

Isomerism of octahedral thiosemicarbazide nickel(II) complexes

A. SIROTA, T. ŠRAMKO, and J. GAŽO

Department of Inorganic Chemistry, Slovak Technical University,
880 37 Bratislava

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Solid nickel(II) complexes with thiosemicarbazide, $\text{CH}_3\text{N}_3\text{S}$ (tsc), of the type $[\text{Ni}(\text{tsc})_3]\text{X}_2$ were prepared, X being NO_3^- (monohydrate and anhydrous), Cl (anhydrous), Br^- (anhydrous), I^- (dihydrate and anhydrous α and β isomer), and ClO_4^- (dihydrate and anhydrous). Their spectral, magnetic, and thermal properties were investigated.

The above complexes are paramagnetic and show electronic absorption spectra typical of octahedral nickel(II) complexes. Thiosemicarbazide molecules were proved to be bidentate ligands, forming NiN_3S_3 environment around the central atom.

Infrared absorption spectra allowed to separate the complexes under investigation into two groups:

1. nitrates, perchlorates, and iodides (dihydrate and anhydrous α isomer),
2. anhydrous chloride, bromide, and iodide (β isomer).

Differences found in electronic absorption spectra were in good agreement with those observed in infrared spectra. Splitting of absorption bands as well as the crystal structure analysis results known for $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2$, make it possible to come to the conclusion that the complexes of the first group have 1,2,3-arrangement of ligands (*cis*), while those of the second group are most probably *trans* isomers with 1,2,6-arrangement. The anhydrous α and β forms of iodide (green or blue, respectively) are considered to be geometrical isomers. Method for preparation of both isomers and their mutual interconversions are given in the present paper. It has been found that the β isomer is thermodynamically more stable.

Были приготовлены комплексы двухвалентного никеля с тиосемикарбазидом (tsc), типа $[\text{Ni}(\text{tsc})_3]\text{X}_2$, где X = NO_3^- (моногидрат и безводный), Cl^- (безводный), Br^- (безводный), I^- (дигидрат и безводный α - и β -изомер) и ClO_4^- (дигидрат и безводный). Были изучены их спектральные, магнитные и термические свойства.

Все комплексы данного типа парамагнитны и их электронные спектры поглощения типичны для октаэдрических комплексов двухвалентного никеля. Молекулы тиосемикарбазидов выступают в роли бидентатного лиганда и образуют хромофор NiN_3S_3 .

На основе инфракрасных спектров можно эти комплексы разделить на две группы:

1. нитраты, перхлораты и йодиды (дигидрат и безводный α -изомер),
2. хлорид, бромид и йодид (β -изомер).

Это разделение находится в согласии с разницей найденными тоже в электронных спектрах поглощения. Принимая во внимание расщепление полос в спектрах и также известные кристаллические структуры $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ и $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2$ комплексы первой группы можно было обозначить как комплексы

с 1,2,3-расположением лигандов (*цис*), между тем как комплексы второй группы, вероятно, имеют лиганды в 1,2,6-положении (*транс*). Безводные α - и β -изомеры $[\text{Ni}(\text{tsc})_3]\text{I}_2$ (зелёный и синий) очевидно являются геометрическими изомерами. В работе описан способ приготовления и взаимные превращения изомеров. Было найдено, что β -изомер является термодинамически стабильнее α -изомера.

Compounds with a molar ratio of $\text{Ni(II)} : \text{tsc} = 1 : 2$ and $1 : 3$ are typical of solid nickel(II) complexes with thiosemicarbazide.

Solid square-planar and octahedral complexes with the molar ratio $1 : 2$, namely their preparations, structural, spectral, and magnetic properties, were thoroughly investigated by many authors [1—10]. It has been proved that two thiosemicarbazide molecules are coordinated through their sulfur and hydrazinic nitrogen atoms in the *trans* or in the *cis* position [3, 5—8]. It was possible to differentiate different arrangement of ligands by comparison of electronic absorption spectra [9]. Moreover, square-planar $[\text{Ni}(\text{tsc})_2](\text{NO}_3)_2$ was the first complex at all, for which *cis-trans* isomerism was proved by monocrystal X-ray structure analysis [7].

On the other hand solid complexes of the type $[\text{Ni}(\text{tsc})_3]\text{X}_2$ were studied so far sporadically. Only preparation of chloride trihydrate [1] and its magnetic moment [2], diffuse reflectance spectrum of a blue iodide [11], and infrared spectra of chloride and bromide [12, 13] are mentioned in the previous papers. The authors believed that three thiosemicarbazide molecules were coordinated as bidentate ligands. This assumption has been supported by X-ray structure analysis, made for $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2$ and $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ [14, 15] which are the only complexes with the molar ratio $1 : 3$ investigated by this method. It has also been shown that molecules of thiosemicarbazide are coordinated in the *cis* position (1,2,3-isomer).

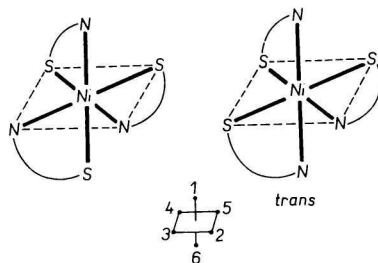


Fig. 1. Two possible arrangements of thiosemicarbazide molecules in cation $[\text{Ni}(\text{tsc})_3]^{2+}$

Three thiosemicarbazide molecules may be bonded, however, both in *cis* and in *trans* position (1,2,6-isomer) (Fig. 1). Systematical spectral investigation, presented in this paper, had the aim to answer the question whether complexes $[\text{Ni}(\text{tsc})_3]\text{X}_2$ could be formed with the *cis* as well as with the *trans* arrangement of ligands. Moreover, an attempt was made to prepare geometrical isomers for the latter complexes, applying the method used for preparation of two isomeric forms of $[\text{Ni}(\text{tsc})_2]\text{SO}_4$ [10].

Experimental

Chemicals and equipments

All chemicals used in preparations were anal. grade. Thiosemicarbazide was recrystallized twice from ethanol (50%). $\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were prepared by reaction of basic Ni(II) carbonate with acids HI and HClO_4 , respectively. Anhydrous NiBr_2 was prepared similarly, but the hydrate was dried at 110°C .

Electronic absorption spectra (350—1300 nm) were measured in Nujol mulls with a Unicam SP 700 spectrophotometer. The values of wavenumbers found for maxima of absorption bands are given in Table 1.

Table 1

Maxima of absorption bands in electronic absorption spectra of solid complexes $[\text{Ni}(\text{tsc})_3]\text{X}_2$

Complex	Absorption maxima $\tilde{\nu} \cdot 10^{-3}$, cm			$\Delta\tilde{\nu}_1$, cm
	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	
$[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	27.4 sh	16.75 ≈ 18.3 sh	10.0 10.95	950
$[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2$	27.2 sh	16.7 ≈ 18.2 sh	10.0 10.95	950
$[\text{Ni}(\text{tsc})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$		18.8 ≈ 18.2 sh	10.0 10.85	850
$[\text{Ni}(\text{tsc})_3](\text{ClO}_4)_2$		16.75 —	10.0 10.85	850
$[\text{Ni}(\text{tsc})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$	27.0 sh	17.3 ≈ 18.1 sh	10.0 11.0	1000
α - $[\text{Ni}(\text{tsc})_3]\text{I}_2$	25.9 sh	17.3 —	10.0 10.9	900
β - $[\text{Ni}(\text{tsc})_3]\text{I}_2$	26.7 sh	16.6 ≈ 18.2 sh	9.55 10.7	1150
$[\text{Ni}(\text{tsc})_3]\text{Br}_2$	26.3 sh	16.7 ≈ 18.2 sh	9.85 10.95	1100
$[\text{Ni}(\text{tsc})_3]\text{Cl}_2$	26.0 sh	16.9 ≈ 18.1 sh	9.3 10.65	1350

Infrared absorption spectra (400 — 3600 cm^{-1}) of solid samples were recorded with a double-beam UR-10 (Zeiss, Jena) spectrophotometer. Spectra taken in Nujol mulls and those made with KBr pellets

technique were not different. Infrared spectra ($200\text{--}400\text{ cm}^{-1}$) were measured in Nujol mulls with a Perkin—Elmer 225 spectrophotometer, using polyethylene plates.

Magnetic susceptibility was measured by Gouy method. Thermal properties were studied with Derivatograph, type OD-102. Powder diffraction patterns were recorded with a goniometer GON 2, using $\text{CuK}\alpha$ radiation.

Analytical procedures

Nickel was determined complexometrically with Chelaton III and sulfur as a sulfate after oxidation by nitrohydrochloric acid and potassium iodide [16]. Content of water was obtained by GTA method with accuracy of $\approx 0.5\%$.

Preparation of complexes

In preparing complexes of the type $[\text{Ni}(\text{tsc})_3]\text{X}_2$, nickel(II) salt (0.02 mole), thiosemicarbazide (0.06 mole), and in some cases also sodium salt with a corresponding anion (0.04 mole), were dissolved in a suitable amount of water at a certain temperature. After filtration solutions were left to crystallize. Crystalline products were washed by cold water and dried at room temperature.

Preparation of $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ — pale blue

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, thiosemicarbazide, and NaNO_3 were dissolved in water (30 ml) at $\approx 40^\circ\text{C}$. The product crystallized at $\approx 2^\circ\text{C}$.

For $[\text{Ni}(\text{CH}_3\text{N}_3\text{S})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (474.16) calculated: 12.38% Ni, 20.29% S, 3.80% H_2O ; found: 12.32% Ni, 20.53% S, 4.0% H_2O .

Preparation of $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2$ — pale blue

It was prepared by dehydration of the above monohydrate at 105°C . It is hygroscopic.

For $[\text{Ni}(\text{CH}_3\text{N}_3\text{S})_3](\text{NO}_3)_2$ (456.15) calculated: 12.87% Ni, 21.09% S; found: 12.71% Ni, 21.28% S.

Preparation of $[\text{Ni}(\text{tsc})_3]\text{Cl}_2$ — blue

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, thiosemicarbazide, and NaCl were dissolved in water (50 ml) at $\approx 80^\circ\text{C}$. Crystallization at room temperature.

For $[\text{Ni}(\text{CH}_3\text{N}_3\text{S})_3]\text{Cl}_2$ (403.04) calculated: 14.57% Ni, 23.87% S; found: 14.61% Ni, 23.52% S.

Preparation of $[\text{Ni}(\text{tsc})_3]\text{Br}_2$ — blue

NiBr_2 and thiosemicarbazide were dissolved in hot water (50 ml). Crystallization at room temperature.

For $[\text{Ni}(\text{CH}_3\text{N}_3\text{S})_3]\text{Br}_2$ (491.95) calculated: 11.93% Ni, 19.55% S; found: 11.76% Ni, 19.38% S.

Preparation of $[\text{Ni}(\text{tsc})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$ — dark blue

$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$ and thiosemicarbazide were dissolved in cold water and solution was left to crystallize at $\approx 2^\circ\text{C}$.

For $[\text{Ni}(\text{CH}_3\text{N}_3\text{S})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$ (621.97) calculated: 9.44% Ni, 15.47% S, 5.79% H_2O ; found: 9.35% Ni, 15.32% S, 5.5% H_2O .

Preparation of α -[Ni(tsc)₃]I₂ — green

It was prepared by dehydration of the dihydrate at 110—120°C.

For [Ni(CH₃N₃S)₃]I₂ (585.94) calculated: 10.02% Ni, 16.42% S; found: 10.06% Ni, 16.30% S.

Preparation of β -[Ni(tsc)₃]I₂ — blue

It was prepared in the same way as the dihydrate but the starting compounds were dissolved in water at higher temperature ($\approx 70^\circ\text{C}$), and crystallization was made at room temperature.

For [Ni(CH₃N₃S)₃]I₂ (585.94) calculated: 10.02% Ni, 16.42% S; found: 10.14% Ni, 16.25% S.

Preparation of [Ni(tsc)₃](ClO₄)₂·2H₂O — dark blue

In dissolving Ni(ClO₄)₂·6H₂O and thiosemicarbazide in water (30 ml at $\approx 60^\circ\text{C}$) a solution was obtained which was left to crystallize at room temperature.

For [Ni(CH₃N₃S)₃](ClO₄)₂·2H₂O (567.07) calculated: 10.35% Ni, 16.96% S; found: 10.27% Ni, 16.68% S.

Preparation of [Ni(tsc)₃](ClO₄)₂ — pale blue

Thiosemicarbazide and Ni(ClO₄)₂·6H₂O were dissolved in ethanol (30 ml) at $\approx 40^\circ\text{C}$. After filtration and stirring, pale blue fine crystalline product was obtained.

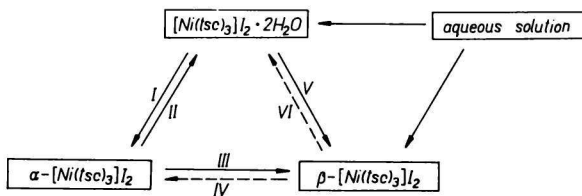
For [Ni(CH₃N₃S)₃](ClO₄)₂ (531.04) calculated: 11.06% Ni, 18.12% S; found: 11.15% Ni, 17.98% S.

Results and discussion

Complexes with the general formula [Ni(tsc)₃]X₂, obtained in the form of crystalline powders, are blue paramagnetic compounds. The only exception is α -[Ni(tsc)₃]I₂ which is green.

Isomers of [Ni(tsc)₃]I₂ differing in their spectral and diffraction properties were prepared analogically as those of [Ni(tsc)₂]SO₄ [10] according to Scheme 1. In studying conditions of their mutual conversions more in detail (in the Scheme 1 marked I—VI), here also, analogy with the sulfates was observed. Transitions I and II are reversible. Conversion of the α isomer to the β isomer (transition III) was observed when the α isomer was slowly heated at 150—160°C. (Conversion III may be realized also at lower temperatures, however, with longer time of heating.) The above transition is an exothermic reaction showing a jump on the DTA curve in the temperature range 170—200°C.

Similar to sulfates, transition V was also observed for iodides, *i.e.* conversion of the hydrate to the β isomer occurs. Left standing at room temperature for some months, humidity of the sample was registered. After short drying at 105°C, a pale blue anhydrous



Scheme 1

Preparation and conversions of α - and β -[Ni(tsc)₃]I₂.

product was obtained which gave the same diffraction powder patterns as β -[Ni(tsc)₃]I₂. Transitions IV and VI were not observed.

The results obtained allow to conclude that the β isomer when compared with the α isomer is thermodynamically more stable.

In order to decide what kind of isomers the two forms of iodide are, spectral properties of complexes [Ni(tsc)₃]X₂ were studied.

While infrared absorption spectra of thiosemicarbazide and those of thiosemicarbazide nickel(II) complexes with a molar ratio of Ni(II) : tsc = 1 : 2 were investigated thoroughly by many authors [9, 12, 13, 17—21] those of complexes [Ni(tsc)₃]X₂ have not been systematically studied. In comparing the infrared spectra we came to the conclusion that the latter compounds can be separated into two groups. Nitrates (monohydrate and anhydrous), perchlorates (dihydrate and anhydrous), and iodides (dihydrate and anhydrous α isomer) belong to the first group, whereas chloride (anhydrous), bromide (anhydrous), and iodide (anhydrous β isomer) represent the second group.

As the X-ray structure analysis made for [Ni(tsc)₃](NO₃)₂·H₂O and its anhydrous form [14, 15] proved the molecules of thiosemicarbazide to be in the *cis* position (1,2,3-isomer), the same arrangement is expected also in the complexes of the first group because their infrared spectra are analogical to those of nitrates (Fig. 2).

Our measurements have shown that for comparison of infrared spectra to differentiate the above groups of complexes, the most suitable is particularly the region 1000—1700 cm⁻¹. Complexes, assumed to have *cis* configuration, show unsplit bands or bands with a shoulder in this region, while those of the second group have most of the bands split (Fig. 3). Differences occur also in the region 400—600 cm⁻¹ where a broad intense band was observed for the complexes of the second group, but only a less distinct band for complexes with *cis* configuration was registered. The vibrations observed in the lower frequency region are probably influenced by ring deformation modes [22] and differences in infrared spectra

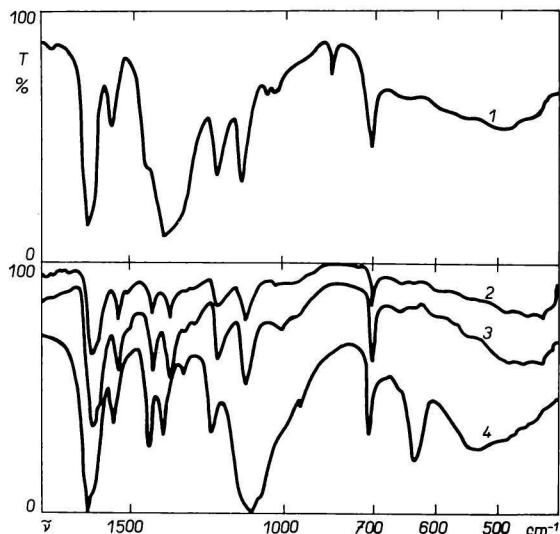


Fig. 2. Infrared absorption spectra (KBr).

1. [Ni(tsc)₃](NO₃)₂·H₂O; 2. α -[Ni(tsc)₃]I₂; 3. [Ni(tsc)₃]I₂·2H₂O; 4. [Ni(tsc)₃](ClO₄)₂·2H₂O.

of the complexes under investigation may be connected with different interactions *via* hydrogen bonds which result in different fixation of thiosemicarbazide molecules as chelate ligands. Spectrum of $[\text{Ni}(\text{tsc})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$ is in this region analogical to that of the α isomer but partly different from those of perchlorates and nitrates (Fig. 2). On the other hand full analogy was found in infrared spectra of chloride and bromide which partly differ from that of β iodide. This can be understood considering the great difference between the radii of I^- and Br^- or Cl^- . The same analogies and differences were observed also in the region of $200\text{--}400\text{ cm}^{-1}$.

The ring deformation modes are most probably responsible for the fact that a correct interpretation cannot be made for differences in the far infrared spectra which should have been observed in stretching vibrations $\tilde{\nu}(\text{Ni}\text{--}\text{N})$ and $\tilde{\nu}(\text{Ni}\text{--}\text{S})$ if complexes have different arrangement of ligands. An assignment of the bands to the above modes and any discussion about the differences observed would have only a speculative basis and has been left out.

All $[\text{Ni}(\text{tsc})_3]\text{X}_2$ show electronic absorption spectra typical of pseudooctahedral $\text{Ni}(\text{II})$ complexes. Absorption bands may be approximately assigned to the three spin-allowed transitions

$$\begin{aligned} {}^3T_{2g} &\leftarrow {}^3A_{2g}(\tilde{\nu}_1), \\ {}^3T_{1g}(F) &\leftarrow {}^3A_{2g}(\tilde{\nu}_2), \\ {}^3T_{1g}(P) &\leftarrow {}^3A_{2g}(\tilde{\nu}_3) \end{aligned}$$

in the O_h ligand-field symmetry (Table 1). Electronic absorption spectra of some complexes $[\text{Ni}(\text{tsc})_3]\text{X}_2$ are given (Fig. 4) only in the region $8000\text{--}20\,000\text{ cm}^{-1}$ (absorption bands $\tilde{\nu}_1$ and $\tilde{\nu}_2$) because the third band ($\tilde{\nu}_3$) in the region $26\,000\text{--}27\,500\text{ cm}^{-1}$ is to a great extent overlapped by charge-transfer band. Thiosemicarbazide molecules form the chromophore NiN_3S_3 in the cation $[\text{Ni}(\text{tsc})_3]^{2+}$. The coordination polyhedron is in fact a considerably

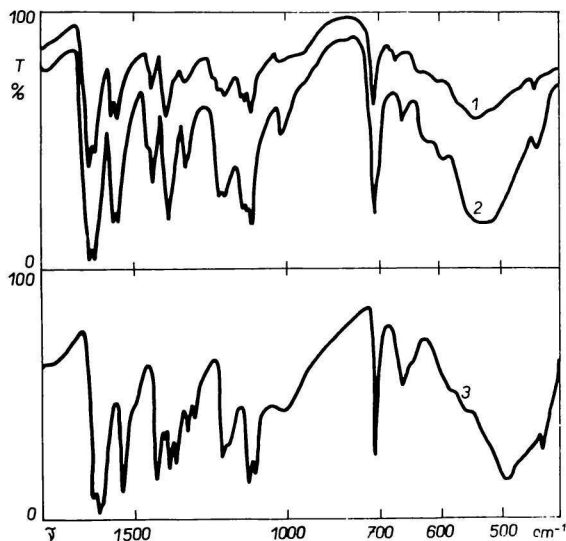


Fig. 3. Infrared absorption spectra (KBr).
1. $[\text{Ni}(\text{tsc})_3]\text{Cl}_2$; 2. $[\text{Ni}(\text{tsc})_3]\text{Br}_2$; 3. $\beta\text{-}[\text{Ni}(\text{tsc})_3]\text{I}_2$.

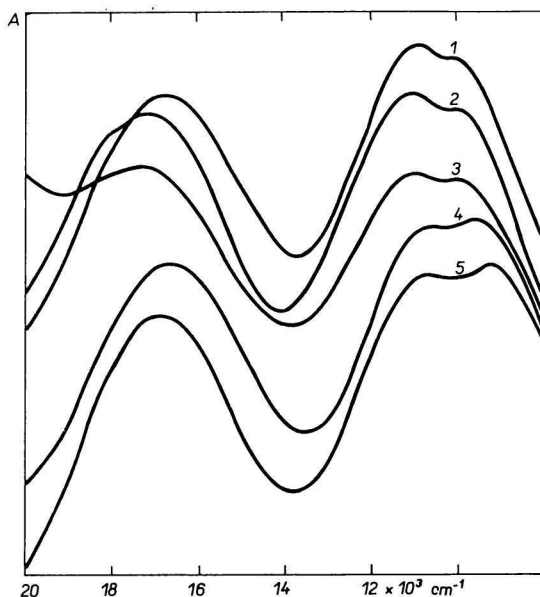


Fig. 4. Electronic absorption spectra (in Nujol).

1. $[\text{Ni}(\text{tsc})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$; 2. $[\text{Ni}(\text{tsc})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$; 3. α - $[\text{Ni}(\text{tsc})_3]\text{I}_2$; 4. β - $[\text{Ni}(\text{tsc})_3]\text{I}_2$; 5. $[\text{Ni}(\text{tsc})_3]\text{Cl}_2$.

distorted octahedron and so it is not surprising that a splitting is observed even in the second absorption band ($\bar{\nu}_2$). As it is known, absorption band with the lowest energy ($\bar{\nu}_1$) is most sensitive to the changes of symmetry. It has been supposed [23, 24] that a greater splitting $\Delta\bar{\nu}_1$ of the first absorption band is expected for complexes with 1,2,6-configuration of ligands (*trans*) when compared with that found for complexes having 1,2,3-NiN₃S₃ chromophore (*cis*). If the values and shapes of the first bands are compared, complexes $[\text{Ni}(\text{tsc})_3]\text{X}_2$ could be separated into two groups which are identical with those obtained by comparison of their infrared spectra. The value of the splitting (Table 1) is in the regions 850–1000 and 1100–1350 cm^{-1} for complexes of the first and the second group, respectively.

The X-ray structure analysis results obtained for nitrates and resemblance in infrared spectra allowed to assign compounds of the first group to the *cis* complexes. Evident mutual resemblance in spectra supports the conclusion that all complexes belonging to the second group have a similar structure. Considering also a greater splitting $\Delta\bar{\nu}_1$, it was possible to assume that anhydrous chloride, bromide, and iodide (β isomer) have most probably the *trans* configuration of ligands. (We have, in fact, no explanation for exchanged values of absorbance in the split band $\bar{\nu}_1$; see Fig. 4.) All the facts mentioned above give support to the assumption that anhydrous α and β form of $[\text{Ni}(\text{tsc})_3]\text{I}_2$ may be considered as geometrical isomers.

In preparing the complexes, attempts were made to obtain isomers also for other compounds of the type under investigation. Attention was paid to those systems, particularly where a hydrate was prepared. In searching for such conditions of dehydration under which two anhydrous isomers would be formed, it has been found that only iodide dihydrate has a different structure of coordination sphere from that of anhydrous form, prepared from

aqueous solution. Although preparation was given for $[\text{Ni}(\text{tsc})_3]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ [1] which should have been blue and after dehydration green, our many attempts were not successful and all preparations gave blue, but anhydrous chloride.

The above-mentioned method of preparation (Scheme 1) is based on the assumption that water molecules being bonded in a complicated system of hydrogen bonds, help to stabilize a certain arrangement of ligands. After dehydration under suitable conditions it is possible to keep the same arrangement also in the anhydrous α isomer. In dehydrating the hydrate, some atoms in the crystal structure show certain shifts into the more advantageous positions, nevertheless, the basic configuration of ligands in cations $[\text{Ni}(\text{tsc})_2]^{2+}$ [10] or $[\text{Ni}(\text{tsc})_3]^{2+}$ is the same as it was in the hydrate.

On the other hand, at a higher temperature (150–160°C), the above shifts may cause such changes in coordination sphere which lead to the formation of a thermodynamically more stable *trans* isomer. From this aspect, behaviour of $[\text{Ni}(\text{tsc})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$ is paradoxical because the dihydrate changes to the β isomer at room temperature, when left standing for a long time in a closed tube. It is worth mentioning that the conversion takes place in a closed room where released water can condense and locally it plays the role of a solvent from which crystallizes a thermodynamically more stable β isomer.

All those changes can be observed in particular when infrared spectra are measured. Absorption bands in the region 1000–1700 cm^{-1} arise due to the combination of several vibrations of coordinated thiosemicarbazide molecules [17–19]. With respect to the possible interactions *via* hydrogen bonds, different contributions to the vibration modes, observed in the given region, can be expected from the different molecules of thiosemicarbazide. It may certainly cause splitting, deformation or shift of the corresponding absorption bands independently from the total symmetry of the complex cation $[\text{Ni}(\text{tsc})_3]^{2+}$. Although those manifestations are unspecific, nevertheless, it seems to be possible to differentiate complexes of the type $[\text{Ni}(\text{tsc})_3]\text{X}_2$ with a different arrangement of ligands.

Electronic absorption spectra ($d-d$ transitions) are not sensitive to such an extent to the changes in the secondary coordination sphere (*cf.* values $\bar{\nu}$ in Table 1 for nitrates and perchlorates). On the other hand if water molecules are released from a hydrate, new interactions may occur and they may influence the bond system in the coordinated thiosemicarbazide molecules and consequently also charge-transfer bands. Electronic absorption spectrum of α - $[\text{Ni}(\text{tsc})_3]\text{I}_2$ serves as a clear example. The charge-transfer band in the α isomer, when compared with that observed in dihydrate, is shifted to lower frequencies and largely overlaps the absorption bands $\bar{\nu}_3$ and $\bar{\nu}_2$.

It is useful to say that any discussion on the structure of two isomeric forms $[\text{Ni}(\text{tsc})_3]\text{I}_2$ would not be possible unless the series of thiosemicarbazide complexes of the same type were available. Preparation of several complexes and comparison of their properties, being supported by some X-ray structure analysis results, allowed to classify the results obtained by indirect structural methods.

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