



Scientific article

UDC 541.49:547-386

DOI: 10.52957/2782-1900-2024-5-3-78-90

SYNTHESIS AND PHYSICOCHEMICAL STUDIES OF IRON(III) COMPLEX COMPOUNDS WITH TSC

T. B. Bobokalonov, S. M. Safarmamadzoda

Tojiddin B. Bobokalonov, Candidate of Chemical Sciences, Senior Lecturer, Safarmamad M. Safarmamadzoda, Doctor of Chemical Sciences, Professor.

Tajik National University, Dushanbe, Republic of Tajikistan, sash65@mail.ru, tojiddin_8989@mail.ru

Keywords:

complexation, synthesis, iron(III), thiosemicarbazide (TSC), IR spectroscopy, conductometry, X-ray diffraction, thermolysis

Abstract. The authors developed methods for the synthesis of coordination compounds of iron(III) with thiosemicarbazide (TSC). The compounds structure was proved by IR spectroscopy, conductometry, X-ray diffraction, and thermogravimetry. The authors found the bidentate coordination of TSC with iron(III) via sulphur and nitrogen atoms. Thermogravimetrically authors have established the proceeding of the complex decomposition in two stages. The first stage involves thermolysis of organic ligands with the formation of the corresponding iron salts; the second one includes decomposition of iron salts and formation of iron(III) oxide. Conductometrically we have established the synthesised complexes are strong electrolytes. X-ray diffraction shows the crystallisation of the complexes into orthorhombic syngonies. There are two structural units in the cell.

For citation:

Bobokalonov, T.B. & Safarmamadzoda, S.M. (2024) Synthesis and physicochemical studies of iron(III) complex compounds with TSC, *From Chemistry Towards Technology Step-By-Step*, Vol. 5(3), pp. 78-90 [online]. Available at: <https://chemintech.ru/ru/nauka/issue/5357/view>

Introduction

Thiosemicarbazides have been of considerable interest for synthetic organic chemistry for many years. They are widely used for the synthesis of nitrogen- and sulphur-containing heterocyclic compounds due to the presence of several active reaction centres. The ability of thiosemicarbazide to form complexes with cations of iron, zinc, copper, nickel, and other metals plays an important role in biological processes. It determines a wide range of biological activity of its derivatives. Among them are substances with antitumour, antimicrobial, antiparasitic, insecticidal, antioxidant, and antiatherosclerotic effects [1]. Iron is an essential microelement for the majority of vital functions of living organisms, such as oxygen transport, DNA synthesis, participation in effector mechanisms of immunity, etc. The microorganisms also require ferrous iron. Bacteria, by consuming iron from the environment, acquire the ability to better resist unfavourable factors. According to many studies of pathogenic bacteria, many genes responsible for pathogenicity are iron regulated [2].

The review paper [3] systematises data on the synthesis, structure, stability of complex compounds of some transition metals with thiosemicarbazide and its derivatives. X-ray



diffraction and IR spectroscopic studies have established the method of thiosemicarbazide coordination and determined the structures of the complexes. In particular, thiosemicarbazide with Cu(II), Zn(II), Fe(II), Ni(II), and Ag(I) coordinates bidentate via the sulphur atom and nitrogen of the hydrazine fragment. Complex compounds of rhenium(V) with thiosemicarbazide were synthesised and studied in [4]. We found that TSC with rhenium(V) coordinates bidentate via sulfur and nitrogen atom. The authors [4, 5] synthesised complexes of rhenium(V) with 4-methylthiosemicarbazide (4MTSC) under identical conditions. The identification of complexes by IR and PMR spectroscopy showed 4MTSC coordination with rhenium(V) monodentate via sulphur atom. The authors explain the change in the dentativity of the 4MTSC molecule by steric factors formed by the methyl group.

The paper [6] studies the processes of complexation in the system Fe(II)-Fe(III)-glycine- $\text{Na(H)ClO}_4\text{-H}_2\text{O}$ by the Clark-Nikolsky oxidation potential method. Experimental curves of system EDS dependence on concentration parameters: pH, $pC_{\text{Fe(III)}}$, $pC_{\text{Fe(II)}}$, $p\text{Cl}$ were obtained. The complex Fe(III) compounds of the composition Fe(III) are formed in the system Fe(II)-Fe(III)-glycine- $\text{Na(H)ClO}_4\text{-H}_2\text{O}$ depending on pH-solution: $[\text{FeHL(H}_2\text{O)}_5]^{3+}$, $[\text{Fe(HL)}_2(\text{H}_2\text{O)}_4]^{3+}$, $[\text{Fe}_2(\text{HL})_2(\text{OH})_2(\text{H}_2\text{O)}_8]^{4+}$, $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HL})_2(\text{OH})_2(\text{H}_2\text{O)}_8]^{3+}$, as well as Fe(II): $[\text{Fe(HL)(H}_2\text{O)}_5]^{2+}$, $[\text{Fe(HL)(OH)(H}_2\text{O)}_4]^+$, $[\text{Fe}^{\text{I}}\text{Fe}^{\text{III}}(\text{HL})_2(\text{OH})_2(\text{H}_2\text{O)}_8]^{3+}$. The paper [7] discusses the conditions for the synthesis of Co(II) acetate complexes with melamine and glycine on the basis of modern physicochemical methods. The authors of [8] studied the condensation of 2-aminopyridine-3-carbaldehyde with 1-hydrazinophthalazine. A new hetarylhydrazone was obtained and its complexation ability towards ions Ni^{2+} , Cu^+ , Cu^{2+} , Zn^{2+} и Co^{3+} was investigated. The authors show dependence of different composition and structure complex compounds formation on the nature of the metal ions and acid residue.

The paper [9] describes the preparation of copper(II) complexes containing a number of salicylaldehyde-semicarbazone ligands. The obtained complexes were characterised by physicochemical methods. The X-ray structure of $[\text{Cu(HBnz}_2\text{)Cl}]\cdot\text{H}_2\text{O}$ shows that the complex is monomeric one; the copper atom is four-coordinated in a distorted plano-square geometry. The ligand chelates copper tridentate via imine(N), carbonyl(O), and phenolato(O) with the fourth position occupied by coordinated Cl. The compound $[\text{Cu(Ph}_2\text{)}\cdot\text{H}_2\text{O}]$ is also formulated as a monomer.

The authors of [10] studied the process of gold(III) complexation with 2-ethylimidazole in solution. To determine the amount of complexes formed, the authors plotted the dependence of ΔE on $\lg C_1$. The authors defined the general stability constants of $[\text{Au(2-EI)Cl}_3]$ and $[\text{Au(2-EI)}_2\text{Cl}_2]\text{Cl}$ complexes. Therefore, the stability of the complexes increases with increasing temperature. The temperature factor affects the stability of the bisubstituted complex to a greater extent. The authors of [11] synthesised and studied the physicochemical properties of gold(III) complex compounds with 1,2,4-triazole, 1,2,3-benztriazole, and 1-furfurylideneamino-1,3,4-triazole. The molecules of 1,2,4-triazole, 1,2,3-benztriazole, and 1-furfurylideneamino-1,3,4-triazole were found to be coordinated to gold(III) via the nitrogen atom of the triazole ring by IR spectroscopic method. The monosubstituted gold(III) complexes in dimethylformamide up to the temperature of 35 °C behave as compounds of non-electrolyte type; above this temperature there is a substitution of intrasphere chloride ions on DMFA molecule with the formation of new complexes of electrolyte type. The gold(III) complexes with 1,2,3-benztriazole were found to be face-centred with the centre at the nodes and the middle of the lattice basic plane. The number of structural units corresponding to them is four.

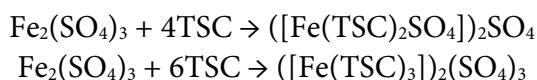


Purpose of the research

Development of optimal methods for the synthesis of iron(III) complexes with thiosemicarbazide, study of their most important physicochemical properties, and establishment of the coordination method of Fe(III) with TSC.

Main body

Studies on the synthesis and establishment of the method of thiosemicarbazide and its derivatives coordination to metal ions indicate that the method of this class of ligands coordination is influenced by the nature of the solvent, the pH of the solution, and the presence of a substituent with donor properties. We obtained complexes of iron(III) with TSC using sulfuric acid solutions (pH<1) at different ratios of initial components. The data of elemental analysis allowed us to establish the formation of iron(III) with TSC complexes with two and three TSC molecules per one metal atom. Moreover, their formation proceeds according to the following reactions:



According to the chemical analysis, both complexes contain sulfate ions. To establish the way of TSC and sulfate ions coordination to iron(III), IR spectra of the initial compounds and synthesised complexes were recorded and compared. The vibrational frequencies in the IR spectrum of TSC and its complexes with some transition metals were interpreted and assigned in [3, 12, 13]. We used these data to establish the mode of coordination of TSC to iron(III). Table 1 shows the characteristic frequencies of infrared absorption of TSC, ferrous sulfate, and iron(III) complexes with TSC at 400-4000 cm⁻¹.

Table 1. Characteristic frequencies of IR absorption of TSC, ferrous sulphate, and Fe(III) complexes

Allocation	Characteristic frequencies, cm ⁻¹			
	TSC	([Fe(TSC) ₂ SO ₄]) ₂ SO ₄	([Fe(TSC) ₃]) ₂ (SO ₄) ₃	Fe ₂ (SO ₄) ₃ ·9H ₂ O
ν(NH)	3367mid.	3396weak	3396weak	-
	3263mid.	3279weak, 3261weak, 3258weak.	3300weak, 3275weak, 3264weak	-
	3176str.	3170mid.	3188str.	-
	2972weak	2970weak	2970weak	-
δ(NH ₂)	1645str.	1635str.	1649str.	-
	1620str.	1612str.	1612str.	-
δ(NH)+ν(CN)	1533str.	1559mid.	1556mid.	-
	1508very weak	1508very weak	1508very weak	-
ν(CN)+δ(NH)	1485weak, 1458very weak	1556mid., 1400weak	1440mid., 1400mid.	-
Amide III	1317mid.	1355mid.	1355mid.	-
Amide III	1287mid.	1203weak	1200weak	-
ρ̇(NH ₂)	1165mid.	1120mid.	1120str.	-
ω(NH ₂) ν(NN)	1001str.	-	-	-
ν(CS)	800str.	694mid.	694mid.	-
SO ₄	-	1080very str.	1099very str.	1186str., 1117str., 1063str., 1015str.



IR-spectrum TSC ($\text{N}^a\text{H}_2\text{N}^b\text{HC}^c\text{SN}^d\text{H}_2$) in the range of $2900\text{--}3500\text{ cm}^{-1}$ has four absorption bands of different intensities (see Table 1). It has the valence vibrations $\nu(\text{N}^d\text{H}_2)\text{--}3367\text{ cm}^{-1}$; $\nu(\text{N}^a\text{H}_2)\text{--}3263\text{ cm}^{-1}$, $\nu(\text{N}^b\text{H})\text{--}3176\text{ cm}^{-1}$ and $\nu(\text{NH})\text{--}2972\text{ cm}^{-1}$, respectively [12]. The above-mentioned bands in the spectra of the composition complexes $([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$ and $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$ show different behaviour. Thus, undergoing slight changes, the band $\nu(\text{N}^b\text{H})\text{--}3176\text{ cm}^{-1}$ in the IR-spectrum of the complex $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$ appears at 3188 cm^{-1} . The band responsible for $\nu(\text{N}^d\text{H}_2)\text{--}3367\text{ cm}^{-1}$ in the spectrum of the complex composition $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$, undergoing a high-frequency shift, appears at 3396 cm^{-1} . The band $\nu(\text{N}^a\text{H}_2)\text{--}3263\text{ cm}^{-1}$ splits into several bands of low intensity in the spectra of the complexes (e.g., the IR spectrum of $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$. It shows three bands of low intensity at 3300 , 3275 and 3264 cm^{-1} , respectively). The TSC band appearing at 2972 cm^{-1} undergoes a slight change in the spectra of the complexes. Two bands of strong intensity at 1645 and 1620 cm^{-1} appear in the IR spectrum of TSC in the range of $1700\text{--}1600\text{ cm}^{-1}$. A slight low-frequency shift of the band appearing in the TSC spectrum at 1620 cm^{-1} occurs in the IR spectrum of the complexes (see Table 1). The TSC band at 1645 cm^{-1} in the spectra of the complexes splits and appears as two bands of strong intensity (see Table 1). The changes observed in the character of absorption bands occurrence are related to valence; strain vibrations of NH groups are related to the coordination of the nitrogen atom of the hydrazine fragment of the TSC molecule to iron(III).

The nitrogen atom of the TSC molecule in coordination is also confirmed by the change in the frequency of the bands related to the valence and strain vibrations of the NH-, CN-, and NN-groups in the spectra of the complexes compared to uncoordinated TSC. Thus, the band related to 'AmideIII' (see Table 1) in the IR spectrum of the complexes undergoes a strong low-frequency shift and appears for $([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$ at 1203 cm^{-1} ; in the spectrum of $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$ it appears at 1200 cm^{-1} . A very intense band in the TSC spectrum appears at 1001 cm^{-1} . According to [3], this band is mainly contributed by $\omega(\text{NH}_2)\text{--}$ and $\nu(\text{NN})\text{--}$ groups. We did not detect this band in the spectra of the complexes, i.e. it disappeared.

Many researchers [3-5, 12, 13] consider the band appearing in the IR spectrum of TSC at $800\text{--}805\text{ cm}^{-1}$ to be the vibrations of the $\nu(\text{CS})\text{--}$ group. This band in the IR spectra of the synthesised complexes, unlike TSC, undergoes a very strong low-frequency shift and appears in the spectra of the synthesised complexes at 694 cm^{-1} (see Table 1). The experimental fact obtained is a strong evidence of participation of sulphur atom of TSC molecule in coordination with iron(III).

The existence of the sulfate ion in the complexes is proved by the appearance of bands characteristic of this ion in the complexes IR spectra. Fig. 1 and 2 show the IR spectra of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$.

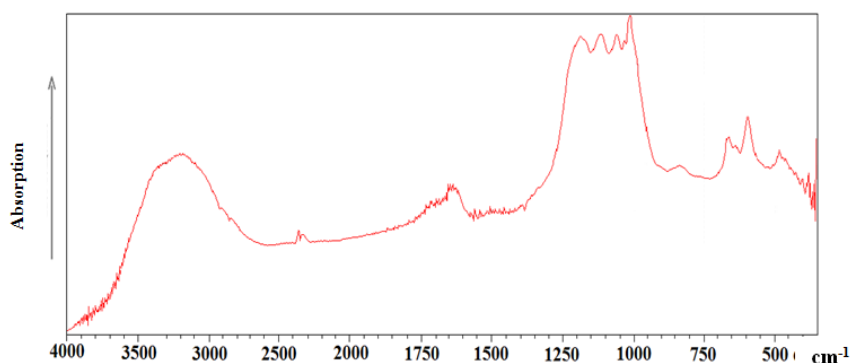


Fig. 1. IR spectrum $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$

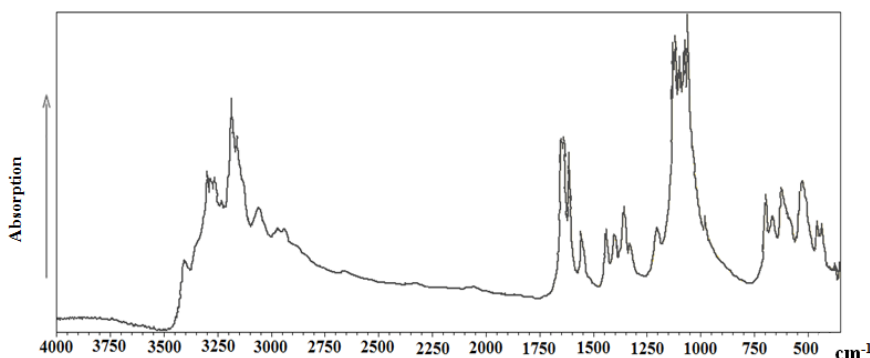


Fig. 2. IR spectrum of the complex $([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$

The infrared spectrum of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ at 3200 and 1614 cm^{-1} shows bands related to valence and strain vibrations of the hydroxyl group of the water molecule. These bands in the IR spectra of $([\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$ and $([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$ could not be interpreted, as these regions show several intense bands of the organic ligand itself.

The oscillation frequencies for the sulphate ion according to [14] are characterised by the oscillation frequencies at ν_1 (983 cm^{-1}), ν_2 (450 cm^{-1}), ν_3 (1105 cm^{-1}), and ν_4 (611 cm^{-1}). A band of weak intensity is evident in the IR spectra of $([\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$ and $([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$, in contrast to the TSC spectrum at 980 cm^{-1} . It likely refers to ν_1 (983 cm^{-1}) of the sulfate ion. The IR spectrum of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ in the range of 1000-1200 cm^{-1} is characterised by a set of alternating bands (see Fig. 1). According to [15], it can be attributed to ν_3 sulphate ions, one of which is a bridge between iron atoms. Two bands, a strong band at 1080 cm^{-1} and a medium band at 1120 cm^{-1} , appear in the IR spectrum of $([\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$ in this range. These bands are absent in the spectrum of TSC. The occurrence of bands related to ν_3 (SO_4) in the spectrum of the complex suggests that one of the two sulfate ions is located in the complex inner sphere. The IR spectrum of the complex composition $([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$ at 1000-1200 cm^{-1} is characterised by four bands (1059, 1072, 1116 and 1126 cm^{-1}). It clearly indicates the presence of sulphate ions in the composition of the complex.

Thus, the synthesised complexes contain bands characteristic of iron(III), TSC, and sulphate ions. Consequently, TSC coordinates with iron(III) bidentate via sulphur and nitrogen atoms of the hydrazine fragment.

Thermogravimetric studies showed the essential difference of complex thermal decomposition process from the thermal decomposition of the initial compounds. The synthesized thiosemicarbazide complexes of iron(III) do not contain crystallisation water molecules in contrast to $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. Thermograms of the complexes also do not contain effects characteristic of organic ligands melting. Therefore, the thermogravigram of the composition complex $([\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$ by the TG curve up to 185 $^\circ\text{C}$ is characterised by mass invariance (Fig. 3).

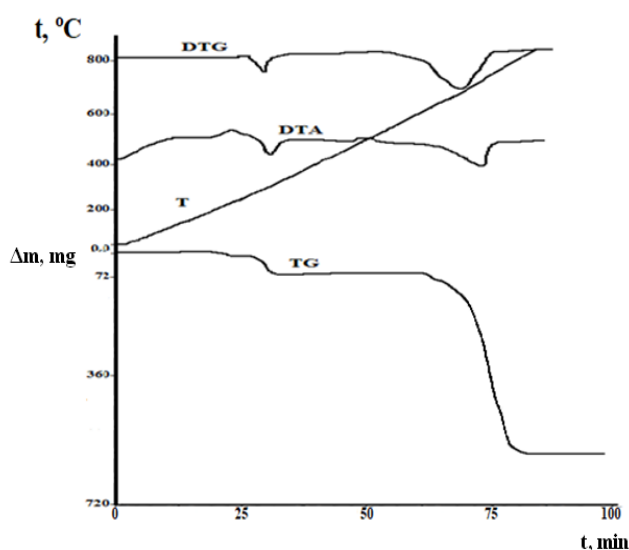


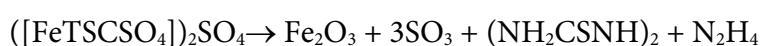
Fig. 3. Thermogram of the composition complex $([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$

No effects are also observed on the DTA curve in this temperature range, although the melting temperature of TSC is 183 °C. The DTA curve of the complex is characterized by alternating exo- and endoeffects in the temperature range of 200 °C – 320 °C. The mass loss from the TG curve for the exoeffect is 2% of the suspension weight; for the endoeffect it is 11%. We performed experiments with a larger weight of the complex in order to determine the specifics of the complex changing in this temperature range. Our results were based on the data of the complex thermogram. For this purpose, 0.5 g of the complex was kept under isothermal conditions to a constant mass at a temperature of 320 °C in a thermo-cabinet. As a result, the complex colour becomes light brown, and the mass loss is 12% of the weight of the suspension. The complex heated at 320 °C was analysed for the content of the corresponding elements, which were as follows: Fe=18.9%; N=14.5%; S=27.2%; C=4.22%; H=1.77%.

Presumably, in the temperature range of 200–320 °C decomposition and removal of one of thiosemicarbazide molecule from the complex occurs as follows:



The temperature ranges 320-530 °C for the complex is characterised by mass invariance. At this temperature range there is no effects observed on the DTA curve. Starting from 550 °C, the complex sharply loses its mass; the process completed at 740 °C. At this temperature range the endoeffect is observed on the DTA curve. The percentage of mass loss on the TG curve at this temperature range is 84% of the suspension weight. The initial complex weighing 0.556 g was held to constant mass in a thermal oven at 750 °C in order to characterise the reaction product. The product is formed as a result of thermal decomposition at the temperature range 550-740 °C. The percentage of mass loss of the complex was 81%. The sample subjected to elemental analysis after decomposition in the thermo-oven contained 68% Fe. According to the obtained experimental data, at the temperature range 550-740 °C there is a complete complex decomposition. The molecule of thiosemicarbazide is first removed from the complex, and then iron(III) sulphate decomposes to form iron(III) oxide according to the equation:





The thermogram of the complex contains three molecules of TSC. It corresponds to the composition $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$, (Fig. 4) and differs from the thermogram of the two-substituted complex (as it was discussed above) because in the thermogram of the former all mass losses are characterised by exoeffects.

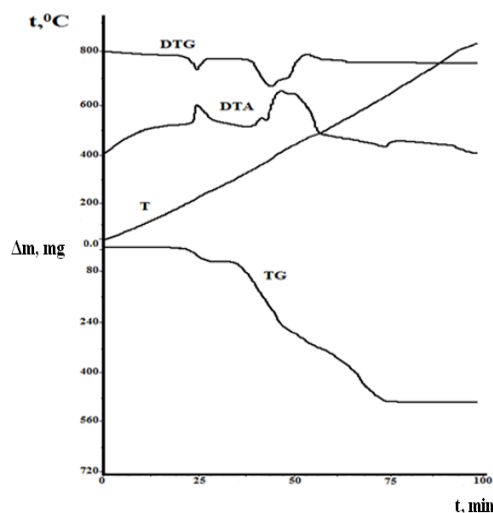
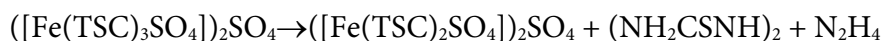


Fig. 4. Thermogram of composition complex $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$

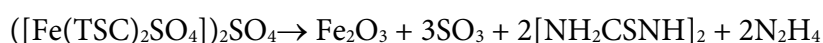
The thermogram of $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$ up to 190 °C along the TG curve is characterised by mass invariance. There are no effects are also observed on the DTA curve of the complex at this temperature range. At the range of 200-280 °C, the complex loses 6% of the total mass. We used the data of thermogravimetry to conduct an experiment with a larger weight of the complex to more accurately establish the nature of thermal decomposition. The complex heated under isothermal conditions of 0.655 g changed its colour from light yellow to ashy. The percentage of mass loss of the sample after heating was 6.9% of the suspension weight. The elemental analysis data were as follows: Fe=14.9%; N=21.6%; S=28.8%; C=6.22%; H=2.77%.

Taking into account the data of elemental analysis, the percentage of mass loss of the complex and the exo-effect on the thermogram, we can assume the occurrence of decomposition of one ligand mole in the complex and its removal according to the equation at this temperature range.



Three exoeffects are observed in the thermogram of the complex in the range 320-660 °C. The first exoeffect occurs at 380 °C; the second and third ones occur at 420-460 °C. For these exoeffects, the mass loss on the TG curve is continuous and there is no clear delineation. The mass loss of the complex at the temperature region 320-660 °C is 65% of the suspension total mass. Under isothermal conditions we have heated the complex; it turned into red-brown in colour. Elemental analysis of the heated sample showed the substance consists of 63% iron.

Taking into account the data of elemental analysis, percentage of the sample mass loss during heating, we can assume decomposition of organic ligands in the complex, their removal, and then decomposition of iron(III) sulfate, according to equation at the temperature range 320-660 °C:





The complex thermogram above the temperature of 650 °C is characterised by an endoeffect on the DTA curve; no mass loss of the complex is observed on the TG curve. The endoeffect without mass loss is most likely related to phase transitions of Fe₂O₃.

The conductometric method is one of the accurate and convenient methods for studying the properties and composition of coordination compounds. Indeed, firstly, the limitation to the application of this method in coordination chemistry is related mainly to hydrolysis of complex compounds in aqueous solutions (thus changing the composition of complexes). Secondly, complex compounds containing complex organic molecules are poorly soluble both in water and in organic solvents. Thirdly, the conductivity limits of different types of electrolytes have been determined only for a limited number of solvents. Therefore, it was difficult to study the electrical conductivity of iron(III) complexes with thiosemicarbazide and its acyl derivative. The synthesised complexes do not dissolve in organic solvents with determined conductivity limit. These compounds are poorly soluble in water. However, we prepared solutions of the synthesised complex compounds with a concentration of less than 0.0014 mol/L in water by heating.

Table 2 shows the values of temperature dependence of the molar electrical conductivity of iron(III) complexes with thiosemicarbazide in water.

Table 2. Data of temperature dependence of molar electrical conductivity of aqueous solutions of synthesised complexes, C=1.4·10⁻³mol/l

item n/a	Complex compounds	μ, Om ⁻¹ ·cm ² ·mol ⁻¹				
		293 K	298 K	303 K	308 K	313 K
1	([Fe(TSC) ₂ SO ₄]) ₂ SO ₄	279	292	331	362	397
2	([Fe(TSC) ₃]) ₂ (SO ₄) ₃	587	648	712	732	760

According to the analysis, the electrical conductivity of all synthesised complexes increases with increasing temperature. This is in agreement with the theory of electrical conductivity on the increase of ion mobility with increasing temperature. If we compare the values of the table (temperature 298 K) with the literature data [16], it is possible to determine the synthesised complexes electrolyte type. The iron(III) sulphate complex containing two molecules of TSC is 2:1 electrolyte. The complex containing three TSC molecules has conductivity characteristic of electrolytes dissociating to form five ions.

The activation energy of electrical conductivity is a quantitative characteristic of ion mobility in solution. To calculate the activation energy, it is sufficient to have experimental data on the temperature dependence of the molar conductivity (see Table 2). The activation energy from the data of the above table can be calculated both analytically and graphically. We chose the graphical method of determining the activation energy using the equation $lg \mu = -\frac{2,3E_a}{R} \frac{1}{T}$, which is recommended in [17]. We determined the activation energy by using the dependence $lg \mu = f(1/T)$ (Fig. 5). For this purpose, we found $tg \alpha$ of the straight lines and then calculated the activation energy using equation $tg \alpha = -\frac{E_a R}{2,3}$.

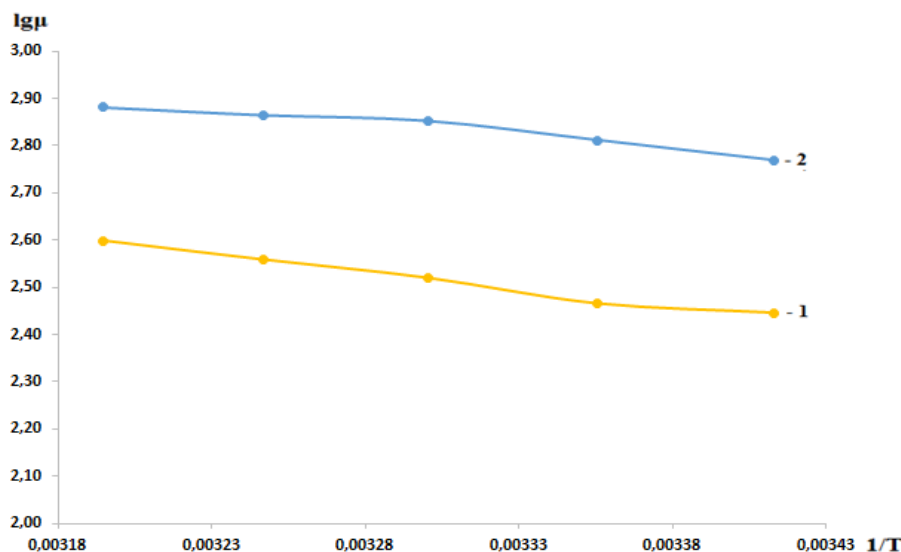


Fig. 5. Dependence of $\lg\mu = f(1/T)$ for complex compounds of composition: 1 – $([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$; 2 – $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$

Table 3 shows the activation energy values of the synthesised complexes electrical conductivity in water.

Table 3. Activation energy of the synthesised iron(III) complexes with thiosemicarbazide

item n/a	Compound	-tgα	E_{act} , cal/mol
1	$([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$	732.18	2646.67
2	$([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$	510.97	1847.05

According to Table 3, the activation energy has a minimum value for the complex that dissociates to form five ions.

Table 4 shows the molar electrical conductivity of the synthesised complexes at dilution.

Table 4. Data of concentration dependence of molar electrical conductivity of complex solutions at 298 K

item n/a	Complex compounds	μ , $\text{Om}^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$			
		Concentration of the complex, mol/l			
		$1.4\cdot 10^{-3}$	$1.3\cdot 10^{-3}$	$1.2\cdot 10^{-3}$	$1.1\cdot 10^{-3}$
1	$([\text{Fe}(\text{TSC})_2\text{SO}_4])_2\text{SO}_4$	274	297	322	343
2	$([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$	532	555	589	615

By Table 4, with dilution for all complex forms, irrespective of the type of electrolyte, the electrical conductivity increases. This dependence in coordinates μ on \sqrt{C} is linear; it is a characteristic of strong electrolytes.

We registered their X-ray diffractograms on X-ray diffractometer ‘Dron-3’ to determine the lattice parameters of the synthesised complexes. We identified radiographs using the Stipple-Lipson method [18]. Fig. 6 and 7 show the X-ray diffraction patterns of the compositions complexes $([\text{Fe}(\text{TSC})_2(\text{SO}_4)])_2\text{SO}_4$ and $([\text{Fe}(\text{TSC})_3])_2(\text{SO}_4)_3$. Both complexes show the presence of a large number of sharp reflexes, indicating their high crystallinity.

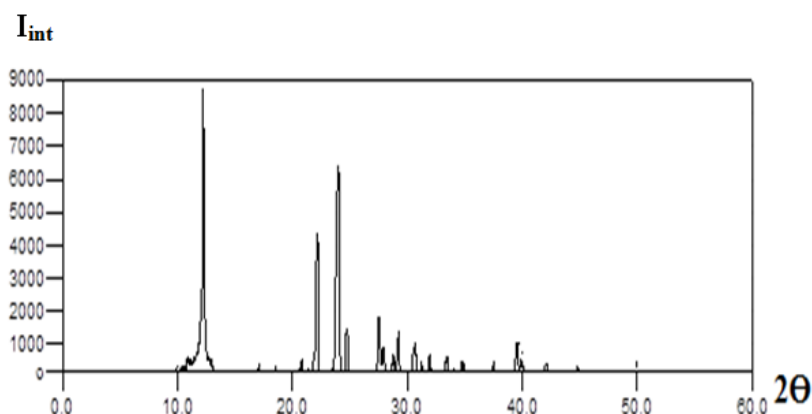


Fig. 6. Line intensity dependence on 2θ for the complex $([\text{Fe}(\text{TSC})_2(\text{SO}_4)]_2)_2\text{SO}_4$

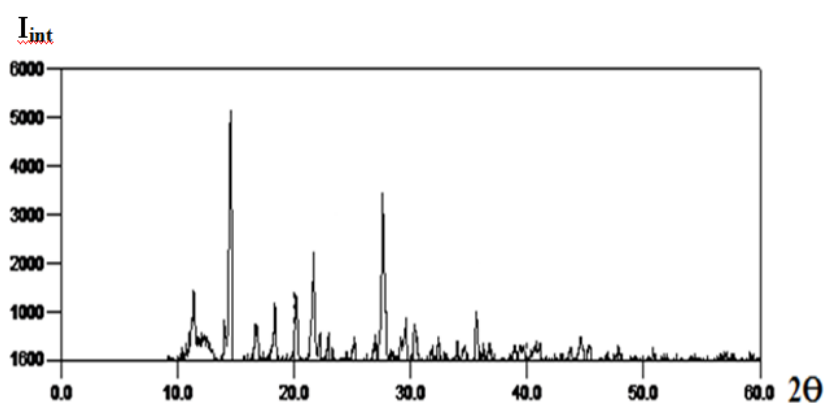


Fig. 7. Line intensity dependence on 2θ for the complex $([\text{Fe}(\text{TSC})_3]_2)_2(\text{SO}_4)_3$

The interplanar distances and unit cell parameters of the complexes calculated from powder X-ray radiographs by the Stipple-Lipson method [18] are given in Tables 5, 6 and 7.

Table 5. Identification of the complex's radiographs $([\text{Fe}(\text{TSC})_2(\text{SO}_4)]_2)_2\text{SO}_4$

item	2θ	$\sin^2\theta_{\text{exp}}$	hkl	$\sin^2\theta_{\text{theor}}$
1	9.732	0.007195	1:0:0	0.0064000
2	10.24	0.007964	0:1:0	0.0079000
3	11.044	0.009260	0:0:1	0.0092600
4	12.308	0.011492	1:1:0	0.0143000
5	14.856	0.016713	1:0:1	0.0156600
6	15.112	0.017291	0:1:1	0.0171600
7	17.406	0.022895	1:1:1	0.0235600
8	18.436	0.025661	2:0:0	0.0256000
9	21.254	0.034009	2:0:1	0.0348600
10	23.534	0.041588	2:1:1	0.0427600
11	25.768	0.049719	1:1:2	0.0513400
12	26.307	0.051784	1:1:2	0.0513400
13	27.631	0.057024	2:2:0	0.0572000
14	28.623	0.061105	2:0:2	0.062640
15	32.942	0.080389	0:3:1	0.0803600
16	34.693	0.088893	1:0:3	0.0897400
17	35.432	0.092598	1:0:3	0.0897400
18	38.598	0.109229	0:3:2	0.1081400



19	40.328	0.118824	2:1:3	0.1168400
20	43.426	0.136869	3:3:1	0.1379600
21	43.929	0.139900	2:2:3	0.1405400
22	45.287	0.148222	3:1:3	0.1488400
23	49.576	0.175781	4:3:0	0.1735000
24	54.177	0.207358	4:3:2	0.2105400
25	55.669	0.218014	0:3:4	0.2192600
26	57.526	0.231542	2:4:3	0.2353400
27	59.329	0.244946	2:3:4	0.2448600

Table 6. Identification of the complex's radiographs $([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$

item	2θ	$\sin^2\theta_{\text{exp}}$	hkl	$\sin^2\theta_{\text{theor}}$
1	10.225	0.007941	1:0:1	0.0080810
2	10.961	0.009122	0:1:1	0.0093420
3	11.382	0.009833	2:0:0	0.0109160
5	14.039	0.014935	0:2:0	0.0149060
6	14.516	0.015961	0:2:0	0.0159600
7	16.695	0.021076	0:2:1	0.0213120
8	16.827	0.021408	0:0:2	0.0214080
9	17.83	0.024015	1:0:2	0.0241370
10	18.335	0.025383	0:1:2	0.0253980
11	20.156	0.030621	3:0:1	0.0299130
12	21.648	0.035266	0:3:0	0.0359100
13	22.168	0.036959	2:1:2	0.0363140
14	22.928	0.039502	1:3:0	0.0386390
15	25.165	0.047457	2:3:0	0.0468260
16	26.979	0.054414	1:1:3	0.0548870
17	27.608	0.056931	0:3:2	0.0573180
18	29.589	0.065205	3:3:1	0.0658230
19	30.329	0.06843	2:3:2	0.0682340
20	32.392	0.077799	3:1:3	0.0767190
21	33.985	0.085408	1:3:3	0.0868070
22	35.671	0.093811	2:3:3	0.0949940
23	41.067	0.123029	1:5:2	0.1238870
24	45.386	0.148836	0:2:5	0.1497600
25	50.816	0.184094	0:5:4	0.1853820
26	57.658	0.232514	0:5:5	0.2335500
27	59.261	0.244436	2:5:5	0.2444660

Table 7. Structural parameters of crystal lattices of iron(III) complex compounds with TSC and FTSC

Compound	Ligand	Unit cell parameters			Number of structural units per cell	Singony
		a, Å	b, Å	c, Å		
$([\text{Fe}(\text{TSC})_3\text{SO}_4]_2\text{SO}_4$	TSC	9.64	8.67	8.01	2	Ortorhombic
$([\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$	TSC	14.76	12.20	10.54	2	Ortorhombic

According to Table 7, iron(III) complexes with TSC have orthorhombic syngony with two structural units in the cell.



Experimental part

We used $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as starting compounds. They were prepared according to the methods described in [19]. TSC-sold was marked as 'T' and was recrystallised from aqueous solutions. We determined Fe^{3+} and Cl^- ions in the complexes composition by the gravimetric method [20]. We determined hydrogen, carbon, nitrogen, and sulphur on a CHNS-element analyser 'Vario-Microcube', SO_4^{2-} and NO_3^- ions by potentiometric method using sulphate- and nitrate-selective electrodes. We prepared solutions of H_2SO_4 , HCl , and HNO_3 of different concentrations using fixanal.

We recorded the infrared spectra of the complexes in the range of 400-4000 cm^{-1} on a FTIR spectrometer IRAffinity-1 (SHIMADZU, Japan) in the form of KBr tablets. The electrical conductivity of solutions of the synthesised complexes was measured in a closed thermostated cell on a HI 8733 Conductivitymeter. We took X-ray diffractograms of powder samples on X-ray diffractometer 'Drone-3' using 'Illumination' and 'Reflection' methods. We studied the process of thermolysis of the formed complexes on a derivatograph 'Q-1500' of the 'Paulik-Paulik-Erdey' system.

Synthesis ($[\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$). We added a solution containing 0.32 g of thiosemicarbazide to 10 ml of acidic solution containing 1.0 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ while stirring on a magnetic stirrer. A yellow sediment precipitates out of the solution after six hours of stirring on a magnetic stirrer. The obtained complex was washed in cold water and dried in a vacuum-exicator over concentrated sulfuric acid. The obtained compound is poorly soluble in water and organic solvents. Found, %: Fe - 14,16; N - 22,64; H - 2,48; C - 6,19; S - 28,88. For ($[\text{Fe}(\text{TSC})_2\text{SO}_4]_2\text{SO}_4$) calculated, %: Fe - 14,66; N - 22,00; H - 2,62; C - 6,28; S - 29,32.

Synthesis ($[\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$). We added a solution containing 0.49 g of thiosemicarbazide to 10 ml of acidic solution containing 1.0 g of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ while stirring on a magnetic stirrer. A brownish-white sediment precipitates out of the solution during three hours of stirring. We washed the compound with cold water and dried it in a vacuum-exicator over concentrated sulfuric acid. The obtained complex is poorly soluble in water and organic solvents. Found, %: Fe - 12.13; N - 26.14; H - 3.05; C - 8.06; S - 30.06. For ($[\text{Fe}(\text{TSC})_3]_2(\text{SO}_4)_3$) is calculated, %: Fe - 11.84; N - 26.64; H - 3.17; C - 7.61; S - 30.44.

Conclusions

1. The authors have developed optimal synthesis techniques and isolated new iron(III) coordination compounds with TSC in solid state. The individuality of the formed complexes was proved by elemental analysis, conductometry, thermogravimetry, IR spectroscopy, and X-ray diffraction. The data of potentiometric titration on the stepwise character of iron(III) complexation with TSC were confirmed. The authors suggested the most probable reactions for the complexes formation.

2. We identified the synthesized complexes electrolyte type by the conductometry method. The authors identified the intermediate and final products of their thermolysis. IR spectroscopy shows the coordination of TSC by iron(III) bidentate via sulphur and nitrogen atoms.



References

1. **Gazieva, G.A. & Kravchenko, A.N.** (2012) Thiosemicarbazides in the Synthesis of Five- and Six-Membered Heterocyclic Compounds, *Uspekhi khimii*, 81(6), pp. 494–523 (in Russian).
2. **Mironov, A.Yu. & Leonov, V.V.** (2016) Iron, virulence and intermicrobial interactions of opportunistic pathogens, *Uspekhi sovremennoi biologii*, 136(3), pp. 285-294 (in Russian).
3. **Campbell, M.J.-M.** (1975) Transition metal complexes of thiosemicarbazideanc, thiosemicarbazones, *Coordination Chemistry Reviews*, 15, pp. 273–319. DOI: 10.1016/S0010-8545(00)80276-3.
4. **Aminjanov, A.A., Kurbanov, N.M. & Akhmedov, K.U.** (1990) Complex compounds of rhenium(V) with stiosemicarbazide, *Zhurn. neorgan. khimii*, 34(10), pp. 2557–2563 (in Russian).
5. **Safarmamadov, S.M.** (1994) Complex compounds of rhenium(V) with 4-methylthiosemicarbazide, 4-methyl-1,2,4-triazolthiol and their derivatives: Ph.D. Dushanbe (in Russian).
6. **Rakhimova, M., Faizullozoda, E.F., Davlatshoeva, J.A. & Eshova, G.B.** (2022) Influence of concentration parameters of solution of the homogeneous system Fe(II) - Fe(III) - glycine - Na(H)ClO₄ - H₂O on the composition of complexes formed, *From Chemistry Towards Technology Step-By-Step*, 4(1), pp. 15–21. DOI: 10.52957/27821900_2023_01_25 [online]. Available at: URL: <https://chemintech.ru/ru/nauka/issue/5032/view> (accessed 10.02.2024) (in Russian).
7. **Buvrayev, E., Kadirova, Sh., Tillayev, S., Abilkasimova, G. & Tursunova, N.** (2021) Synthesis and investigation of mixed bioligand complexes with melamin and glycine, *Universum: Chemistry and Biology : electronic scientific journal*, 10(88). DOI: 10.32743/UniChem.2021.88.10.12332 [online]. Available at: <https://7universum.com/ru/nature/archive/item/12332> (accessed 02.01.2024).
8. **Popov, L.D., Raspopova, E.A., Borodkin, S.A., Tupolova, Y.P., Levchenkov, S.I. & Shcherbakov, I.N.** (2020) Synthesis and physicochemical study of phthalazinyldiazone 2-aminopyridine-3-carbaldehyde and metal complexes on its basis, *Zhurnal obshchey khimii*, 90(3), pp. 432–440. DOI: 10.31857/S0044460X20030138 (in Russian).
9. **Lee, H.F., Yang, C.-T., Fan, D., Vittal, J.J. & John, D.** (2003) Ranford Synthesis, characterization and physicochemical properties of copper(II) complexes containing salicylaldehydesemicarbazone, *Polyhedro*, 22(20), pp. 2781–2786. DOI: 10.1016/S0277-5387(03)00402-9.
10. **Safarmamadzoda, S.M., Kurbonbekov, D.S. & Muborakkadamov, D.A.** (2022) Influence of temperature on the stability of 2-ethylimidazole Au (III) complexes, *From Chemistry Towards Technology Step-By-Step*, 3(3), pp. 58–64. DOI: 10.52957/27821900_2022_03_58 [online]. Available at: <https://chemintech.ru/ru/nauka/issue/5031/view> (accessed 23.02.2024) (in Russian).
11. **Safarmamadov, S.M., Muborakkadamov, D.A. & Mabatkadamzoda, K.S.** (2020) Synthesis and physico-chemical exploration complex compounds of gold (3) with triazoles, *Vestnik Tadzhijskogo natsionalnogo universiteta. seriya estestvennykh nauk*, 1, pp. 154–167 (in Russian).
12. **Mashima, M.** (1964) The Infrared Absorption Spectra of (NH₂CONH-)₂, NH₂CONHNH₂, (NH₂CSNH-)₂ and NH₂CSNHNH₂, *Bulletin of the Chemical Society of Japan in 1964*, 37(7).
13. **Wiles, A. & Suprunchuk, T.** (1969) The infrared absorption spectra of thiosemicarbazide and related compounds: NH and NH vibrations, *Canadian Journal of Chemistry*, 47. 1087. DOI: 10.1139/V69-173.
14. **Lane, M.D.** (2007) Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals, *American Mineralogist*, 92, pp. 1–18. DOI: 10.2138/AM.2007.2170.
15. **Nakamoto, K.** (1991) *IR- and Raman spectra of inorganic and coordination compounds*. M.: Mir (in Russian).
16. **Kukushkin, Y.N.** (1985) *Chemistry of coordination compounds*. M.: Vysshaya shkola (in Russian).
17. **Gorbacheva, S.V.** (1974) *Practicum on physical chemistry*. M.: Vysshaya shkola (in Russian).
18. **Lipson, G. & Stuil, G.M.** (1972) *Interpretation of powder radiographs*. M.: Mir (in Russian).
19. **Karyakin, Y.V. & Angelov, I.I.** (1974) *Pure Chemical Substances*. M.: Mir (in Russian).
20. **Norova, M.T., Shodiyeva, S.F., Khamzayeva, G.C., Rachinskaya, G.F. & Vakhobova, R.U.** (2015) *Gravimetry and Vatrmetry*. Dushanbe: Tadh. nats. un-t (in Russian).

Received 05.04.2024

Approved 16.05.2024

Accepted 02.07.2024