

COORDINATION COMPOUNDS OF NICKEL AND COBALT WITH THE SCHIFF BASE DERIVED FROM THIOSEMICARBAZIDE AND DIACETYLMONOOXIME

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Coordination compounds with the compositions $[\text{Ni}(\text{H}_2\text{TSD})_2]\text{Cl}_2$, $[\text{Co}(\text{H}_2\text{TSD})_2]\text{Cl}_2$, $[\text{NiH}_2\text{O}(\text{TSD})]$, $[\text{CoH}_2\text{O}(\text{TSD})]$ and $[\text{Co}(\text{TSD})(\text{HTSD})] \cdot 2 \text{H}_2\text{O}$ were prepared, where $\text{H}_2\text{TSD} = \text{HON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{N.NH.CS.NH}_2$. Cyclic voltammetry indicated that $[\text{NiH}_2\text{O}(\text{TSD})]$ can be oxidized and reaction of this compound with bromine yielded the nickel compound with the composition $[\text{Ni}(\text{TSD})\text{Br}]$. The properties of the ligand that make it useful for stabilizing the higher oxidation states of nickel are discussed.

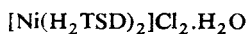
The coordination compounds of nickel in less common oxidation states have recently been systematically studied^{1,2}. The results obtained so far permit fairly reliable prediction of the properties of ligands that can stabilize nickel in the oxidation states III and IV. Amongst other factors, these are polydentate N-ligands with strong σ -donor properties. It could be expected that this property will be exhibited by the Schiff base obtained by the condensation of diacetylmonooxime and thiosemicarbazide with the composition $\text{HON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{N}-\text{NH}-\text{C}(\text{S}).\text{NH}_2 - \text{H}_2\text{TSD}$. Although the complex compounds of nickel and other transition elements with Schiff bases derived from thiosemicarbazide have been studied³⁻⁵, no systematic investigation of the coordination compounds of nickel or cobalt with this Schiff base has been carried out. This work describes the preparation and some of the properties of nickel(II) and cobalt(II) complexes with this ligand and the characteristics of the nickel(III) and cobalt(III) compounds.

EXPERIMENTAL

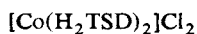
Diacetylmonooxime was the product of Loba-Chemie (Vienna); the other chemicals of p.a. purity were provided by Lachema (Brno).

The infrared absorption spectra were recorded on a Specord IR 75 instrument by the nujol technique and the electron absorption spectra were recorded on a Specord M 40 instrument (both manufactured by Carl Zeiss, Jena). The magnetic susceptibility was measured at normal temperatures by the Gouy method on magnetic scales constructed in the laboratory, calibrated

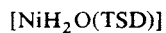
using $\text{Co}[\text{Hg}(\text{NCS})_2]$. The thermal decomposition was studied using the Derivatograph Q 1 500 D instrument (MOM, Budapest) using a sample weight of 120–150 mg and temperature gradient of $2.5^\circ\text{C}/\text{min}$. The electrical conductivity was measured in sample solutions in methanol with a concentration of $5 \cdot 10^{-4} \text{ mol l}^{-1}$ on a Conductivity meter 102/1 instrument (Radelkis, Budapest). The electrochemical measurements were carried out in dimethylformamide, methanol and in a dimethylformamide/methanol 1 : 1 mixture. The concentration of the complex varied in the range 0.2 to 1.5 mmol l^{-1} and the base electrolyte was 0.1 mol l^{-1} LiCl. Cyclic voltammograms (c.v.) were measured on an EG & G Princeton Applied Research Model 273 potentiostat/galvanostat in a three-electrode arrangement. The working electrode was glassy carbon (gC) with an area of 0.08 cm^2 and porosity of 1 to 3%. The reference electrode was a saturated calomel electrode and the auxiliary electrode was a platinum foil with a large surface area. The potential change velocity was 0.005 to 1.0 V/s .



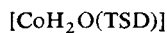
Thiosemicarbazide (0.45 g, 5 mmol) was dissolved in 15 ml of ethanol and 1.25 g (12.3 mmol) of diacetylmonooxime were added to this solution. The reaction mixture was refluxed for half an hour and then a hot solution of 1.2 g (5 mmol) $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ in 12 ml ethanol was added; after stirring for a further half hour without heating, the precipitated yellow-brown powder product was filtered off on a frit and washed with ethanol, and ether and dried in a vacuum desiccator over KOH.



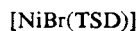
This product was obtained using a procedure identical with that described for the above compound; the reaction was carried out in an argon atmosphere. The compound is brick red in colour.



Thiosemicarbazide (0.9 g, 10 mmol) was dissolved in 30 ml of ethanol and mixed with 2.5 g (24.7 mmol) of diacetylmonooxime. The solution formed was refluxed for two hours. A hot solution of 2.4 g (10 mmol) $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ in 25 ml ethanol was then added, the solution was stirred for 15 min and then 2 ml of 27% ammonia were added. The reaction mixture was stirred for 1 h and left to stand overnight at a temperature of -10°C . The red-brown substance formed was filtered off on a frit and washed with ethanol and ether and dried in the air.



This substance which is brown in colour was obtained by carrying out a reaction analogous to that described for the nickel compound in an argon atmosphere.



Red brown $[\text{NiH}_2\text{O}(\text{TSD})]$ (0.5 g, 2 mmol) was suspended in 10 ml of chloroform and stirred at laboratory temperature for 10 min. Then 0.1 ml (3.9 mmol) of Br_2 in 5 ml of chloroform were added and the reaction mixture was stirred for 15 min. The dark brown substance was filtered off on a frit, washed with chloroform and dried in a vacuum desiccator over KOH.

[Co(HTSD)(TSD)].2 H₂O

Thiosemicarbazide (0.9 g, 10 mmol) was dissolved in 30 ml of ethanol, mixed with 2.5 g (24.7 mmol) of diacetylmonooxime and the mixture was refluxed for 5 h. Then a solution of 2.4 g (10 mmol) of CoCl₂.6 H₂O, 3 ml of a conc. aqueous ammonia solution and, in two aliquots, 2 ml of conc. H₂O₂ were added. After stirring for two hours, the yellow-brown precipitate was filtered off and washed on the frit with ethanol and ether; it was then dried in a vacuum dessicator over KOH.

RESULTS AND DISCUSSION

Table I lists the chemical compositions of the prepared substances. The Schiff base apparently acts as an electroneutral ligand in neutral solutions, while it has the character of a dibasic acid in basic medium. The Schiff base was not prepared, but the nickel(II) or cobalt(II) complex can be obtained under the conditions used here. The ligand is formed by the condensation of a single molecule of diacetylmonooxime with thiosemicarbazide. Similar results were obtained by Gerbeleu et al.³ in a study of the nickel(II) complexes with Schiff base produced by the condensation of salicylaldehyde and thiosemicarbazide. These authors demonstrated that only template synthesis can be employed to produce the Schiff base in which

TABLE I

The chemical compositions of the substances prepared (%)

Compound	Formula (M _r)	Found/Calculated				
		Ni(Co)	C	H	N	Cl(Br)
[Ni(H ₂ TSD) ₂]Cl ₂ .H ₂ O	C ₁₀ H ₂₂ Cl ₂ N ₈ . .NiO ₃ S ₂ (496.0)	12.28	24.36	4.46	22.34	14.06
		11.84	24.21	4.47	22.53	14.28
[Co(H ₂ TSD) ₂]Cl ₂	C ₁₀ H ₂₀ Cl ₂ Co. .N ₈ O ₂ S ₂ (478.2)	11.69	25.74	4.35	22.93	14.06
		12.32	25.11	4.23	23.43	14.82
[NiH ₂ O(TSD)]	C ₅ H ₁₀ N ₄ NiO ₂ S (248.9)	23.28	24.60	3.96	22.98	
		23.58	24.12	4.04	22.51	
[CoH ₂ O(TSD)]	C ₅ H ₁₀ CoN ₄ O ₂ S (249.1)	23.84	24.90	4.36	22.88	
		23.63	24.10	4.05	22.50	
[NiBr(TSD)]	C ₅ H ₈ BrN ₄ NiOS (310.8)	18.81	19.75	2.70	17.92	25.08
		18.89	19.32	2.59	18.03	25.71
[Co(HTSD)(TSD)].2 H ₂ O	C ₁₀ H ₂₁ CoN ₈ O ₄ S ₂ (440.4)	13.52	27.03	4.81	25.58	
		13.38	27.27	4.46	25.45	

two salicylaldehyde molecules can be bonded to the two thiosemicarbazide amino groups in the condensation reaction.

The compound $[\text{Ni}(\text{H}_2\text{TSD})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ is a yellow-brown powder with a magnetic moment (Table II) corresponding to an octahedral complex. It follows from the thermal decomposition (Table II) that dehydration occurs at 65°C and that the anhydrous compound formed is then stable up to a temperature of 200°C . A further increase in the temperature leads to its decomposition to form the oxide, without the formation of a defined intermediate. The molar conductivity value measured in ethanol solution with a concentration of 0.5 mmol l^{-1} corresponds⁶ to a ternary (1 : 2) electrolyte, indicating dissociation of both chloride ions in solution. Thus, the Schiff base acts as a tridentate ligand and two of these ligands octahedrally coordinate the nickel(II) ion. Thus it appears that, in agreement with the conclusions of Gerbeleu et al.³, the ligands are coordinated to the nickel through the nitrogen atoms.

The cobalt salt obtained under similar conditions has the composition $[\text{Co}(\text{H}_2\text{TSD})_2]\text{Cl}_2$ and is precipitated from solution as a brick red powder. The magnetic moment value corresponds to an octahedral high-spin cobalt(II) complex with three unpaired electrons. Thus, the molar conductivity value (Table II) measured in methanol solution with a concentration of 0.5 mmol l^{-1} indicates that both chloride ions are dissociated. This compound is thermally less stable than the analogous nickel complex. Its thermal decomposition begins at a temperature of 110°C and occurs without the formation of a defined intermediate. When ammonia was added to the reaction mixture, a compound with the composition $[\text{NiH}_2\text{O}(\text{TSD})]$ or $[\text{CoH}_2\text{O}(\text{TSD})]$ can be isolated from this solution. Magnetochemical studies indicate that both these compounds can be considered to be square planar complexes that first lose water on heating, followed by decomposition of the organic moiety. The nickel(II) complex is thermally more stable.

TABLE II

Magnetic moment, temperature of thermal decomposition and molar conductivity of the substances prepared

Compound	μ_{cf} , BM	$T(\text{GTA})$, $^\circ\text{C}^a$	Λ , $\text{S cm}^2 \text{ mol}^{-1}$
$[\text{Ni}(\text{TSD}) \cdot \text{H}_2\text{O}]$	dia	150 (270)	
$[\text{Ni}(\text{H}_2\text{TSD})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$	2.92	65 (200)	152
$[\text{Ni}(\text{TSD})\text{Br}]$	1.72	80 (- Br)	
$[\text{Co}(\text{TSD}) \cdot \text{H}_2\text{O}]$	3.08	80 (270)	
$[\text{Co}(\text{H}_2\text{TSD})_2]\text{Cl}_2$	4.23	110	152
$[\text{Co}(\text{HTSD})(\text{TSD})] \cdot 2 \text{H}_2\text{O}$	dia	80 (195)	15.1

^a In case of hydrates, the first value represents the beginning of dehydration.

Electrochemical oxidation and oxidation by bromine of the $[\text{NiH}_2\text{O}(\text{TSD})]$ complex were studied. The electrochemical measurements were carried out in dimethylformamide, in methanol and in a dimethylformamide-methanol (1 : 1) mixture. In all the media, the $[\text{NiH}_2\text{O}(\text{TSD})]$ complex oxidizes at a potential of 0.5 to 0.6 V (Fig. 1). The cyclic voltammogram with the undeveloped reverse peak is typical for irreversible electrode processes. With increasing potential scan rate, the oxidation potentials shift to higher values. The linear dependence of the height of the anodic peak on the concentration and on the square root of the potential scan rate indicate that the anodic oxidation is diffusion controlled and these values approach those for a one-electron irreversible process⁷. The reaction with bromine yielded a compound with the composition $[\text{NiBr}(\text{TSD})]$ with a magnetic moment value corresponding to that for the nickel(III) compound⁸. This is a dark brown substance that is stable at room temperature and loses bromine at a temperature of 80°C. Thus, the initial nickel(II) complex can be oxidized to the nickel(III) compound both electrochemically and using bromine.

The diamagnetic cobalt(III) complex $[\text{Co}(\text{TSD})(\text{HTSD})] \cdot 2\text{H}_2\text{O}$ begins to lose both water molecules at a temperature of 80°C and decomposes above 195°C. It can be assumed that the water in this compound is not coordinated and that both anions of the Schiff base act as tridentate ligands.

The absorption maxima in the infrared absorption spectra (Table III) were assigned to the corresponding vibrations of the important functional groups in agreement with the literature data⁹⁻¹¹.

The valence vibrations $\nu(\text{NH})$ or $\nu(\text{OH})$ lie in the region above $3\,000\text{ cm}^{-1}$. These vibrations for the compound $[\text{Ni}(\text{H}_2\text{TSD})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ lie at wavenumbers of 3 000 (s), 3 100 (s), 3 250 (s) and 3 420 (s); the last of these absorption maxima is absent from

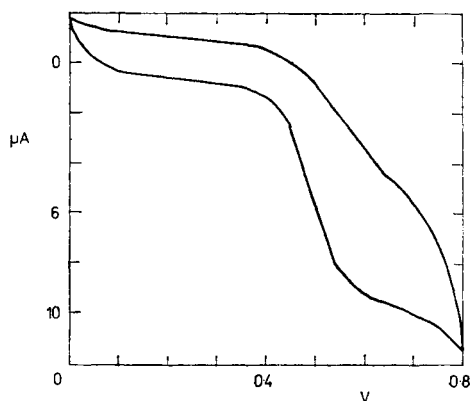


FIG. 1
Cyclic voltammogram of $[\text{Ni}(\text{TSD}) \cdot \text{H}_2\text{O}]$

TABLE III
Infrared absorption spectra of studied compounds

Compound	$\tilde{\nu}$, cm^{-1}									
	$\nu(\text{CNO})$	$\nu(\text{CS})$ $\delta(\text{CNO})$	$\nu(\text{NO})$	$\delta(\text{NH}_2)$	$\nu(\text{CS})$ $\nu(\text{CN})$ $\delta(\text{NH}_2)$	$\nu(\text{CN})$ $\delta(\text{NH}_2)$	$\delta(\text{NH})$	$\nu(\text{CN})$	$\delta(\text{NH}_2)$ ($-\text{CSNH}_2$)	$\delta(\text{NH}_2)$ ($-\text{NHNH}_2$)
[Ni(TSD).H ₂ O]	500 (w)	780 (w)	1 080 (s) 1 210 (s)	1 160 (s)	1 320 (s) 1 480 (s)	1 510 (m) 1 550 (m)	1 530 (w)	1 570 (s)		1 640 (s)
[Ni(H ₂ TSD) ₂ Cl ₂].H ₂ O	480 (w)	760 (m)	1 050 (s) 1 220 (s)	1 005 (m) 1 150 (s)	1 350 (s) 1 470 (m)	1 510 (m) 1 540 (s)	1 500 (m) 1 525 (m)	1 575 (s)	1 610 (s)	1 640 (m)
[Ni(TSD)Br]	500 (w)	750 (w)	1 070 (s) 1 270 (m)	1 020 (w) 1 170 (m)	1 315 (m) 1 480 (m)	1 505 (m) 1 540 (m)	1 500 (m) 1 535 (m)	1 585 (s)		1 640 (w)
[Co(TSD).H ₂ O]	500 (m)	750 (m)	1 050 (s) 1 210 (s)	1 155 (s)	1 320 (s) 1 480 (s)	1 515 (m) 1 545 (s)	1 500 (m) 1 530 (m)	1 585 (s)		1 620 (s)
[Co(H ₂ TSD) ₂ Cl ₂]	480 (w)	755 (m)	1 050 (s) 1 205 (s)	1 000 (s) 1 150 (s)	1 355 (s) 1 475 (s)	1 515 (m) 1 535 (m)	1 500 (m) 1 530 (m)	1 575 (s)	1 620 (s)	1 640 (s)
[Co(TSD)(HTSD)].2 H ₂ O	475 (w)	750 (w)	1 080 (s) 1 210 (m)	980 (m) 1 150 (m)	1 325 (s) 1 475 (s)	1 515 (w) 1 540 (w)	1 500 (m) 1 530 (w)	1 580 (m)	1 610 (w)	1 640 (w)

the spectra of the other studied substances and the remaining maxima lie at approximately the same wavenumbers as for $[\text{Ni}(\text{H}_2\text{TSD})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

The region $1450-1700\text{ cm}^{-1}$ is less clear; here, the absorption maxima correspond to the deformation vibrations $\delta(\text{NH}_2)$ or $\delta(\text{NH})$ and valence vibrations $\nu(\text{CN})$. The interval $900-1400\text{ cm}^{-1}$ contains the absorption maxima corresponding to the valence vibrations $\nu(\text{NO})$ of the oxime group, $\nu(\text{CS})$, $\nu(\text{CN})$ and also the deformation vibration $\delta(\text{NH}_2)$. In addition, the spectra of the compound $[\text{Ni}(\text{H}_2\text{TSD})_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{H}_2\text{TSD})_2]\text{Cl}_2$ contain absorption maxima at a wavenumber of 960 cm^{-1} (m), corresponding to the valence vibrations $\nu(\text{OH})$ of the oxime group, confirming that the Schiff base acts as a molecular ligand in both these compounds. As the Schiff base itself could not be prepared, it was not possible to compare its spectrum with those of these complexes.

It follows from these results that the Schiff base employed acts as a tridentate ligand. When it is an electroneutral ligand, it forms an octahedral complex with Ni(II) or Co(II), which is high-spin for the cobalt compound. Deprotonization of the ligand produces such a strong ligand field that the formation of a square planar complex is facilitated. The electron density is apparently greatly increased on the donor atoms in this anionic form. Thus, this anion acts as a strong σ -donor, leading to stabilization of nickel in the III oxidation state. These results thus confirm the assumption that polydentate N-ligands can be used to stabilize higher oxidation states of nickel, especially when the increased electron density on the donor atoms increases their σ -donor ability.

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