

# Dithiocarbamate Complexes of Nickel with Triphenylphosphine and Isothiocyanate as Mixed Ligands

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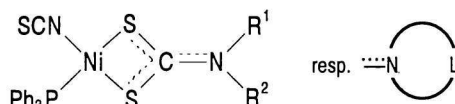
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The new complex compounds of bivalent nickel with dithiocarbamates, triphenylphosphine and isothiocyanate as mixed ligands of the composition Ni(NCS)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>) and Ni(NCS)(Ldtc)(PPh<sub>3</sub>), respectively, have been isolated. By the X-ray analysis of Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>) the distorted square-planar coordination around of nickel (NiS<sub>2</sub>PN) was confirmed. The monocrystal is monoclinic and the basic data are as follows: Space group of symmetry P2<sub>1</sub>/c; a = 9.891(1) 10<sup>-10</sup> m; b = 14.661(2) 10<sup>-10</sup> m; c = 21.002(3) 10<sup>-10</sup> m; β = 102.65(1)°; V = 2972.3 10<sup>-30</sup> m<sup>3</sup>; Z = 4; ρ<sub>X-ray</sub> = 1.304 g cm<sup>-3</sup>; ρ<sub>exp</sub> = 1.32 g cm<sup>-3</sup>; R = 3.90 %; R<sub>w</sub> = 4.21 %.

By oxidation of initial Ni(II) complexes by bromine the Ni(III) complexes of the composition Ni(SCN)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>)Br and Ni(NCS)(Ldtc)(PPh<sub>3</sub>)Br, respectively, have been prepared (R<sup>1</sup> = H, et, but; R<sup>2</sup> = et, but; L = morph = C<sub>4</sub>H<sub>8</sub>O, pip = C<sub>5</sub>H<sub>10</sub>; dtc = S<sub>2</sub>CN<sup>-</sup>; PPh<sub>3</sub> = C<sub>18</sub>H<sub>15</sub>P). By the method of cyclic voltammetry it was found that the electrochemical oxidation can be described as a reversible diffusion-controlled process. All the prepared complexes were studied in detail by X-ray powder diffractograms, magnetochemical measurements, thermogravimetric method, conductivity measurements, IR and UV VIS spectroscopy; in the case of compound Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>) the <sup>13</sup>C NMR spectroscopy was used.

The complexes of nickel with dithiocarbamates, triphenylphosphine and isothiocyanate have never been studied. Only the Ni(II) dithiocarbamates of the formulas NiX(R<sup>2</sup>dtc)(PPh<sub>3</sub>) [1—3] and NiX(HRdtc)(PPh<sub>3</sub>) [4] (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, PF<sub>6</sub><sup>-</sup>; R = alkyl, aryl) are described. In our previous paper [5] we studied the Ni(II) complexes with composition of NiX(Ldtc)(PPh<sub>3</sub>) (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>; L = morph, pip) and their oxidation products NiX(Ldtc)(PPh<sub>3</sub>)Br, respectively. By complete X-ray analysis of NiCl(et<sub>2</sub>dtc)(PPh<sub>3</sub>) [6, 7] and NiBr(morphdtc)(PPh<sub>3</sub>) [5] the distorted square-planar coordination of NiS<sub>2</sub>PX chromophore was confirmed.

The aim of this work was the synthesis of Ni(II) dithiocarbamate complexes with PPh<sub>3</sub> and NCS<sup>-</sup> as further ligands and the study of influence of these ligands on the structure and properties of the prepared complexes of the type



The possibility of participation of the Ni(III, IV) compounds in some biological systems [8] led us to the tracking of using these ligands to the stabilization of higher oxidation states of nickel.

## EXPERIMENTAL

The Ni(II) complexes of the formulas Ni(NCS)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>) and Ni(NCS)(Ldtc)(PPh<sub>3</sub>), respectively, have been prepared by the reaction of the suspension of 0.002 mol of fine pulverized Ni(R<sup>1</sup>R<sup>2</sup>dtc)<sub>2</sub> respectively Ni(Ldtc)<sub>2</sub> [9] in 20 cm<sup>3</sup> of CHCl<sub>3</sub> with 0.002 mol of pulverized Ni(NCS)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [10]. The suspensions were thoroughly stirred for ca. 45 min till the dissolving of the components. After filtration 50 cm<sup>3</sup> of ether was added to the filtrate and the mixture was left to crystallize (ca. 15 min). The red-violet crystals were sucked, washed with ether and dried at 40 °C under the infralamp. In the case of compound III the solution was evaporated nearly to dryness and the pulverized substance was obtained by stirring in hexane, then it was washed with hexane and dried.

Ni(III) complexes of the composition Ni(NCS)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>)Br and Ni(NCS)(Ldtc)(PPh<sub>3</sub>)Br, respectively, have been prepared by oxidation of the fine suspension of Ni(NCS)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>) and

Ni(NCS)(Ldtc)(PPh<sub>3</sub>), respectively (0.0015 mol in 10 cm<sup>3</sup> of hexane) by bromine (0.0016 mol Br<sub>2</sub> in 5 cm<sup>3</sup> of hexane). The oxidant was added by parts and the mixture was stirred for 30 min (in the case of compound X for 10 min only). After this time the brown material was formed. Product was decanted several times with hexane, sucked, washed with hexane and dried over H<sub>2</sub>SO<sub>4</sub>. The X-ray structure analysis was carried out on the KUMA diffractometer at 20 °C (dimensions of single crystal 0.2 mm × 0.3 mm × 0.5 mm). The graphite monochromatic CuK<sub>α</sub> radiation was used; 6094 diffractions (5764 unique, 4532 observed), 2θ-range (2°—60°) (ω/2θ scan), 2 reference reflections (crystal stability control after 100 diffractions), range *h* (0—11); *k* (0—18); *l* (−26—26). Hydrogen atoms were calculated in the expected positions; the corrections for absorption and extinction were neglected. The structure was solved by using of the SHELX 86 (direct methods), SHELX 76, PARST 91 programs on PC 486.

The powder diffractograms were recorded on the HZG4/c diffractometer (Präzisionsmechanik, Freiberg); Cu-radiation, Ni-filter.

The cyclic voltammetry was carried out on the EG8G Princeton Applied Research, Model 273 potentiostat/galvanostat with three-electrode system. As the working glassy carbon electrode (*S* = 0.08 cm<sup>2</sup>, 1—3 % porosity) was used; saturated calomel electrode served as the reference electrode and as the auxiliary electrode the Pt-foil with great surface was used. The potential scan rate was in the range 0.05—0.5 V s<sup>−1</sup>. The measurements were made in dimethylformamide with 0.01 M-LiCl as basic electrolyte ([Ni<sup>2+</sup>] = 10<sup>−3</sup> mol dm<sup>−3</sup>).

<sup>13</sup>C NMR spectroscopy was recorded on the GE GN-300 NMR spectrometer in CDCl<sub>3</sub> solution at room temperature according to [11].

Thermogravimetric study was performed on the derivatograph Q-1500 (MOM, Budapest) with sample mass of 150 mg and the temperature gradient 2.5 °C min<sup>−1</sup>.

The magnetochemical measurements were carried out by the Faraday method at 20 °C on laboratory designed device (Development Laboratories and Workshops, Palacký University, Olomouc) using Co[Hg(SCN)<sub>4</sub>] as standard. The diamagnetic corrections constants were used according to [12].

The molar conductivities  $\Lambda$  were measured on Conductivity Meter OK 102/1 (Radelkis, Budapest) at (25 ± 0.2) °C in nitromethane solution.

The electron absorption spectra EAS were recorded in nujol mull on the Specord M40 UV VIS spectrophotometer (Zeiss, Jena) in the range of  $\tilde{\nu}$  = 13 000—45 000 cm<sup>−1</sup>.

The IR spectra were recorded on Specord IR-75 spectrophotometer in the range of  $\tilde{\nu}$  = 400—4000 cm<sup>−1</sup> by the nujol technique.

The content of nickel was estimated by the chelatometric method with murexide as indicator. The C, H, and N analyses were carried out by the CHN-analyzer (Laboratorní přístroje, Prague). The content of bromine was estimated by the Schöniger method.

## RESULTS AND DISCUSSION

The chemical compositions and results of analyses of the prepared complexes are given in Table 1, the important results of the physicochemical study are collected in Table 2. The crystalline red-violet Ni(II) complexes Ni(NCS)(R<sup>1</sup>R<sup>2</sup>dtc)(PPh<sub>3</sub>) and Ni(NCS)(Ldtc)(PPh<sub>3</sub>), respectively, are diamagnetic and nonelectrolytic (in nitromethane solution). The single crystal of the model complex Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>) is monoclinic; the other crystallographic data are: Space group of symmetry P2<sub>1</sub>/c; *a* = 9.891(1) 10<sup>−10</sup> m; *b* = 14.661(2) 10<sup>−10</sup> m; *c* = 21.002(3) 10<sup>−10</sup> m;  $\beta$  = 102.65(1)°; *V* = 2972.3 10<sup>−30</sup> m<sup>3</sup>; *Z* = 4;  $\rho_{X\text{-ray}}$  = 1.304 g cm<sup>−3</sup>;  $\rho_{\text{exp}}$  = 1.32 g cm<sup>−3</sup>; *R* = 3.90 %; *R*<sub>W</sub> = 4.21 %.

The results of X-ray structure analysis of this complex (Tables 3 and 4, Fig. 1) confirm the slightly distorted square-planar coordination around the central atom of the molecule. This fact is apparent from the different values of the bond lengths and angles between the nickel and coordinated atoms of ligands, and is confirmed by calculated differences  $\Delta$  of coordinates for the respective atoms from "ideal" plane, atom ( $\Delta/10^{-10}$  m): Ni (−0.04), N-1 (−0.01), P (+0.03), S-1 (+0.04), S-2 (−0.01). It was found that the NCS<sup>−</sup> group is coordinated on central atom of nickel by nitrogen atom. The deviation of the nickel from "ideal" line formed by N-1, C-1, S-3 is ca. 0.26 10<sup>−10</sup> m. The value of length of N-1—C-1 bond (1.162 10<sup>−10</sup> m) nearly corresponds with the value of C≡N bond in NCS<sup>−</sup> group [11]. The great deal of  $\pi$ -bond is apparent on C-2—N-2 bond (1.307 10<sup>−10</sup> m) when for instance for C<sup>⋯</sup>N bond in pyridine the value of 1.339 10<sup>−10</sup> m was published [12]; but this fact is for dithiocarbamate complexes known [1].

The three phenyl rings are situated in three different planes; the dihedral angles between the Ni, P, N-1, S-1, S-2 "ideal" plane and phenyl planes are: 45.1° (Ph-1 = C-11—C-16); 63.3° (Ph-2 = C-21—C-26); 90.8° (Ph-3 = C-31—C-36); the angles between the phenyl planes are: 101.8° (Ph-1—Ph-2); 71.9° (Ph-1—Ph-3); 83.9° (Ph-2—Ph-3).

The refinement of the structure shows the best results for the presumption that the C-9 and C-10 atoms from butyl group possess two statistically equivalent positions (*i.e.* besides C-9, C-10 also C-91, C-92 with occupying factor 0.5 are taken into account). This interesting fact was confirmed by the results of <sup>13</sup>C NMR spectroscopy (Table 5). The C- $\gamma$

Table 1. The Results of Elemental Analysis

Compound	Formula $M_r$	$w_i(\text{calc.})/%$ $w_i(\text{found})/%$					
		Ni	C	H	N	P	Br
<i>I</i>	Ni(NCS)( $\text{et}_2\text{dtc}$ )( $\text{PPh}_3$ ) 527.34	11.13	54.66	4.78	5.31	5.87	
		11.45	54.42	5.23	4.84	6.26	
<i>II</i>	Ni(NCS)( $\text{but}_2\text{dtc}$ )( $\text{PPh}_3$ ) 583.45	10.06	57.64	5.70	4.80	5.31	
		10.32	57.87	5.23	4.38	6.00	
<i>III</i>	Ni(NCS)( $\text{Hetdtc}$ )( $\text{PPh}_3$ ) · $\text{H}_2\text{O}$ 517.30	11.35	51.08	4.48	5.41	5.99	
		10.92	51.63	4.37	5.23	6.33	
<i>IV</i>	Ni(NCS)( $\text{Hbutdtc}$ )( $\text{PPh}_3$ ) 527.34	11.13	54.66	4.78	5.31	5.87	
		11.51	53.97	4.76	5.86	6.26	
<i>V</i>	Ni(NCS)( $\text{morphdtc}$ )( $\text{PPh}_3$ ) 541.32	10.84	53.25	4.28	5.17	5.72	
		10.87	53.86	4.37	4.63	5.97	
<i>VI</i>	Ni(NCS)( $\text{pipdtc}$ )( $\text{PPh}_3$ ) 539.35	10.88	55.66	4.67	5.19	5.74	
		10.34	55.19	4.87	4.77	5.41	
<i>VII</i>	Ni(NCS)( $\text{et}_2\text{dtc}$ )( $\text{PPh}_3$ )Br 607.24	9.67	47.47	4.15	4.61	5.10	13.16
		10.19	47.89	4.53	4.39	5.84	12.58
<i>VIII</i>	Ni(NCS)( $\text{but}_2\text{dtc}$ )( $\text{PPh}_3$ )Br 663.35	8.85	50.70	5.01	4.22	4.67	12.04
		9.34	50.34	5.29	4.55	4.55	11.62
<i>IX</i>	Ni(NCS)( $\text{Hetdtc}$ )( $\text{PPh}_3$ )Br 579.18	10.13	45.62	3.65	4.84	5.35	13.80
		9.86	45.23	3.48	4.46	5.51	13.38
<i>X</i>	Ni(NCS)( $\text{Hbutdtc}$ )( $\text{PPh}_3$ )Br 607.24	9.66	47.47	4.15	4.61	5.06	13.16
		10.03	47.45	4.17	4.12	5.59	12.69
<i>XI</i>	Ni(NCS)( $\text{morphdtc}$ )( $\text{PPh}_3$ )Br 621.22	9.45	46.40	3.73	4.51	4.99	12.86
		9.51	45.95	3.72	4.06	5.51	12.49
<i>XII</i>	Ni(NCS)( $\text{pipdtc}$ )( $\text{PPh}_3$ )Br 619.25	9.48	48.49	4.07	4.52	5.00	12.90
		9.15	47.78	4.17	4.11	5.16	13.28

and C- $\delta$  atoms show two signals, whereas the C- $\beta$  (C-8) atom only one peak. Atom C- $\alpha$  (C-7) exhibits one peak but little broader than the other C-signals, with two maxima. This phenomenon can be attrib-

uted to the "hindered rotation" around C $\cdots$ N bond in  $\text{S}_2\text{C}\cdots\text{NC}_2$  arrangement, which was in the case of dithiocarbamate and diselenocarbamate recently observed [13, 14]. The complexes  $\text{Ni}(\text{but}_2\text{dtc})_2$ ,

Table 2. The Results of Physicochemical Study

Compound	$\mu_{\text{eff}}/\mu_B$	$\Lambda$ $\text{S cm}^2 \text{ mol}^{-1}$	IR data, $\tilde{\nu}/\text{cm}^{-1}$					EAS $\tilde{\nu} \cdot 10^{-3}/\text{cm}^{-1}$	
			$\nu(\text{C}\cdots\text{S})$	$\nu(\text{C}\cdots\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}-\text{S})$		
<i>I</i>	dia	6.7	992 w	1536 m	–	2096 s	840 m	21.1	30.0
<i>II</i>	dia	7.5	992 w	1535 m	–	2100 m	830 w	36.1	40.2
								20.9	29.7
<i>III</i>	dia	21.8	995 w	1552 m	3140 w	2120 m	828 w	36.4	40.1
								21.0	29.1
<i>IV</i> <sup>a</sup>	dia	–	995 w	1535 m	3140 w	2124 m	828 w	–	39.5
								20.8	29.4
<i>V</i>	dia	5.4	995 w	1534 m	–	2100 vs	832 m	36.6	40.9
								21.0	29.5
<i>VI</i>	dia	3.8	996 w	1547 m	–	2092 m	832 w	36.4	40.1
								20.6	30.0
<i>VII</i>	1.69	19.3	995 w	1520 m	–	2095 s	830 m	–	40.2
								–	30.4
<i>VIII</i>	1.94	22.8	995 vw	1520 m	–	2090 m	830 w	37.5	43.8
								–	30.6
<i>IX</i>	1.79	9.7	995 w	1524 m	3130 m	2105 m	830 w	34.9	40.1
								–	30.5
<i>X</i>	1.98	10.7	995 w	1545 m	3135 m	2124 s	830 w	36.8	41.2
								–	30.0
<i>XI</i>	1.74	16.2	995 w	1520 w	–	2100 m	833 w	37.6	42.9
								–	30.3
<i>XII</i>	2.04	21.8 <sup>b</sup>	995 w	1540 w	–	2097 m	833 w	38.4	43.7
								–	30.0
								38.3	42.9

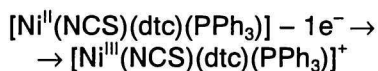
a) Insoluble, b)  $[\text{Ni}] = 3 \times 10^{-4} \text{ mol dm}^{-3}$ .

**Table 3.** Fractional Coordinates of Atoms of Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>)

Atom	10 <sup>4</sup> · (x/a)	10 <sup>4</sup> · (y/b)	10 <sup>4</sup> · (z/c)
Ni	2438(1)	3444(1)	3093(1)
P	1356(1)	4015(1)	3824(1)
S-1	3785(1)	2829(1)	2493(1)
S-2	3669(1)	2498(1)	3785(1)
S-3	193(2)	5124(1)	1316(1)
N-1	1605(3)	4211(2)	2422(1)
N-2	5548(3)	1646(2)	3236(2)
C-1	1019(4)	4586(2)	1956(2)
C-2	4519(3)	2222(2)	3176(2)
C-3	6217(4)	1467(3)	2682(2)
C-4	7441(4)	2087(3)	2703(2)
C-5	8109(4)	1877(3)	2145(2)
C-6	9414(6)	2419(4)	2168(3)
C-7	6158(5)	1192(3)	3860(2)
C-8	5599(11)	196(6)	3840(5)
C-9	4347(14)	3(9)	3916(6)
C-10	4033(22)	- 1037(13)	3937(14)
C-91	6017(19)	- 287(12)	4295(10)
C-92	5135(21)	- 1244(12)	4246(12)
C-11	1416(3)	3300(2)	4541(1)
C-12	1014(4)	2393(2)	4450(2)
C-13	1010(4)	1836(3)	4982(2)
C-14	1436(5)	2174(3)	5610(2)
C-15	1860(4)	3070(3)	5701(2)
C-16	1848(3)	3632(2)	5174(2)
C-21	- 470(3)	4325(2)	3569(1)
C-22	- 1463(3)	3956(3)	3872(2)
C-23	- 2851(4)	4203(3)	3661(2)
C-24	- 3243(4)	4806(3)	3167(2)
C-25	- 2277(4)	5195(3)	2868(2)
C-26	- 885(4)	4947(3)	3067(2)
C-31	2220(3)	5068(2)	4136(2)
C-32	3634(4)	5146(3)	4158(2)
C-33	4338(5)	5928(3)	4407(3)
C-34	3667(6)	6634(3)	4622(2)
C-35	2240(5)	6574(3)	4594(2)
C-36	1538(4)	5787(2)	4354(2)

NiCl(but<sub>2</sub>dtc)(PPh<sub>3</sub>), and NiBr(but<sub>2</sub>dtc)(PPh<sub>3</sub>) exhibit by C- $\alpha$  and C- $\gamma$  atoms one peak only [15].

The electrochemical oxidation of Ni(II) complexes was studied by cyclic voltammetry in dimethylformamide (the results are given in Table 6). The solution of Ni(NCS)(pipdtc)(PPh<sub>3</sub>) was turbid and cannot be measured. The cyclic voltammograms of all compounds exhibit a well developed anodic peak, but the cathodic peaks are missing. The oxidation of the complexes causes a shoulder on the anodic part of record. The magnitudes of peaks were deducted against the current of basic electrolyte. The heights of the anodic peaks depend linearly on the square root of the polarization rate and reach 78—92 % of theoretical value for one-electron oxidation. It can be affirmed that it is a one-electron diffuse-controlled oxidation [16].



This conclusion agrees with the results of

Hofbauerová *et al.* obtained by investigation of Ni(II) complexes with bis(2-hydroxyethyl)dithiocarbamate [17]. From Table 6 it is apparent that all complexes undergo the oxidation in the interval 0.5—1.1 V. The peaks of anodic oxidation potentials are in the range 0.67—0.95 V.

By chemical oxidation of Ni(II) complexes dark-brown coloured compounds of the general composition Ni<sup>III</sup>(NCS)(dtc)(PPh<sub>3</sub>)Br were obtained. Whereas the initial Ni(II) complexes are diamagnetic, the oxidation products are paramagnetic with magnetic moments  $\mu_{\text{eff}}$  in the range 1.61—2.04  $\mu_{\text{B}}$ , which corresponds with literature data for Ni(III) complexes [18—20]. The values of  $\mu_{\text{eff}}$  (measured at room temperature only) cannot be rigorously discussed without additional measurements.

The important difference of X-ray powder diffractograms of initial Ni(II) complexes and oxidation products confirms their different structures and absence of starting material in the oxidation products.

The EAS spectra of both of them in nujol are different, too. Ni(II) complexes exhibit medium intense bands in the range  $\tilde{\nu} = 20\,600$ — $21\,300\text{ cm}^{-1}$  (probably  $d-d$  transition  $^1A_{1g} \rightarrow ^1E_g$  according to [4] respectively  $^1A_{1g} \rightarrow ^1A_{2g}$  [21]), which is characteristic of square-planar Ni(II) complexes. This maximum has not been found in oxidation products. The values of other absorption bands are similar and can be attributed to the interligand transitions of S<sub>2</sub>CN<sup>-</sup> group (the band near  $\tilde{\nu} = 30\,000\text{ cm}^{-1}$  corresponds with  $n \rightarrow \pi^*$  transition on the sulfur atom, the second one near  $\tilde{\nu} = 40\,000\text{ cm}^{-1}$  corresponds with  $\pi \rightarrow \pi^*$  transition at the NCS<sup>-</sup> group and the third one around  $\tilde{\nu} = 37\,000\text{ cm}^{-1}$  ( $\pi \rightarrow \pi^*$ ) to the transition at phenyl groups [4, 22]).

The form of IR records of starting Ni(II) materials and their oxidation products is very similar. This fact agrees with the assumption that neither dithiocarbamate nor triphenylphosphine is oxidized [23] because no absorption maximum of P—O vibration at  $\tilde{\nu} = 1200\text{ cm}^{-1}$  in the IR spectrum was found. All complexes exhibit the absorption maximum of  $\nu(\text{C}\equiv\text{N})$  vibration at  $\tilde{\nu} = 2100\text{ cm}^{-1}$  and of  $\nu(\text{C}-\text{S})$  from NCS<sup>-</sup> group at  $\tilde{\nu} = 828$ — $840\text{ cm}^{-1}$  (generally above  $\tilde{\nu} = 750\text{ cm}^{-1}$ ). This fact indicates the coordination of NCS<sup>-</sup> group by nitrogen atom, whereas the coordination by sulfur brings about  $\nu(\text{C}-\text{S})$  vibration lower than  $\tilde{\nu} = 750\text{ cm}^{-1}$  [24]. The Ni—N bond was confirmed by X-ray structure analysis in the case of complex II. The values of  $\nu(\text{C}\equiv\text{N})$  vibrations around  $\tilde{\nu} = 2120\text{ cm}^{-1}$  (observed at complexes III, IV, X) were described at square-planar isothiocyanato Ni(II) complexes by other authors [25]. At complexes, containing N—H bond (III, IV, IX, X) the maxima of  $\nu(\text{N}-\text{H})$  vibrations were found in the interval  $\tilde{\nu} = 3130$ — $3140\text{ cm}^{-1}$ . All these complexes exhibit the

**Table 4.** Important Interatomic Distances and Angles of Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>)

Bond	Distance/10 <sup>-10</sup> m	Atoms	Angle/°
Ni—P	2.219(1)	P—Ni—S-1	171.2(1)
Ni—S-1	2.217(1)	P—Ni—S-2	93.6(1)
Ni—S-2	2.178(1)	S-1—Ni—S-2	78.6(1)
Ni—N-1	1.850(3)	P—Ni—N-1	95.6(1)
P—C-11	1.825(3)	S-1—Ni—N-1	92.1(1)
P—C-21	1.826(3)	S-2—Ni—N-1	170.5(1)
P—C-31	1.816(3)	Ni—P—C-11	114.9(1)
S-1—C-2	1.709(3)	Ni—P—C-21	119.2(1)
S-2—C-2	1.725(4)	C-11—P—C-21	103.7(1)
S-3—C-1	1.616(4)	Ni—P—C-31	108.0(1)
N-1—C-1	1.162(4)	C-11—P—C-31	105.3(1)
N-2—C-2	1.307(5)	C-21—P—C-31	104.5(1)
N-2—C-3	1.482(6)	Ni—S-1—C-2	86.1(1)
N-2—C-7	1.476(5)	Ni—S-2—C-2	87.0(1)
C-3—C-4	1.507(6)	Ni—N-1—C-1	170.9(3)
C-4—C-5	1.498(7)	C-2—N-2—C-3	120.8(3)
C-5—C-6	1.508(8)	C-2—N-2—C-7	122.3(4)
C-7—C-8	1.558(10)	C-3—N-2—C-7	116.8(3)
C-8—C-9	1.314(18)	S-3—C-1—N-1	178.9(4)
C-8—C-91	1.188(21)	S-1—C-2—S-2	108.3(2)
C-9—C-10	1.559(23)	S-1—C-2—N-2	126.5(3)
C-9—C-91	1.723(21)	S-2—C-2—N-2	125.2(3)
C-10—C-92	1.180(28)	N-2—C-3—C-4	111.4(3)
C-91—C-92	1.644(26)	C-3—C-4—C-5	110.1(3)
C-11—C-12	1.389(5)	C-4—C-5—C-6	112.9(4)
C-11—C-16	1.392(4)	N-2—C-7—C-8	109.0(4)
C-12—C-13	1.386(5)	C-7—C-8—C-9	122.4(9)
C-13—C-14	1.385(5)	C-7—C-8—C-91	118.6(11)
C-14—C-15	1.380(6)	C-9—C-8—C-91	86.9(13)
C-15—C-16	1.378(5)	C-8—C-9—C-10	114.4(13)
C-21—C-22	1.391(5)	C-8—C-9—C-91	43.5(9)
C-21—C-26	1.386(5)	C-10—C-9—C-91	85.5(11)
C-22—C-23	1.395(5)	C-9—C-10—C-92	95.8(16)
C-23—C-24	1.354(6)	C-8—C-91—C-9	49.6(9)
C-24—C-25	1.376(6)	C-8—C-91—C-92	111.9(15)
C-25—C-26	1.397(5)	C-9—C-91—C-92	74.9(11)
C-31—C-32	1.394(5)	C-10—C-92—C-91	103.3(16)
C-31—C-36	1.383(5)	P—C-11—C-12	118.6(2)
C-32—C-33	1.383(6)	P—C-11—C-16	122.3(2)
C-33—C-34	1.359(7)	C-12—C-11—C-16	119.1(3)
C-34—C-35	1.403(8)	C-11—C-12—C-13	120.2(3)
C-35—C-36	1.383(6)	C-12—C-13—C-14	120.2(4)
		C-13—C-14—C-15	119.5(4)
		C-14—C-15—C-16	120.6(3)
		C-11—C-16—C-15	120.2(3)
		P—C-21—C-22	121.4(2)
		P—C-21—C-26	119.8(3)
		C-22—C-21—C-26	118.8(3)
		C-21—C-22—C-23	119.9(3)
		C-22—C-23—C-24	120.6(4)
		C-23—C-24—C-25	120.5(4)
		C-24—C-25—C-26	119.6(4)
		C-21—C-26—C-25	120.5(4)
		P—C-31—C-32	118.1(3)
		P—C-31—C-36	122.8(3)
		C-32—C-31—C-36	119.0(3)
		C-31—C-32—C-33	120.0(4)
		C-32—C-33—C-34	121.0(5)
		C-33—C-34—C-35	119.9(4)
		C-34—C-35—C-36	119.2(4)
		C-31—C-36—C-35	120.9(4)

characteristic vibration  $\nu(\text{C}\equiv\text{N})$  in the range  $\tilde{\nu} = 1520\text{--}1555\text{ cm}^{-1}$  and  $\nu(\text{C}\equiv\text{S})$  at  $\tilde{\nu} = 995\text{ cm}^{-1}$  for dithiocarbamate [4, 23]. In the case of oxidation products the shift of the  $\nu(\text{C}\equiv\text{N})$  vibration to the lower wavenumbers was indicated with regard to the initial Ni(II) complexes, which may be caused by the reduced character of the  $\pi$ -bond  $\text{C}\equiv\text{N}$  [4].

From the molar conductivity measurements it follows that Ni(II) complexes are nonelectrolytes [26], which corresponds with the square-planar configuration of NiS<sub>2</sub>PN chromophore. The oxidation products exhibit under the same circumstances slightly higher conductivities; however their  $\Lambda$  values are significantly lower than the values typical for 1 : 1 electrolyte in nitromethane (75–95 S cm<sup>2</sup> mol<sup>-1</sup>) and they can be considered as nonelectrolyte. Slightly higher values of molar conductivities  $\Lambda$  can be explained by partial dissociation of these complexes in the used solvent. At Ni(III) complexes we can on

plained by partial dissociation of these complexes in the used solvent. At Ni(III) complexes we can on

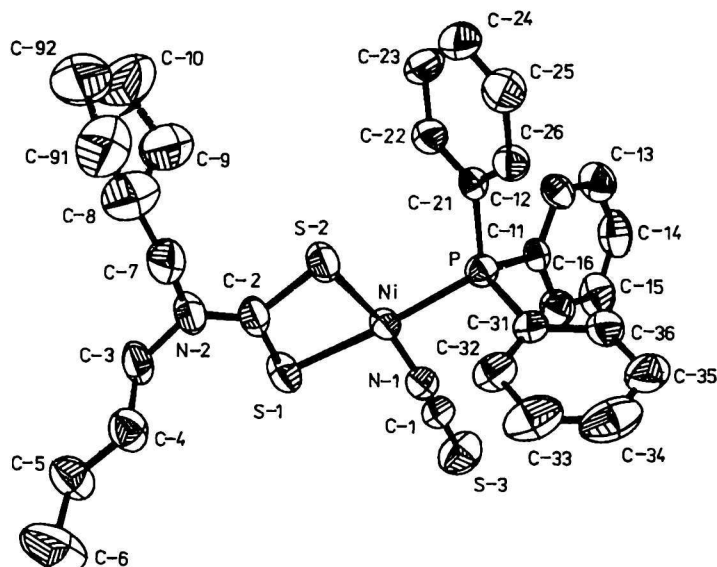


Fig. 1. The skeleton of the molecule of Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>).

Table 5. The <sup>13</sup>C NMR Spectrum of Ni(NCS)(but<sub>2</sub>dtc)(PPh<sub>3</sub>)

δ (Maximum)	Specification
203.14	CS <sub>2</sub>
134.07; 134.21	P—C (splitting by <sup>31</sup> P)
128.68; 128.81; 130.96	the other C-atoms in PPh <sub>3</sub>
128.00	NCS
48.88; 48.99	C-α
29.11	C-β
19.71; 19.96	C-γ
13.52; 13.66	C-δ

C-α carbon in dithiocarbamate C≡N bond.

the basis of conductivity measurements conclude that the increase of the oxidation state leads to the decrease of coordination number of the central atom.

The change of the sulfur atoms in NiS<sub>4</sub> chromophore by the P and N atoms leads to the significant decrease of the thermal stability of Ni(II) dithiocarbamates. While the basic complexes decompose at the temperature over 120 °C (Ni(Hbutdtc)<sub>2</sub> at 135 °C, Ni(et<sub>2</sub>dtc)<sub>2</sub> at 150 °C, Ni(Hetdtc)<sub>2</sub> at 150 °C, Ni(morphdtc)<sub>2</sub> at 120 °C, Ni(pipdtc)<sub>2</sub> at 170 °C, and Ni(but<sub>2</sub>dtc)<sub>2</sub> at 155 °C), the thermal decomposition of our complexes starts in the range 50—70 °C. The decomposition is continual without thermally stable intermediate products and cannot be rigorously interpreted. An exception is Ni(NCS)(Hetdtc)(PPh<sub>3</sub>) · H<sub>2</sub>O; the beginning of dehydration is at 70 °C and the DTA curve exhibits a small *endo*-effect at 90 °C. The dehydrated compound is stable in the temperature range 100—130 °C. The thermal decomposition of studied complexes was not finished at 900 °C.

With respect to all experimental data for Ni(II) complexes we can conclude that there is a slightly distorted square-planar coordination around the central atom. In the case of oxidation products we can sup-

Table 6. Results of Electrochemical Oxidation of Ni(II) Complexes

Complex	<i>v</i> mV s <sup>-1</sup>	<i>R</i> V	<i>E</i> <sub>p</sub> V	<i>I</i> <sub>p,exp</sub> μA cm <sup>-2</sup>	<i>I</i> <sub>p,ir,th</sub> μA cm <sup>-2</sup>
I	50	0.5—0.8	0.67	117	134
II	100	0.6—0.9	0.78	175	190
III	50	0.7—1.1	0.95	106	134
V	50	0.5—0.9	0.77	104	134
VI	50	0.5—0.9	0.70	107	134

*v* – scan rate, *R* – interval of anodic oxidation, *E*<sub>p</sub> – peak potential, *I*<sub>p,exp</sub> – experimental estimate of current density from peak height, *I*<sub>p,ir,th</sub> – theoretical current density for irreversible process.

pose that the decrease of coordination number was connected with the raising of the oxidation state. Unfortunately we are not able to grow the single crystal suitable to the X-ray analysis to confirm these conclusions.

## REFERENCES

1. Maxfield, P. L., *Inorg. Nucl. Chem. Lett.* 6, 693 (1970).
2. McCleverty, J. A. and Morrison, N. J., *J. Chem. Soc., Dalton Trans.* 6, 541 (1976).
3. Fackler, J. P., Lin, I. J. B., and Andrews, J., *Inorg. Chem.* 16, 450 (1977).
4. Tsipis, C. A., Kessissoglou, D. P., and Katsoulos, G. A., *Chimica Chronica, New Series* 14, 195 (1985).
5. Pastorek, R., Kameníček, J., Březina, F., Hamrusová, M., Šindelář, Z., and Lasovský, J., *Chem. Papers* 47, 210 (1993).
6. Ramalingam, B. K. and Aravamudan, G., *Acta Crystallogr., C* 40, 965 (1984).
7. Pastorek, R., Kameníček, J., Březina, F., Lasovský, J., Šindelář, Z., and Ondráček, J., *Acta Univ. Palacki. Olomuc., Fac. Rerum Nat.* 112, 7 (1993).
8. Lancaster, J. R., *The Bioinorganic Chemistry of Nickel*. VCH Publishers, New York, 1988.

9. *Gmelins Handbuch der anorganischen Chemie, Nickel*, Teil C, Lief. 2. P. 997. Verlag Chemie, Weinheim, 1969.
10. *Gmelins Handbuch der anorganischen Chemie, Nickel*, Teil C, Lief. 2. P. 1043. Verlag Chemie, Weinheim, 1969.
11. Dietzsch, W., Duffy, N. V., Katsoulos, G. A., and Olk, B., *Inorg. Chim. Acta* **184**, 89 (1991).
12. Cotton, F. A. and Wilkinson, G., *Inorganic Chemistry*. P. 112. Academia, Prague, 1973.
13. Ravidelya, A. A. and Ponomarevoi, A. V., *Korotkii spravochnik fizicheskko-khimicheskikh velichin*. P. 192. Khimiya, Leningrad, 1983.
14. Duffy, N. V. and Appleton, T. G., *Inorg. Chim. Acta* **145**, 273 (1988).
15. Duffy, N. V., unpublished results.
16. Beck, F., *Elektroorganische Chemie*. P. 80. Verlag Chemie, Weinheim, 1974.
17. Hofbauerová, H., Beinrohr, E., and Mocák, J., *Chem. Papers* **41**, 441 (1987).
18. Asoke Das, K. and Ramana Rao, D. V., *J. Indian Chem. Soc.* **LX**, 718 (1983).
19. Neiding, A. B., *Magnetokhimiya kompleksnykh soedinenii perekhodnykh metallov*. P. 149. Mir, Moscow, 1970.
20. Landolt—Börnstein, *Neue Serie, II/2, Magnetische Eigenschaften der Koordinations- und metalloorganischen Verbindungen der Übergangselemente*. P. 305. Springer-Verlag, Berlin, 1966.
21. Lever, A. B. P., *Inorganic Electronic Spectroscopy*. P. 343. Elsevier Publishing Company, Amsterdam, 1968.
22. Tsipis, C. A., Meleziadis, I. J., Kessissoglou, D. P., and Katsoulos, G. A., *Inorg. Chim. Acta* **90**, L19 (1984).
23. Larionov, S. V., Patrina, L. A., Oglezneva, I. M., and Uskov, E. M., *Koord. Khim.* **10**, 92 (1984).
24. Chernikova, I. E., Khartonik, I. A., Umreiko, D. S., Kavrikov, A. B., and Afanov, V. I., *Koord. Khim.* **15**, 1695 (1989).
25. Mašlejová, A. and Kováčik, I., *Z. Anorg. Chem.* **604**, 151 (1991).
26. Geary, J. W., *Coord. Chem. Rev.* **7**, 81 (1971).

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## Studies on Organomercury(II) Complexes of 5-Fluorouracil

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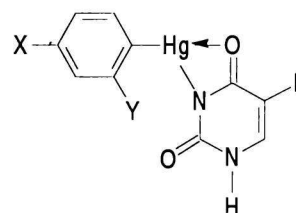
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A number of organomercury(II) complexes involving 5-fluorouracil (HL) of the type RHgL (R = *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, *p*-HOC<sub>6</sub>H<sub>4</sub>, *o*-HOC<sub>6</sub>H<sub>4</sub>) have been synthesized. Conductance measurements reveal that the compounds are nonelectrolytes. From IR and UV spectral studies the bonding modes of the ligand to the mercury(II) ion have been deduced. <sup>1</sup>H and <sup>13</sup>C NMR spectral studies confirm the stoichiometry of the complexes. The fragmentation pattern has been analyzed on the basis of mass spectral studies.

5-Fluorouracil is an anti-cancer drug [1]. For many decades, drugs used for cancer chemotherapy were predominantly derived from organic and biochemical preparations. When in 1969 *Rosenberg et al.* [2] discovered the strongly cell-mitosis-depressing, broad spectrum, inorganic anti-cancer agent, cisplatin, the use of metal coordination compounds in the search for new drugs for cancer treatment started to evolve. In the following years, numerous interesting results have attracted the attention of inorganic chemists [3–5]. There are possibilities for

improving therapeutic activity and suppressing side effects of currently used anti-neoplastic drugs by using their metal complexes [6]. With this aim, we synthesized a few organomercury(II) complexes RHgL involving the ligand 5-fluorouracil (Formula 1).



Formula 1

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