

Complexes of Nickel with Heterocyclic Dithiocarbamates and Triphenylphosphine as Mixed π -Acceptor Ligands

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Received 8 July 1992

The new complex compounds of bivalent nickel with heterocyclic dithiocarbamates (dtc) and triphenylphosphine (PPh_3) as mixed π -acceptor ligands of composition $\text{NiX}(\text{Rdtc})(\text{PPh}_3)$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$; $\text{R} = \text{morph} (\text{C}_4\text{H}_8\text{O})$, $\text{pip} (\text{C}_5\text{H}_{10})$; $\text{dtc} = \text{S}_2\text{CN}^-$; $\text{PPh}_3 = \text{C}_{18}\text{H}_{15}\text{P}$) have been isolated. By the X-ray analysis of the model complex $\text{NiBr}(\text{morphdtc})(\text{PPh}_3)$ the distorted square-planar coordination around of nickel (NiS_2BrP) was detected. The monocrystal is triclinic — basic data are as follows: space group of symmetry $\text{P}\bar{1}$, $a = 9.765(2) \text{ \AA}$, $b = 10.943(3) \text{ \AA}$, $c = 13.008(3) \text{ \AA}$, $\alpha = 112.18(2)^\circ$, $\beta = 90.89(2)^\circ$, $\gamma = 109.18(2)^\circ$, $V = 1200.1 \text{ \AA}^3$, $Z = 2$, $\rho_{\text{X-ray}}/\rho_{\text{exp}} = 1.558/1.55 \text{ g cm}^{-3}$, $R = 5.3 \%$. By oxidation of initial Ni(II) complexes by bromine the Ni(III) complexes of the composition $\text{NiX}(\text{Rdtc})\text{Br}$ have been isolated. All the prepared complexes were studied by X-ray diffractograms, magnetochemical measurements, thermogravimetric methods, conductivity measurements, IR and VIS spectroscopy and for Ni(II) complexes the method of cyclic voltammetry was used.

The complex compounds of nickel with heterocyclic dithiocarbamates (dtc) and triphenylphosphine (PPh_3) have never been studied yet. Only the Ni(II) complexes of the formulas $\text{NiX}(\text{HRdtc})(\text{PPh}_3)$ [1], $\text{NiX}(\text{R}_2\text{dtc})(\text{PPh}_3)$ [2–4] and the dimeric complex $[\text{Ni}(\text{S}_2\text{C}=\text{NR})(\text{PPh}_3)_2]$ [5] ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{PF}_6^-$; $\text{R} = \text{alkyl, aryl}$) are described. The X-ray structure of $\text{NiCl}(\text{et}_2\text{dtc})(\text{PPh}_3)$ complex is known [6]. The results point to triclinic crystal with nearly square-planar configuration around the metal atom (NiS_2ClP).

The paper is given as a contribution to solution of the problems concerning Ni(II) dithiocarbamate complexes with mixed ligands. The great interest of this group of compounds is due to the fact that the Ni(III) and Ni(IV) complexes play an important role in some microorganisms or biological systems [7].

Our aim was the isolation of the new morpholine and piperidine dithiocarbamate complexes of bivalent nickel and the attempt of their oxidation by chemical and electrochemical methods. The goal of more detailed studies of the prepared compounds was to find out the influence of the used ligands on the structure and properties of the complexes by using of the current physicochemical methods.

EXPERIMENTAL

The Ni(II) complexes of the formula $\text{NiX}(\text{Rdtc})(\text{PPh}_3)$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$; $\text{R} = \text{morph} (\text{C}_4\text{H}_8\text{O})$, $\text{pip} (\text{C}_5\text{H}_{10})$, $\text{dtc} (\text{S}_2\text{CN}^-)$) have been isolated by the reaction of the suspension of pulverized $\text{Ni}(\text{Rdtc})_2$ (0.002 mol) [8, 9] in CHCl_3 (20 cm^3) with pulverized

$\text{NiX}_2(\text{PPh}_3)_2$ (0.002 mol) [10]. The suspensions were at slightly higher temperature stirred for ca. 30 min. After the dissolving of the components, the reaction mixture was filtered and 25 cm^3 of ether (compounds I–III) or 20 drops of benzene (compounds IV–VI) were added to the crystallization. After 30 min the violet crystals were sucked, washed with ether and dried at 40°C under the infralamp.

The Ni(III) complexes with the composition $\text{NiX}(\text{Rdtc})(\text{PPh}_3)\text{Br}$ have been prepared by oxidation of the suspension of $\text{NiX}(\text{Rdtc})(\text{PPh}_3)$ (0.0015 mol in 10 cm^3 of hexane) by bromine (0.0016 mol in 5 cm^3 of hexane). The oxidant was added by parts and the mixture was stirred for ca. 30 min. After this time the brown material was formed. The mixture was filtered and the product was washed by hexane and dried *in vacuo* over H_2SO_4 in desiccator.

The X-ray structure analysis was carried out on the KUMA diffractometer at 20°C (dimensions of single crystal $0.5 \times 0.5 \times 0.2 \text{ mm}$). The graphite monochromated $\text{MoK}\alpha$ radiation was used; 5746 diffractions (3511 observed), 2θ -range (4 – 56°), hkl -range h {12, 0}, k {–13, 13}, l {–16, 16}, $\omega/2\theta$ scan, 2 reference reflections (crystal stability control after 100 diffractions). Hydrogen atoms were calculated in the expected positions; the correction for absorption was neglected. The structure was solved by using of the SHELX86, SHELX76, XTL programs on the NETmate/dx-25 computer. The final value of R -factor is 5.3 %.

The magnetochemical measurements were carried out by the Faraday method on laboratory-designed device (Development laboratories and workshops,

Palacký University, Olomouc) with Sartorius ultramicrobalance, model MP8-4433 at 20 °C and using Co[Hg(SCN)₄] as the magnetic susceptibility standard. The diamagnetic correction constants were used according to [11].

The molar conductivities were measured on Conductivity Meter OK-102/1 (Radelkis, Budapest) at (25 ± 0.2) °C in a nitromethane solution containing 10⁻³ mol dm⁻³ of the complex. The VIS diffuse-reflectance spectra were recorded on the Specord UV-VIS spectrophotometer (Zeiss, Jena) in the range $\tilde{\nu} = 13\,000\text{--}45\,000\text{ cm}^{-1}$. The IR spectra were recorded on the Specord 75 IR instrument (Zeiss, Jena) by the nujol technique in the range of wavenumbers 400–4000 cm⁻¹. The remaining methods were the same as in the papers [12, 13].

The content of nickel in the complex compounds was estimated by the chelatometric method with murexide as indicator, that of bromine by the Schöniger method, of phosphorus by the gravimetric method and C, H, N was determined by CHN-analyzer (Laboratorní přístroje, Prague).

RESULTS AND DISCUSSION

The chemical compositions of the prepared substances are given in Table 1. Important results of the physicochemical study are given in Table 2. The crystalline complexes of bivalent nickel NiX(Rdct)(PPh₃) are blue-violet, diamagnetic and

nonelectrolyte in nitromethane. The single crystal of the model compound NiBr(morphdct)(PPh₃) is triclinic. The other crystallographic data are: space group P $\bar{1}$, Z = 2, V = 1200.1 Å³, a = 9.765(2) Å, b = 10.943(3) Å, c = 13.008(3) Å, $\alpha = 112.18(2)^\circ$, $\beta = 90.89(2)^\circ$, $\gamma = 109.18(2)^\circ$, $\rho_{X\text{-ray}}/\rho_{\text{exp}} = 1.558/1.55\text{ g cm}^{-3}$, R = 5.3 %. The results of the complete X-ray structure analysis of this complex (Tables 3 and 4; Fig. 1) confirm the distorted square-planar coordination around the central atom of nickel. This fact is apparent from the different values of the bond lengths and angles between the nickel and donor atoms of ligands. The differences of positions (in Å) for atoms from "ideal" plane which is formed by Ni, Br, P, S1, S2 are: Br + 0.04; P - 0.10; Ni - 0.06; S1 - 0.07; S2 + 0.11. The three phenyl rings are situated in three different planes; the dihedral angles between the above ideal plane and phenyl planes are: 60.5° (Ph1=C11-C61), 122.7° (Ph2=C12-C62), 101.6° (Ph3=C13-C63), the angles between the phenyl planes are: 83.1° (Ph1-Ph2), 78.1° (Ph1-Ph3), 112.9° (Ph2-Ph3). The values of the bond lengths Ni-S1 and Ni-S2 are more different above 0.03 Å than for Ni(Hpropdct)₂ (0.01 Å) [14]. This behaviour can be explained by the fact that PPh₃ is better π -acceptor than Br⁻ ion. The angle S1-Ni-S2 is smaller (difference 1.1°) and the bond length C1-N is longer (difference 0.21 Å) in this comparison.

The electrochemical oxidation of the Ni(II) complexes was studied by cyclic voltammetry in

Table 1. The Results of Elemental Analysis

Compound	Formula <i>M_r</i>	<i>w_i</i> (calc.)/%					
		Ni	C	H	N	P	Cl(Br)
I	NiCl(morphdct)(PPh ₃)	11.31	53.27	4.17	2.70	5.97	6.84
	518.69	11.32	53.13	4.11	2.53	5.71	7.41
II	NiBr(morphdct)(PPh ₃)	10.42	49.06	4.12	2.49	5.50	14.19
	563.14	10.48	49.52	4.18	1.98	5.42	14.57
III	NiI(morphdct)(PPh ₃)	9.62	45.28	3.80	2.30	5.08	
	610.14	9.53	44.93	3.92	2.22	4.91	
IV	NiCl(pipdct)(PPh ₃)	11.36	55.79	4.88	2.71	5.99	6.86
	516.72	11.38	55.75	4.80	2.13	6.04	6.39
V	NiBr(pipdct)(PPh ₃)	10.46	51.37	4.49	2.50	5.52	14.24
	561.17	10.28	52.09	4.40	2.41	5.48	14.92
VI	NiI(pipdct)(PPh ₃)	9.65	47.40	4.14	2.30	5.09	
	608.17	9.62	47.23	4.23	1.85	4.98	
VII	NiCl(morphdct)(PPh ₃)Br	9.80	46.15	3.87	2.34	5.17	
	598.60	10.03	45.69	3.68	2.22	4.98	
VIII	NiBr(morphdct)(PPh ₃)Br	9.13	42.96	3.60	2.18	4.82	24.85
	643.05	9.50	42.38	2.89	1.88	4.63	25.15
IX	NiI(morphdct)(PPh ₃)Br	8.50	40.00	3.36	2.03	4.49	
	690.04	8.33	39.29	3.21	1.86	4.07	
X	NiCl(pipdct)(PPh ₃)Br	9.84	48.32	4.42	2.35	5.19	
	596.62	10.11	48.23	3.91	2.15	5.02	
XI	NiBr(pipdct)(PPh ₃)Br	9.15	44.97	3.93	2.18	4.83	24.94
	641.07	8.87	44.29	3.58	1.82	4.46	25.01
XII	NiI(pipdct)(PPh ₃)Br	8.53	41.89	3.66	2.04	4.50	
	688.07	8.76	42.38	3.20	2.21	4.12	

Table 2. The Results of Physicochemical Study

Compound	$\mu_{\text{eff}}/\mu_{\text{B}}$	IR data				EAS			TA/°C			
		λ S cm ² mol ⁻¹	$\tilde{\nu}/\text{cm}^{-1}$		$\tilde{\nu} \cdot 10^{-3}$ cm ⁻¹			θ_1	θ_2	Exo	Plateau	
			$\nu(\text{C}\cdots\text{S})$	$\nu(\text{C}\cdots\text{N})$								
I	dia	4.7	992 m	1518 m	19.4	29.8	38.6	75	175	185	—	
II	dia	8.2	990 m	1508 m	19.1	30.0	39.1	75	160	170	—	
III	dia	9.1	980 m	1528 vs	19.0	30.0	39.0	50	140	150	575–625	
IV	dia	8.8	1000 s	1535 s	19.4	29.1	39.0	60	170	180	—	
V	dia	3.6	999 s	1534 vs	19.4	29.2	39.1	75	160	170	—	
VI	dia	6.7	980 m	1520 vs	19.0	29.6	39.1	50	130	145	550–650	
VII*	1.81	—	996 m	1500 s	—	29.7	38.4	50	155	175	—	
VIII*	1.83	—	992 m	1500 s	—	30.0	38.6	60	150	170	—	
IX*	2.07	—	990 m	1510 m	—	29.8	39.1	50	130	140	575–630	
X*	1.69	—	998 m	1510 m	—	30.0	39.2	50	—	175	—	
XI*	2.09	—	992 m	1510 m	—	29.0	38.3	75	—	145	500–620	
XII*	1.81	—	995 m	1505 vs	—	29.3	39.3	55	—	130	540–680	

*Unsoluble. θ_1 – initial temperature of decomposition, θ_2 – beginning of the mass increase, exo – top of exo-effect.

Table 3. Fractional Coordinates of Atoms of NiBr(morphdte)-(PPh₃)

Atom	$10^4 \cdot (x/a)$	$10^4 \cdot (y/b)$	$10^4 \cdot (z/c)$
Ni	2161(1)	8418(1)	6219(1)
Br	1744(1)	7557(1)	7613(1)
P	2105(1)	0482(1)	7334(1)
S1	1887(2)	6305(1)	4920(1)
S2	2549(2)	8892(1)	4739(1)
N	2208(5)	6496(4)	2927(3)
O	1563(5)	5093(5)	0574(3)
C1	2222(6)	7120(5)	4015(4)
C2	2621(7)	7284(6)	2207(5)
C3	1586(7)	6498(7)	1104(5)
C4	0981(8)	4350(7)	1248(5)
C5	1963(7)	4981(6)	2375(5)
C11	3360(6)	1471(5)	8656(4)
C21	4344(6)	0938(6)	8962(5)
C31	5325(7)	1723(6)	9958(5)
C41	5367(7)	3051(6)	0670(5)
C51	4409(7)	3596(6)	0370(5)
C61	3415(7)	2828(6)	9376(5)
C12	0243(6)	0126(5)	7660(5)
C22	-0078(7)	0490(6)	8755(5)
C32	-1514(8)	0068(8)	8936(6)
C42	-2656(7)	9267(7)	8052(6)
C52	-2355(7)	8921(8)	6970(6)
C62	-0907(7)	9345(7)	6775(5)
C13	2428(6)	1842(5)	6778(4)
C23	1452(7)	2531(6)	6801(5)
C33	1837(8)	3637(7)	6427(7)
C43	3128(8)	4028(7)	6067(6)
C53	4117(7)	3331(6)	6022(5)
C63	3754(6)	2240(6)	6378(4)

nitromethane solutions ($[\text{Ni(II)}] = 2 \times 10^{-3} \text{ mol dm}^{-3}$) in the presence of LiCl (0.02 mol dm^{-3}). Other solvents are unsuitable for lower solubility of the studied compounds. The compound NiCl(pipdte)(PPh₃) cannot be studied by this method because its solution is unstable. The cyclic voltammograms of the complexes NiCl(morphdte)(PPh₃), NiBr(morphdte)(PPh₃), and NiBr(pipdte)(PPh₃) cannot be interpreted because these redox processes are irreversible and

Table 4. Important Interatomic Distances and Angles of NiBr(morphdte)(PPh₃)

Bond	Distance/Å	Atoms	Angle/°
Ni—Br	2.325(1)	Br—Ni—P	96.85(6)
Ni—P	2.196(2)	Br—Ni—S1	92.12(5)
Ni—S1	2.214(2)	P—Ni—S2	96.85(6)
Ni—S2	2.182(2)	S1—Ni—S2	78.82(6)
S1—C1	1.703(6)	Ni—S1—C1	85.62(20)
S2—C1	1.719(6)	Ni—S2—C1	86.25(19)
C1—N	1.316(6)	S1—C1—S2	109.29(31)
N—C2	1.475(8)	S1—C1—N	125.76(44)
C2—C3	1.507(9)	S2—C1—N	124.94(43)
C3—O	1.420(9)	Ni—P—C11	118.53(19)
C4—O	1.414(8)	Ni—P—C12	105.52(19)
C5—N	1.469(8)	Ni—P—C13	117.80(19)
P—C11	1.812(5)		
P—C12	1.822(6)		
P—C13	1.833(6)		
C11—C21	1.398(5)		
C21—C31	1.384(8)		
C31—C41	1.384(9)		
C41—C51	1.383(10)		
C51—C61	1.388(8)		
C61—C11	1.407(8)		
C12—C22	1.397(8)		
C22—C32	1.379(10)		
C32—C42	1.376(10)		
C42—C52	1.377(10)		
C52—C62	1.395(11)		
C62—C12	1.380(9)		
C13—C23	1.390(9)		
C23—C33	1.412(11)		
C33—C43	1.344(11)		
C43—C53	1.404(11)		
C53—C63	1.383(9)		

irreproducible (decomposition of the indifferent electrolyte). The anodic oxidation of NiI(morphdte)(PPh₃) occurs at the potential 0.9 V and of NiI(pipdte)(PPh₃) at the potential 0.7 V. The polarization rate was 20 mV s^{-1} . The potentials of the above anodic peaks depend on the rate of polarization; they varied in the interval $0.005\text{--}5 \text{ V s}^{-1}$. The heights of the peaks

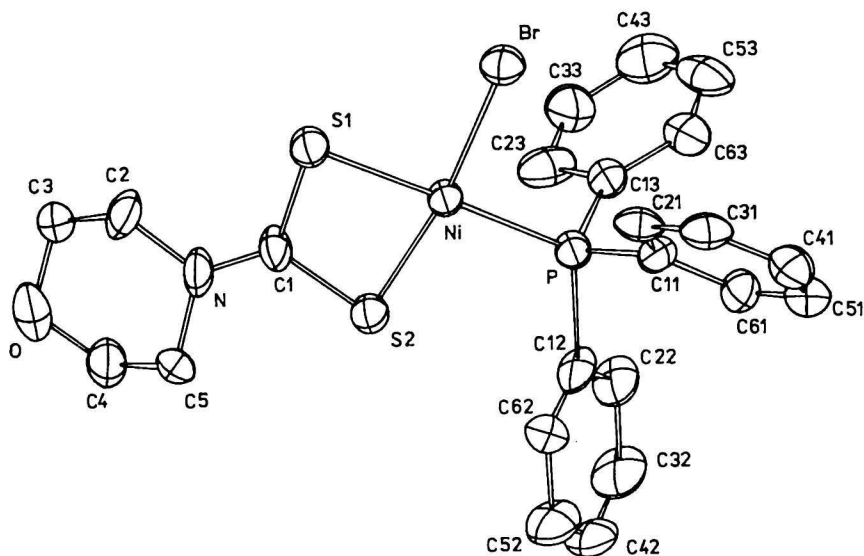
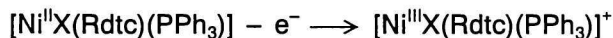


Fig. 1. The skeleton of the molecule of NiBr(morphdtc)(PPh₃).

depend linearly on the square root of the polarization rate and nearly agree with the theoretical values for one-electron diffuse-controlled oxidation [15].



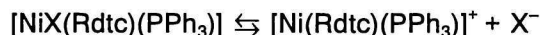
This conclusion agrees with the results obtained by investigation of Ni(II) complexes with bis(2-hydroxyethyl)dithiocarbamate [16]. The comparison of oxidation potentials of our complexes of Ni(II) with potentials for complexes Ni(morphdtc)₂ and Ni(pipdte)₂ cannot be made because these complexes are insoluble in organic solvents.

The oxidation of Ni(II) complexes by bromine leads to dark-brown Ni(III) compounds of the composition NiX(Rdte)(PPh₃)Br. Their X-ray diffractograms are different from diffractograms of the starting material (starting compounds are X-ray amorphous substances). This fact can be interpreted as absence of the starting material in products. The diffuse-reflectance VIS spectra of initial Ni(II) complexes are different from the spectra of products of oxidation. While the Ni(II) complexes exhibit a medium intense band in the range $\tilde{\nu} = 19\,000\text{--}19\,400\text{ cm}^{-1}$ (for the transition ${}^1A_{1g} \rightarrow {}^1E_g$) characteristic of square-planar Ni(II) complexes [1], in the products of oxidation this absorption band has not been found. The values of the next two bands are slightly different and this fact can be assigned to the S₂CN⁻ group of the dithiocarbamate [1, 5]. The first absorption band ($\tilde{\nu} = 30\,000\text{ cm}^{-1}$) corresponds with $n \rightarrow \pi^*$ transition at the sulfur atom and the second one ($\tilde{\nu} = 39\,000\text{ cm}^{-1}$) corresponds with $\pi \rightarrow \pi^*$ transition at the N=C=S group.

The initial complexes are diamagnetic (as against the oxidation products). Magnetic moments μ_{eff} for

paramagnetic oxidation products are in the range 1.69–2.09 μ_{B} . This fact is in accordance with literature data for Ni(III) complexes [7, 17, 18]. The width of this interval of the effective magnetic moments for room temperature only is difficult to simply explain. The additional measurements of magnetic properties are necessary.

Ni(II) complexes are nonelectrolytes [19]. Slightly higher values of molar conductivity Λ can be explained by partial dissociation of these compounds in solution



The Ni(III) complexes are little soluble in the organic solvents, that is why their molar conductivities cannot be estimated.

The IR spectra were not studied in detail, only the characteristic vibrations $\nu(\text{C}\equiv\text{N})$ and $\nu(\text{C}\equiv\text{S})$ are interpreted. All oxidation products exhibit with regard to the original Ni(II) complexes the shift of the vibration $\nu(\text{C}\equiv\text{N})$ to the lower wavenumbers. This fact can be explained by the reduced character of the C≡N double bond [1]. The form of IR records of the starting Ni(II) complexes and their oxidation products is very similar; not even the absorption maximum of (P—O) vibration at 1 200 cm^{-1} in the IR spectrum of products was found. This fact agrees with the assumption that neither dithiocarbamate nor triphenylphosphine is oxidized [20].

The interchange of the donor sulfur atoms in NiS₄ chromophore by the P and X atoms (X = Cl⁻, Br⁻, I⁻) leads to the significant decreasing of the thermal stability. While the decomposition of the complexes [Ni(pipdte)₂] and [Ni(morphdte)₂] occurs at above 170 °C and 120 °C, respectively, the thermal decompo-

sition of Ni(II) complexes NiX(pipdte)(PPh₃), NiX(morphdte)(PPh₃) and their oxidation products started in the range of 50–75 °C. The influence of oxidation on thermal stability of Ni(III) complexes was not observed. The thermal decomposition of all the compounds is not simple. The initial mass loss (probably dehalogenation) in the temperature range 130–175 °C coincides with the insertion of oxygen into the Ni—P bond (the Ni—O—P bond is formed). These conclusions are supported on the TG curves by the slight increasing of mass (for complexes X, XI, XII by a small plateau) and on the DTA curves by a small exo-effect within the temperature range 130–185 °C. The problem of oxygen insertion reactions was studied previously in compounds NiX₂(PPh₃)₂ (X = Cl⁻, Br⁻, I⁻, NCS⁻, NO₃⁻) [21]. The further course of the TG curves indicates the decomposition without the formation of a definite or perceptible intermediate, only in the case of complexes III, VI, IX, XI, XII the thermal decomposition leads according to [22] to formation of Ni₂P₂O₇ as intermediate (plateau within the temperature range 500–680 °C). The thermal decomposition of studied compounds was not finished even at 900 °C.

With respect to all experimental facts 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 are not able to confirm the coordination number of nickel, *i.e.* four or five.

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Translated by J. Kameníček and F. Březina