **TTA** takes place. No complexing process in the triple systems in nickel(II)hexacyanoferrate(II) gelatin-immobilized matrix was found.

Keywords: Complexing reactions; Nickel(II) chelate complexes; N,S-donor atomic ligand

1. Introduction

M(II)-thiocarbohydrazide-propanone and M(II)-thiocarbohydrazide-diacetyl triple systems ($M = Ni, Cu$) with nickel(II)- or copper(II)-hexacyanoferrate(II) gelatin-immobilized matrices were studied with an aqueous-alkaline solution containing ligand [1–5]. Template synthesis occurs in these systems and chelate complexes having various structure and ligand coordination to M(II) are formed. Mobility and flexibility of thiocarbohydrazide and free rotation around C–C and C–N bonds are important. To ascertain the possibility of template synthesis with participation of a (N, S)-containing ligand with a fixed structural N–N–C(S)–N–N fragment, we chose a derivative of thiocarbohydrazide 5-methyl-4-amino-3-thiooxo-1,2,4-triaza-pentene-1 (**TTA**) which may exist in thione and thiol forms [6].

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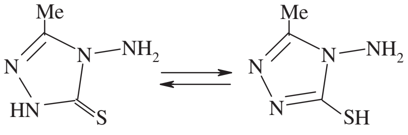


TTA

TTA is easily synthesized from thiocarbohydrazide and acetic acid [7]. Complexing processes with this ligand have not been studied previously and are the subject of this communication.

2. Experimental

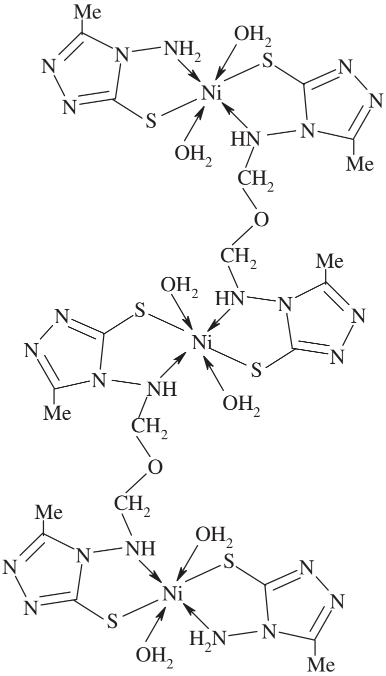
Synthesis of **TTA** was carried out by mixing 0.1 mol of thiocarbohydrazide and 0.1 mol of acetic acid with reflux for 15 min. The transparent solution obtained was cooled to room temperature. White crystals formed and were filtered, recrystallized from distilled water and dried by vacuum. Purity of the **TTA** was verified by melting point (Found: 216°C, according to the data [7] 217°C). Chemical analysis: (Found, %: C, 27.2; H, 4.1; S, 25.0; Calculated value for $C_3H_6N_4S$, %: C, 27.69; H, 4.62; S, 24.62). The yield is 80.4%.

To study complexation in EtOH, anhydrous $NiCl_2$ **TTA** and methanal/propanone (molar ratios $NiCl_2$: **TTA**: methanal; $NiCl_2$: **TTA**: propanone) triple systems (**A** and **B**, respectively) were varied from 1 : 2 : 1 to 1 : 2 : 4. The [$NiCl_2$ + **TTA** + methanal (propanone)] mixtures were refluxed in EtOH (78°C) for 3 h. The products were then removed from the mother solution by filtration, washed with distilled H_2O and EtOH, and dried at 100C. When studying complexation in nickel(II)hexacyanoferrate(II) gelatin-immobilized matrix, this matrix was in a contact with aqueous-alkaline solutions containing **TTA** and methanal or propanone with molar ratio of 0.5–2.0. All experimental techniques were as reported earlier in Refs [1–4, 8].

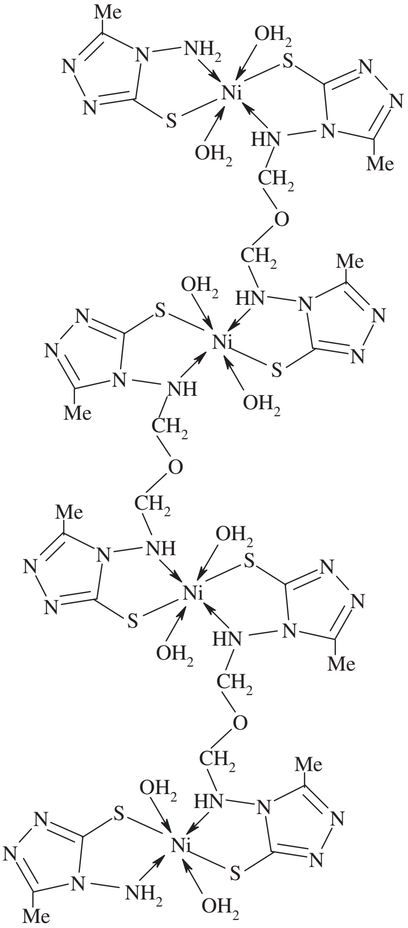
3. Results and discussion

Complexation between $NiCl_2$, **TTA**, and methanal gives turquoise substance (**1**), soluble in DMF, DMSO, and MeCN but insoluble in water, ethanol, or chloroform. This substance shows in the MALDI TOF mass-spectrum of two intense peaks of molecular ions having molecular masses $M = 1142$ and 1538 c.u. with 1561 c.u. [molecular ion with $M = 1538 + (Na^+)$] and 1578 c.u. [molecular ion with $M = 1538 + (K^+)$]. No other peaks are observed in the mass-spectrum; formation of two coordination compounds having molecular masses more than 1000 occurs in the triple system.

In IR spectra of these complexes, ν(C=S) shifts to higher frequency (70 cm^{-1}) in comparison to free **TTA** (745 cm^{-1}). There are broad and weak bands corresponding to ν(N–H) at 3220–3200 cm^{-1} and a band corresponding to ν(CH_2–O–CH_2) at 1160–1170 cm^{-1}. The IR spectra of complexes provide evidence that ligand is coordinated to Ni(II) through sulfur and nitrogen of amino- or imino groups. The unusual molecular masses provide evidence that complexes formed in triple system **A**, have oligomeric structures. MALDI TOF mass-spectroscopy, elemental analysis, and IR spectroscopy, indicate two complexes having the same monomeric fragment. Computer analysis of possible products show that molecular masses $M = 1142$ and 1538 c.u. may correspond to only Ni(II) trimeric and tetrameric compounds **I** and **II**



I



II

having $Ni_3C_{22}N_{24}S_6O_8H_{46}$ and $Ni_4C_{30}N_{32}S_8O_{11}H_{62}$ empirical formulas (Calcd values $M = 1142.8$ and 1537.8 c.u., respectively). Analyses cannot distinguish between the trimer and tetramer for (**1**) ((%): Ni, 15.4; C, 23.5; N, 29.3; S, 16.9; H, 4.1. Calcd for $Ni_3C_{22}N_{24}S_6O_8H_{46}$ formula: Ni, 15.41; C, 23.12; N, 29.42; S, 16.83; H, 4.02. Calcd for $Ni_4C_{30}N_{32}S_8O_{11}H_{62}$ formula (%): Ni, 15.27; C, 23.43; N, 29.15; S, 16.68; H, 4.03). As seen from formulas **I** and **II**, formation of these compounds is not a template synthesis.

Complexing between $NiCl_2$, **TTA**, and propanone gives green substance (**2**) with blue tinge which is soluble in water, DMF, DMSO, and MeCN but insoluble in ethanol and chloroform. According to chemical analysis data, it is nickel(II) complex with singly deprotonated **TTA** (HL), $Ni(HL)_2(H_2O)_2$ ($NiC_6N_8S_2O_2H_{14}$; Found, %: Ni, 16.9; C, 20.0; N, 31.4; S, 17.5; H, 4.0. Calcd for given formula, %: Ni, 16.63; C, 20.42;

N, 31.75; S, 18.17; H, 3.97). The composition is supported by MALDI TOF mass-spectroscopy of (**2**) with a molecular ion $M = 354$ c.u. (Calcd value of molecular mass for the $NiC_6N_8S_2O_2H_{14}$ formula is 352.9 c.u.). The same complex is formed when propanone is absent confirming that propanone does not participate in the reaction. Neither formation of oligomeric compounds similar to **I** and **II**, nor template synthesis occurs in the propanone triple system (**B**).

Neither template synthesis nor complexation occur in triple systems (**A**) and (**B**) in $Ni_2[Fe(CN)_6]$-gelatin-immobilized matrix. In a series of binary and triple systems M(II)–(N, S)–ligand synthon–carbonyl-containing ligand synthon, complexation does not occur in solution, but takes place in gelatin-immobilized matrix [3–5]. To understand the cause of this phenomenon, comparative stability of the coordination compound of Ni(II) with **TTA** and nickel(II)hexacyanoferrate(II) is important. $Ni_2[Fe(CN)_6]$ and **TTA** have no interaction. Hence, nickel(II) complex with **TTA** is less stable than $Ni_2[Fe(CN)_6]$. Complexation in the triple system (**A**) accompanied by reaction of formation of oligomers **I** or **II**, would proceed in ethanol for $NiCl_2$ but would not proceed in nickel(II) hexacyanoferrate(II) gelatin-immobilized matrix where initial substance is $Ni_2[Fe(CN)_6]$. In the case of triple system (**B**) oligomeric coordination compounds of types **I** and **II** are not observed, perhaps, inhibited by steric interactions of methyl groups in propanone.

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