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Square Planar Ni^{II} Complexes of Thiosemicarbazide

A. SIROTA and T. ŠRAMKO
Department of Inorganic Chemistry, Slovak Technical University, Jánska 1, 880 37 Bratislava, Czechoslovakia
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Square planar Ni^{II} complexes of thiosemicarbazide with the general formula $Ni(Htsc)_2X_2 \cdot nH_2O$ have been studied. Their electronic and infrared absorption spectra are presented. It is shown that the electronic absorption spectra may distinguish the trans or cis arrangement of two thiosemicarbazide ligands while this differentiation is not possible on basis of the infrared absorption spectra although it was supposed before.

Introduction

Isomerism of Ni^{II} complexes was studied in our laboratory for several years. In connection with this study Ni^{II} complexes with thiosemicarbazide ligand, $NH_2NHCSNH_2$ (Htsc), were investigated because they were assumed to form geometric isomers when suitable Ni^{II} salts were used.[1,2] Although several papers have been published in this field,[3–6] our attention has been taken by a particular paper published by Haines and Sun.[7] The criteria given by these authors were based on infrared absorption spectra and seemed to be very useful for differentiation of the cis and trans arrangement of two thiosemicarbazide molecules in the complex cation $[Ni(Htsc)_2]^{2+}$.

Since some already known experimental results have not been taken into consideration and meanwhile new papers have appeared it was necessary to check the mentioned criteria and if possible to extend their validity to other complexes of the type of $[Ni(Htsc)_2]X_2$.

Experimental

Preparation of Complexes

All chemicals were made in Czechoslovakia by Lachema, Brno.

The complexes under investigation were prepared by a method based on the conclusion that the perchlorate Ni^{II} complexes of thiosemicarbazide are by far more readily soluble than complexes with other anions. When a calculated amount of a Ni^{II} salt was added to an aqueous solution of the perchlorate Ni^{II} complex of thiosemicarbazide the expected complex was precipitated and after washing and drying a fine crystalline powder was obtained. Analysis of these products gave good results (Table I).

Measurements

All analyses were carried out in our laboratory by methods given in ref. 2. Infrared absorption spectra were obtained with a Perkin Elmer 225 spectrophotometer and a Carl Zeiss (Jena) UR–10 spectrophotometer using potassium bromide disks and Nujol mulls. Reflectance spectra were measured using an Optica

TABLE I. Analysis for complexes.

Complex	% Ni Calc.	Found	% S Calc.	Found
$[Ni(Htsc)_2]SO_4 \cdot 3H_2O$	15.01	15.02	24.60	24.53
α-$[Ni(Htsc)_2]SO_4$	17.42	17.28	28.54	28.30
β-$[Ni(Htsc)_2]SO_4$	17.42	17.39	28.54	28.80
$[Ni(Htsc)_2(H_2O)_2](NO_3)_2$	14.64	14.70	15.99	15.65
$[Ni(Htsc)_2](NO_3)_2$	16.08	16.10	17.57	17.36
$[Ni(Htsc)_2]Cl_2$	18.82	18.51	20.56	20.40
$[Ni(Htsc)_2]Br_2$	14.65	14.69	16.00	16.34
$[Ni(Htsc)_2]I_2$	11.86	11.81	12.96	13.16
$[Ni(Htsc)_2(H_2O)_2](ClO_4)_2 \cdot H_2O$	11.88	11.96	12.98	13.18

Milano CF–4 spectrophotometer with a standard reflectance attachment, the absorption spectra in Nujol mulls were recorded on a Specord UV VIS (Carl Zeiss Jena) spectrophotometer. Powder patterns were obtained with a powder diffractograph model GON 2 (Chirana, Czechoslovakia) using copper K_α radiation. Magnetic moments were measured on a Gouy balance and tubes were calibrated with aqueous solution of $NiCl_2$. Thermal properties were investigated by means of a derivatograph OD 102 (MOM Budapest).

Results and Discussion

While in previous papers[1,2] syntheses and some physico-chemical properties of complex compounds with a molar ratio of Ni^{II}:Htsc = 1 : 2 were investigated, possibilities of identification of both *cis* and *trans* configuration in the complex cation $[Ni(Htsc)_2]^{2+}$ are pointed out in this paper.

Complexes with the general formula $Ni(Htsc)_2X_2 \cdot nH_2O$, in the form of fine crystalline powders, are green for X = 1/2 SO_4^{2-} (trihydrate), 1/2 SO_4^{2-} (α), Cl^-, Br^-, and I^-; red for X = 1/2 SO_4^{2-} (β) and NO_3^-; blue for X = NO_3^- (dihydrate) and ClO_4^- (trihydrate). The green and red compounds are diamagnetic, whereas the blue species are paramagnetic and their electronic absorption spectra are typical of pseudo-octahedral Ni^{II} complexes. The coordination of two water molecules in the blue nitrate dihydrate was proved by X-ray structure analysis.[8] The same coordination is assumed to be also in the perchlorate trihydrate and thus its formula is $[Ni(Htsc)_2(H_2O)_2](ClO_4)_2 \cdot H_2O$. Spectral, magnetic and thermal behaviour of this compound support the above conclusion.

The visible electronic absorption spectra of the above diamagnetic compounds are typical of square planar Ni^{II} complexes with a π-interaction supposed to occur between a ligand and the central atom. Similar spectra are shown by square planar Ni^{II} complexes with sulfur containing ligands where the sulfur atom is bonded to the nickel atom.[9] The X-ray structure analysis results found for some Ni^{II} complexes of thiosemicarbazide confirmed the partial π-bonding nature of the Ni–S bond.[5,6,8,10]

Comparison of the electronic absorption spectra showed that all the green compounds have similar spectra to that of $[Ni(Htsc)_2]SO_4 \cdot 3H_2O$ (Fig. 1, spectra 1–5) and thus they can be referred to as the complexes with *trans* configuration since this configuration was proved to be in the sulfate trihydrate.[5] Some differences in the spectra were observed in the region of 350–450 nm where charge-transfer bands occured and overlapped the d–d transition bands.

The visible spectra of the red compounds differ from those of the green ones in their wavenumbers and relative intensities of the corresponding absorption bands (Fig. 1, spectra 6 and 7). Since the crystal structures of both the red anhydrous sulfate *(cis–trans)*[6] and the red nitrate *(cis)*[11] are known the above mentioned differences can be easily explained. The spectrum of the red β-$[Ni(Htsc)_2]SO_4$, as expected in accordance with its crystal structure, must partially differ from the spectra of the green complexes of the type discussed, as well as from that of the red nitrate.

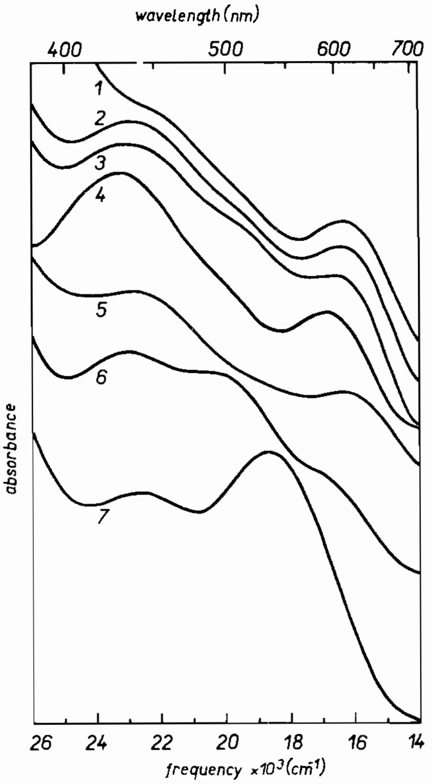

Figure 1. Electronic absorption spectra (in Nujol mulls) for complexes of the type $[Ni(Htsc)_2]X_2$. Spectrum 1: iodide, 2: bromide, 3: chloride, 4: sulfate trihydrate, 5: sulfate (α-isomer), 6: sulfate (β-isomer), 7: nitrate.

Thus, as it has been shown, the visible electronic absorption spectra of square planar Ni^{II} complexes of thiosemicarbazide may help differentiate the *cis* and *trans* configuration of the ligands.

Distinct differences in infrared absorption spectra were recorded for some complexes under investigation when measured both in KBr pellets and in Nujol mulls. The spectra were identical for both techniques in the case of chloride, bromide, iodide, anhydrous red sulfate and nitrate. On the other hand differences were found for hydrates of the sulfate, nitrate and perchlorate as well as for the anhydrous green sulfate and at the same time a striking similarity was observed between their infrared spectra measured in KBr pellets and that of $[Ni(Htsc)_2]Br_2$.

On grinding nickel(II) salts with thiosemicarbazide and also some Ni^{II} complexes of thiosemicarbazide with alkali halides a great reactivity was observed.[2] Since in preparing KBr pellets an intense grinding was necessary there arose the suspicion that in some cases the following reaction took place:

$$\mathrm{Ni(Htsc)_2X_2 \cdot nH_2O + 2\ KBr = [Ni(Htsc)_2]\,Br_2 + 2\ KX + nH_2O.}$$

Model mixtures of $[\mathrm{Ni(Htsc)_2]Br_2 + 2\ KX}$ and those of the starting compounds $\mathrm{Ni(Htsc)_2X_2 \cdot nH_2O + 2\ KBr}$ were prepared by grinding under the same conditions as the samples for infrared spectra measurements in potassium bromide pellets. In comparing the X-ray powder patterns taken from the mixtures it was proved that the above reaction occurred when sulfate trihydrate and its anhydrous green form, nitrate dihydrate and perchlorate trihydrate were the starting complexes and the resulting mixture contained always $[\mathrm{Ni(Htsc)_2]Br_2 + K_2SO_4}$, $\mathrm{KNO_3}$ and $\mathrm{KClO_4}$, respectively.

This conclusion is contradictory to that given by Haines and Sun.[7] These authors compared infrared absorption spectra of sulfates (trihydrate and the anhydrous red form), and those of nitrates (dihydrate and the anhydrous form) and chloride. For comparison of the *cis–trans* isomers certain regions of the infrared absorption spectra were suggested to be entirely distinctive.

Our experiments showed that Haines and Sun measured and then compared in fact most probably the infrared spectrum of the mixture of $[\mathrm{Ni(Htsc)_2]Br_2 + K_2SO_4}$ with that of β-$[\mathrm{Ni(Htsc)_2]SO_4}$ and similarly the infrared spectrum of the mixture of $[\mathrm{Ni(Htsc)_2]Br_2 + KNO_3}$ with that of $[\mathrm{Ni(Htsc)_2](NO_3)_2}$, and therefore their criteria for the differentiation of the *cis* and *trans* isomers were not correct. Moreover it was known that the β-form of the sulfate, considered by those authors for the pure *cis* isomer, contains cations of $[\mathrm{Ni(Htsc)_2}]^{2+}$ with both *cis* and *trans* configuration of ligands.[12]

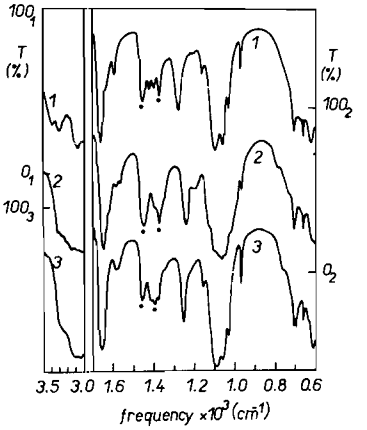

Figure 2. Infrared absorption spectra (in Nujol mulls) of $[\mathrm{Ni(Htsc)_2]SO_4 \cdot 3H_2O}$ (spectrum 1), α-$[\mathrm{Ni(Htsc)_2]SO_4}$ (2), and β-$[\mathrm{Ni(Htsc)_2]SO_4}$ (3). The absorption bands corresponding to Nujol are marked by little circles.

The infrared absorption spectra of the sulfates (trihydrate and both anhydrous forms) measured in Nujol mulls are shown in Fig. 2. Two sharp bands in the region of 3000–3400 cm^{-1}, suggested by Haines and Sun to be characteristic of the *trans* configuration, were not recorded for the green α-$[\mathrm{Ni(Htsc)_2]SO_4}$ (Figure 2, spectrum 2) and a distinct splitting of the absorption band in the region of 1600–1700 cm^{-1}, supposed also for the *trans* isomer, was not observed even for $[\mathrm{Ni(Htsc)_2]SO_4 \cdot 3H_2O}$ (spectrum 1).

A similar comparison of infrared absorption spectra was made for all complexes with a molar ratio of Ni^{II} : Htsc = 1 : 2. Considering electronic absorption spectra and all known X-ray structure analysis results for the above complexes we may come to the conclusion that there are no common criteria for the differentiation of the *cis* and *trans* configuration on the basis of their infrared absorption spectra.

The lowering of symmetry in the case of the *cis* isomer need not cause splitting of the absorption bands corresponding to the vibrations of the ligand as it is often considered. Interactions between molecules in the crystal structure may be of a great importance when vibrations of ligands are studied. Such interactions were supposed to occur in all known crystal structures of thiosemicarbazide nickel(II) complexes. Infrared absorption spectra show good agreement with those results, in particular when absorption bands are considered which correspond to the vibrations of the $\mathrm{SO_4}^{2-}$, $\mathrm{ClO_4}^{-}$, and $\mathrm{NO_3}^{-}$ anions.

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