

Complex compounds of nickel with salicylaldoxime

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Some octahedral complexes of the $\text{Ni}(\text{HSal})_2 \cdot \widehat{\text{LL}} \cdot n\text{H}_2\text{O}$ type ($\widehat{\text{LL}} = 1,10$ -phenanthroline, α, α' -bipyridyl or ethylenediamine and $n = 0, 1$) were prepared by using the reaction of $\text{Ni}(\text{HSal})_2$ ($\text{H}_2\text{Sal} = \text{salicylaldoxime} - \text{C}_7\text{H}_7\text{NO}_2$) with bidentate ligands. The reaction of $\text{Ni}(\text{HSal})_2$ with bromine results in bromination of the aromatic ring of ligand. The possibility of oxidizing $\text{Ni}(\text{HSal})_2$ with peroxodisulfate or hydrogen peroxide has been studied.

Реакцией $\text{Ni}(\text{HSal})_2$ ($\text{H}_2\text{Sal} = \text{салицилальдоксим} - \text{C}_7\text{H}_7\text{NO}_2$) с бидентатными лигандами были получены октаэдрические комплексы типа $\text{Ni}(\text{HSal})_2 \cdot \widehat{\text{LL}} \cdot n\text{H}_2\text{O}$, где $\widehat{\text{LL}} = 1,10$ -фенантролин, α, α' -бипиридил или этилендиамин, а $n = 0, 1$. Реакция $\text{Ni}(\text{HSal})_2$ с бромом приводит к бромированию ароматического ядра лиганда. Изучалась возможность окисления $\text{Ni}(\text{HSal})_2$ пероксодисульфатом или перекисью водорода.

The nickel(II) complex of the composition $\text{Ni}(\text{HSal})_2$ ($\text{H}_2\text{Sal} = \text{salicylaldoxime} - \text{C}_7\text{H}_7\text{NO}_2$) has been known for some time [1]. It is a green crystalline substance which has diamagnetic properties [2]. It is soluble in pyridine and from this solution the octahedral coordination compounds [3] of the chemical composition $\text{Ni}(\text{HSal})_2\text{py}_2$ ($\text{py} = \text{pyridine}$) were obtained. As some oximes [4] stabilize nickel in higher oxidation states, we investigated the reactions of $\text{Ni}(\text{HSal})_2$ with selected agents of oxidation. We were also interested in the chance of transforming this planar complex in an octahedral one by the effect of some bidentate ligands the coordination of which should be manifested by a more obvious change in internal coordination sphere.

Experimental

Ethylenediamine was product of Downs Development Chemicals. Salicylaldoxime, α, α' -bipyridyl, and 1,10-phenanthroline as well as other anal. grade chemicals were supplied by Lachema, Brno.

We obtained the infrared absorption spectra with an instrument Specord IR 75 (Zeiss, Jena) by using the nujol technique, the electronic absorption spectra with a spectrometer Specord M 40 (Zeiss, Jena), and diffuse reflectance spectra with an instrument Specord

UV VIS (Zeiss, Jena) by using the nujol technique [5]. The magnetic susceptibility was measured at 293 K with laboratory constructed magnetic balance by the Gouy method. The thermal decomposition was investigated with a Derivatograph Q 1500 D (MOM, Budapest) by using weighed amounts in the range 120—140 mg and temperature gradient of $2.5\text{ }^{\circ}\text{C min}^{-1}$.

Preparation of complex compounds

$\text{Ni}(\text{HSal})_2$: The solution containing 1.5 g (6.6 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 15 cm^3 of water was added into the solution of 1 g of ligand (7.3 mmol) in 5 cm^3 of ethanol. The formed green precipitate was sucked after 10 min stirring, washed with water on the fritted glass and purified by recrystallization from chloroform.

$\text{Ni}(\text{H}_3\text{Sal}_2\text{Br}_2)\text{Br}$: 0.1 cm^3 (1.95 mmol) of bromine dissolved in 1 cm^3 of chloroform was dropwise and under stirring added into the solution of 0.66 g (1.94 mmol) of $\text{Ni}(\text{HSal})_2$ in 75 cm^3 of chloroform. The excluded precipitate was stirred for 10 min, sucked on a fritted glass filter and washed with chloroform.

$\text{Ni}(\text{HSal})_2 \cdot \text{bpy}$: 0.5 g (1.47 mmol) of $\text{Ni}(\text{HSal})_2$ was dissolved in 50 cm^3 of boiling chloroform and mixed with the solution of 0.55 g (3.52 mmol) of α, α' -bipyridyl (bpy) in 5 cm^3 of ethanol. Then the boiling reaction mixture was for a short time stirred under reflux. In the course of stirring a violet precipitate separated from the solution. This precipitate was sucked and for a while extracted with hot chloroform.

$\text{Ni}(\text{HSal})_2 \cdot \text{phen} \cdot \text{H}_2\text{O}$: The hot solution containing 0.6 g (3.03 mmol) of the monohydrate of 1,10-phenanthroline (phen) dissolved in 5 cm^3 of ethanol was added into the boiling solution of 0.5 g (1.47 mmol) of $\text{Ni}(\text{HSal})_2$ in 50 cm^3 of chloroform. A violet solution originated in this mixture from which a preparation of the above composition separated after a few minutes' boiling under reflux. It was sucked on a fritted glass filter and washed with hot chloroform.

$\text{Ni}(\text{HSal})_2 \cdot \text{en} \cdot \text{H}_2\text{O}$: 0.5 g of $\text{Ni}(\text{HSal})_2$ (1.47 mmol) was dissolved in 50 cm^3 of boiling chloroform and the formed solution was mixed with 0.4 g (5.98 mmol) of ethylenediamine (en). After 0.5 h stirring, the solution was concentrated on a water bath and the solid residue was recrystallized from the ethanol—acetone mixture (volume ratio = 1 : 1).

Results and discussion

The analytical composition of the obtained preparations is given in Table 1. The single compound which was prepared earlier is nickel(II) salicylaldoximate. It has been evidenced on the basis of X-ray structural analysis and infrared spectra [6] that both ligands are joined by a hydrogen bond existing between the $=\text{N}-\text{O}-\text{H}$ group of the first salicylaldoxime and the phenolic oxygen of the second one.

We may assume that, in order to facilitate the oxidation of the bivalent nickel in this complex, it should be convenient to bring the oxidizing agent in direct contact with the central atom. That might result in an increase (maybe temporary) in

Table 1

Chemical composition of the investigated preparations

Compound	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$				
	Ni	C	H	N	Br
Ni(HSal) ₂	17.74	50.80	3.65	8.46	
	16.89	50.58	3.38	8.11	
Ni(H ₃ Sal ₂ Br ₂)Br	10.27	29.41	1.94	4.90	41.93
	10.44	29.81	1.73	5.03	41.95
SalBr ₂		28.50	1.71	4.75	54.19
		28.38	1.55	4.86	54.35
Ni(HSal) ₂ ·bpy	12.05	59.17	4.11	11.50	
	11.80	59.97	3.91	11.26	
Ni(HSal) ₂ ·phen·H ₂ O	11.09	59.00	4.19	10.50	
	11.34	58.88	4.10	10.40	
Ni(HSal) ₂ ·en·H ₂ O	14.35	46.97	5.42	13.69	
	14.27	46.71	5.56	14.09	

coordination number of the central atom. For this reason, we investigated the reaction of Ni(HSal)₂ with other ligands in order to verify the possibility of its transformation into a complex with higher coordination number. The only one hitherto described complex of this type of the composition Ni(HSal)₂py₂ was obtained by dissolving nickel(II) salicylaldoximate in pyridine [3] under rather drastic conditions. Our attempt to link lutidine by boiling a chloroform solution of Ni(HSal)₂ with this potential ligand dissolved in acetone (mole ratio = 1 : 10) failed. Similarly, the reaction of Ni(HSal)₂ with triphenylphosphine performed under analogous conditions was without much result. The use of bidentate ligands, such as ethylenediamine, α, α' -bipyridyl or 1,10-phenanthroline enabled us to isolate substances of the composition Ni(HSal)₂bpy, Ni(HSal)₂·en·H₂O or Ni(HSal)₂·phen·H₂O. The presence of water bound in the investigated preparations manifests itself in thermograms (Fig. 1) and infrared absorption spectra of these substances which are relatively stable violet-coloured compounds. Their thermal decomposition (Table 2) starts at the temperature of about 200 °C after preceding dehydration. In the infrared absorption spectrum of these substances, we may observe an absorption maximum at the wavenumber of 1620 cm⁻¹ (for en and phen) corresponding to the bending vibration $\delta(\text{H}-\text{OH})$ and a maximum at the wavenumber of 3240—3210 cm⁻¹ (phen) or 3220—3210 cm⁻¹ (en) corresponding to the vibration $\nu(\text{OH})$. The values of their magnetic moments enable us to presume octahedral coordination. This conclusion is in harmony with the results obtained from the study of reflectance spectra where we can observe maxima at the

wavenumber of $12\,500\text{ cm}^{-1}$ (for complex with bpy) or $12\,700\text{ cm}^{-1}$ (for complex with en) corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition, maxima at $\tilde{\nu} = 18\,000\text{ cm}^{-1}$ (bpy), $18\,500\text{ cm}^{-1}$ (phen) or $18\,400\text{ cm}^{-1}$ (en) corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition, and maxima at $\tilde{\nu} = 27\,000\text{ cm}^{-1}$ (bpy) or $28\,000\text{ cm}^{-1}$ (for phen

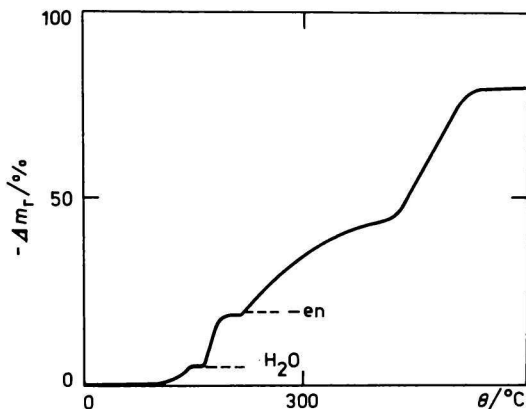


Fig. 1. Thermal decomposition of $\text{Ni}(\text{HSal})_2 \cdot \text{en} \cdot \text{H}_2\text{O}$ (GTA).

and en) corresponding to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition. As $\text{Ni}(\text{HSal})_2 \cdot \text{en} \cdot \text{H}_2\text{O}$ is soluble in methanol (other described compounds are practically insoluble in water and common organic solvents), we [7] have been able to estimate from the positions of the absorption spectra of this solution ($\tilde{\nu} = 29\,140\text{ cm}^{-1}$, $18\,260\text{ cm}^{-1}$, $11\,660\text{ cm}^{-1}$) the CF parameters: $10\text{ Dq} = 11\,660\text{ cm}^{-1}$, $B = 828\text{ cm}^{-1}$, and $\beta = 0.804$. The infrared absorption spectra of the studied compounds are rather unclear. The absorption maxima corresponding to characteristic stretching vibrations $\nu(\text{OH})$, $\nu(\text{NO})$, and $\nu(\text{CN})$ have been assigned in line with papers [8] and [9] and are described in Table 3. We may state that the stretching vibration $\nu(\text{CN})$ shifts by the effect of coordination to lower values of wavenumbers when compared with nonbonded (free) ligand, in the same manner as the stretching vibration $\nu(\text{NO})$. This fact is in agreement with the statement that the above-mentioned maxima [9] exhibit the greatest changes owing to coordination.

The reaction of nickel(II) salicylaldoximate with bromine was carried out by two procedures. In the first case, bromine was dropwise added under stirring at laboratory temperature into the methanolic solution of NiBr_2 and H_2Sal ($n(\text{NiBr}_2 \cdot 3\text{H}_2\text{O}) : n(\text{HSal}) : n(\text{Br}) = 1 : 2 : 2$). The brominated derivative of salicylaldoxime was separated from this reaction mixture in the form of greenish compound as the least soluble component (for $\text{Sal} \cdot \text{Br}_2$ $w_i(\text{calc.})$: 28.50 % C, 4.75 % N, 1.71 % H, 54.19 % Br; $w_i(\text{found})$: 28.40 % C, 4.82 % N, 1.55 % H,

Table 2

Some properties of the investigated substances

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}$	GTA — temperature of the start of decomposition/°C
Ni(HSal) ₂	dia	235
Ni(H ₃ Sal ₂ Br ₂)Br	dia	240
Ni(HSal) ₂ · bpy	3.22	210
Ni(HSal) ₂ · phen · H ₂ O	2.99	105 (–H ₂ O), 210
Ni(HSal) ₂ · en · H ₂ O	3.22	105 (–H ₂ O), 180

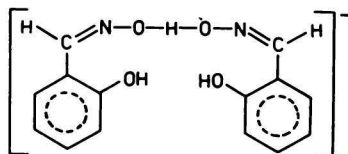
Table 3

Infrared absorption spectrum of the investigated substances
Characteristic absorption maxima

Compound	$\bar{\nu}/\text{cm}^{-1}$		
	$\nu(\text{OH})$	$\nu(\text{NO})$	$\nu(\text{CN})$
H ₂ Sal	960 m	1190 m, 1255 m	1620 m
Ni(HSal) ₂	940 m	1200 m	1590 m
Ni(H ₃ Sal ₂ Br ₂)Br	940 m	1190 w, 1225 m	1615 m
Ni(HSal) ₂ · bpy	950 m	1100 m, 1220 m	1580 m
Ni(HSal) ₂ · phen · H ₂ O	950 m	1100 m, 1210 m	1580 m
Ni(HSal) ₂ · en · H ₂ O	940 m	1120 m	1580 s

w — weak, m — medium, s — strong.

54.05 % Br). In the second case, bromine was added into the solution of Ni(HSal)₂ in chloroform. A green precipitate of the composition Ni(H₃Sal₂) · Br₃ separated from the solution. As it was diamagnetic, it could be regarded as a complex of tetravalent nickel with negatively univalent anion of disalicylaldoxime (Scheme 1) and three Br[–] anions. The second alternative is based on the idea that bromine is



Scheme 1

bonded to both aromatic rings in the ligand H_3Sal_2^- (Scheme 1) so that a planar nickel(II) complex of the composition $\text{Ni}(\text{H}_3\text{Sal}_2-\text{Br}_2)\text{Br}$ is formed. The isolated substance was rather insoluble in water and organic solvents so that we could not perform conductivity measurements. The reflectance spectrum of this substance exhibits maxima at $\tilde{\nu} = 16\,000\text{ cm}^{-1}$ and $\tilde{\nu} = 25\,000\text{ cm}^{-1}$ and almost does not differ from the spectrum of $\text{Ni}(\text{HSal})_2$ which has maxima at $\tilde{\nu} = 16\,100\text{ cm}^{-1}$ and $\tilde{\nu} = 25\,000\text{ cm}^{-1}$. In the infrared absorption spectrum of this substance, there are absorption maxima at $\tilde{\nu} = 520\text{ cm}^{-1}$, 540 cm^{-1} , 1120 cm^{-1} , and 1225 cm^{-1} which do not occur in the infrared spectra of other investigated complexes. However, we found them in the spectrum of brominated salicylaldehyde. The thermal decomposition of this substance proceeds analogously as decomposition of $\text{Ni}(\text{HSal})_2$. Therefore we may assume that bromine preferentially attacks the aromatic components of ligand and the investigated species may be regarded as a planar nickel(II) complex.

The reaction of bromine with a solution of $\text{Ni}(\text{HSal})_2 \cdot \text{en} \cdot \text{H}_2\text{O}$ in methanol gave rise to violet crystals of NiBr_2 ($w_i(\text{calc.})$: 18.06 % C, 6.07 % H, 21.07 % N, and 40.07 % Br; $w_i(\text{found})$: 17.70 % C, 5.98 % H, 20.68 % N, and 39.58 % Br).

Peroxosulfates which are soluble in water cannot be used for oxidation of nickel(II) salicylaldehyde. $\text{Ni}(\text{HSal})_2$ is separated from reaction mixtures which contain relatively very small amount of water. The reaction with hydrogen peroxide was carried out in the solution acidified with perchloric acid. In this considerably acid medium, salicylaldehyde functions as a molecular ligand. A mixture of $\text{Ni}(\text{H}_2\text{Sal})(\text{ClO}_4)_2$ with $\text{H}_2\text{Sal} \cdot \text{HClO}_4$ was separated from the red-coloured solution after a few days.

It is obvious from the presented results that different quite stable octahedral complexes may be prepared by the effect of convenient bidentate ligands on $\text{Ni}(\text{HSal})_2$. The reaction of $\text{Ni}(\text{HSal})_2$ with bromine involves a preferential attack on the aromatic ring of ligand. The possibility of oxidizing with peroxodisulfate is negatively affected by separation of nickel(II) salicylaldehyde from the water—organic solvent (ethanol, acetone) mixture. In acid medium salicylaldehyde functions as a molecular ligand (H_2Sal), which brings about a decrease in electron density on donor atoms when compared with the HSal^- anion. Thus the ability of the used ligand to stabilize the central atom in unusually high oxidation states is impaired.

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