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ETHYLXANTHATES AND ISOPROPYLXANTHATES OF NICKEL WITH TRIPHENYLPHOSPHINE AS MIXED π-ACCEPTOR LIGAND

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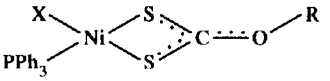
Abstract—Nickel(II)xanthates with triphenylphosphine as mixed π-acceptor ligand of the composition [NiX(RXa)(PPh$_3$)] (X = Cl, Br, I, NCS; R = Et, i-Pr; Xa = S$_2$CO have been prepared. All of these complexes have been characterized by elemental analysis, infrared and electronic absorption spectroscopy, magnetochemical measurements, thermal analysis and conductivity measurements. The [NiI(RXa)(PPh$_3$)] complexes have been one-electron irreversibly oxidized which was determined by cyclic voltammetry. A distorted square-planar arrangement of the coordination sphere with chromophore NiS$_2$ClP has been proved by the X-ray structural analysis of the model [NiCl(i-PrXa)(PPh$_3$)] complex.

Owing to the possible exploitation of xanthates of some transition metals as fungicides, pesticides, vulcanization accelerators, flotation agents and high pressure lubricants,[1–3] considerable attention has been paid to these compounds. Only a few ethyl- or isopropylxanthates of nickel with triphenylphosphine have been studied so far. Before we started our work the complexes of the composition [(η^5-C$_5$H$_5$)Ni(RXa)(PPh$_3$)] (R = Me, Et) were known. A square-planar arrangement of coordination sphere with coordination of xanthate anion as monodentate ligand was proved by the X-ray structural analysis for the above mentioned compounds.[4,5] A distorted square-pyramidal arrangement around the Ni atom was determined[6] by the X-ray structural analysis of [Ni(EtXa)$_2$(PPh$_3$)]. Diamagnetic complexes of [Ni(NO)(RXa)PPh$_3$)] (R = Me, Et, n-Pr, n-Bu, c-Hex) were also isolated[7] and the complex with R = *c*-Hex was structurally characterized.[8]

The aim of this work has been the preparation of the new complexes [NiX(RXa)(PPh$_3$)] and the study of the influence of radical R and ligand X on the structure and properties of these complexes:



Possibilities of exploitation of nickel(III), and Nickel(IV) compounds in living organisms[9] led us to try to increase the oxidation number of nickel in this type of complex.

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EXPERIMENTAL

Preparation of [Ni(RXa)$_2$]

These complexes were synthesized according to the literature procedure.[10]

Preparation of [NiX$_2$(PPh$_3$)$_2$]

These compounds were prepared by the method described in Ref. 11.

Preparation of [NiX(RXa)(PPh$_3$)]

Fine pulverized [NiX$_2$(PPh$_3$)$_2$] (0.002 mol) was added to a solution of [Ni(RXa)$_2$] (0.002 mol) in 15 cm^3 of CHCl$_3$. The mixture was intensively stirred till the reaction components were dissolved (*ca* 30 min). The reaction mixture was filtered and 30 cm^3 of ether (excess n-hexane for complexes **IV, VII**) was added to make it crystallize. After standing for *ca* 10 min at laboratory temperature black–violet crystals (dark brown powder for complexes **IV, VII**) were obtained. These were filtered off, washed with ether (n-hexane) and dried at 40°C under the infralamp.

General methods

The Ni content was determined by the chelatometric method with murexide as indicator, bromine by the Schöniger method, phosphorus by the gravimetric method. The C, H, N analyses were performed on a CHN-Analyser (Laboratorní přístroje Praha). IR spectra were measured on a Specord M80 (Carl Zeiss, Jena) within the region $\nu = 4000$–400 cm^{-1}. Diffuse-reflectance spectra (in the range 45 000–13 000 cm^{-1}) were recorded on a Specord M40 UV/vis (Carl Zeiss, Jena). Magnetochemical measurements were carried out at 20°C on a laboratory-designed device (Development Laboratories of Palacký University, Olomouc) by the Faraday method. [CoLHg(NCS)$_4$] was used as calibrant. The corrections for diamagnetism were performed according to Ref. 12. The thermal stability was studied on a Q-1500 Derivatograph (MOM, Budapest) with a sample of weight *ca* 150 mg over the temperature range 20–900°C and gradient 2.5°C min^{-1}. The molar conductivities λ_M were measured on a Conductivity Meter OK 102/1 (Radelkis, Budapest) at 25 ± 0.2°C in nitromethane.

Cyclic voltammograms were obtained on a Polarographic Analyzer PA3 (Laboratorní přístroje, Praha) in a three-electrode arrangement using a Pt working electrode (surface area 0.32 cm^2), a saturated calomel electrode (SCE) as reference electrode, and Pt foil with a large surface area as auxiliary eletrode. The polarization scan rate varied from 0.05 to 0.5 V s^{-1}. The measurements were performed in the polarization range -0.2 to $+0.8$ V in dimethyl sulphoxide in the presence of N(Me)$_4$Cl (0.05 mol l^{-1}) as supporting electrolyte. The concentrations of the complexes were 8×10^{-5} mol l^{-1}.

Determination of the structure of [NiCl(i-PrXa)(PPh$_3$)].

The diffraction experiment was performed using a KUMA KM4 diffractometer at 20°C with graphite-monochromatized Mo$-K_\alpha$ radiation ($\lambda = 0.71073$ Å) and a crystal of dimensions $0.2 \times 0.2 \times 0.05$ mm. The experimental density of the crystals was estimated picnometrically under water solution of KI at laboratory temperature. Final values of the lattice parameters were determined from 25 reflection in the range $11.1 < 2\Theta < 17.2$. Intensities were measured using ω–2Θ scan techniques within the $4 < 2\theta < 45°$ region. Index ranges: $-13 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 17$. The two standard reflections (-2 -3 -2, 1 1 -4) were checked after every 200 measurements (deviation max. 1.1%). Extinction and absorption corrections were not applied.

The phase problem was solved by the heavy-atom method and the structure was anisotropically refined by the full-matrix least-squares procedure with weight $w = 1/[\sigma^2(F_o^2) + (0.0641P)^2]$, where $P = [(F_o^2) + 2F_c^2]/3$. The H atoms were positioned theoretically. The maximum and minimum electron density on the final difference Fourier map were 0.374 and -0.527 e Å^{-3}. Refinement of the structure was based on F^2. The weighted R-factor, wR, and goodness of fit, S, were based on F^2, the conventional R-factor, R, was based on F. The following programs were used: SHELXS-86,[13] SHELXL-93[14] and ORTEP.[15] Basic crystallographic data and structure refinement are reported in Table 1. The structure is shown in Fig. 1.

RESULTS AND DISCUSSION

The chemical compositions and the results of analyses of these new compounds are given in Table 2. Their important physico-chemical properties are listed in Table 3.

The new complexes are diamagnetic, non-electrolytes (like the starting [Ni(EtXa)$_2$] and [Ni(i-PrXa)$_2$] complexes, whose square-planar arrangement of NiS$_4$-coordination sphere was determined by the X-ray structural analysis[16,17]). The slight increase of conductivities of the same complexes can be explained by their partial dissociation in nitromethane.

$$[NiX(RXa)(PPh_3)] \rightleftharpoons [Ni(RXa)(PPh_3)]^+ + X^-$$

The measurements of electronic spectra confirmed a square-planar arrangement of coordinating atoms. Medium strong absorption maxima in the region of 18 400–20 500 cm^{-1} and 23 700–24 000 cm^{-1} have been found for all complexes. These maxima to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions have been assigned.[1,18] The maximum near 31 000 cm^{-1} is ascribed to the $\pi \rightarrow \pi^*$ transition of the xanthate ligand by the authors.[1] The maxima about 39 000 and 45 000 cm^{-1} are apparently connected with the same intraligand transition.

The following maxima characteristic for nickel (II) xanthates[1] have been observed in the IR spectra: ν(C—S), ν_{as}(C—O—C) and ν_s(C—O—C). It has been found for complexes *IV* and *VIII* that the NCS$^-$ group is coordinated through the nitrogen

Table 1. Crystal data and structure refinement for [NiCl(i-PrXa)(PPh$_3$)]

Empirical formula	$C_{22}H_{22}ClNiOPS_2$
Formula weight	491.65
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 12.972(3)$ Å $b = 11.072(2)$ Å $c = 15.858(3)$ Å $\beta = 98.36(3)$
Volume	2253.4(8) Å^3
Z	4
Density ($\rho_{rtg./exp.}$)	1.499/1.45 Mg m^{-3}
Absorption coefficient	1.246 mm^{-1}
$F(000)$	1016
Reflections collected	3068
Independent reflections	2945 [$R_{int} = 0.0368$]
Data/restraints/parameters	2931/0/271
Goodness of fit$_{obs/all}$	1.181/0.927
$R_{obs}[I > 2\sigma(I)]$	$R = 0.0360$, $wR = 0.0972$
R_{all}	$R = 0.1656$, $wR = 0.1633$

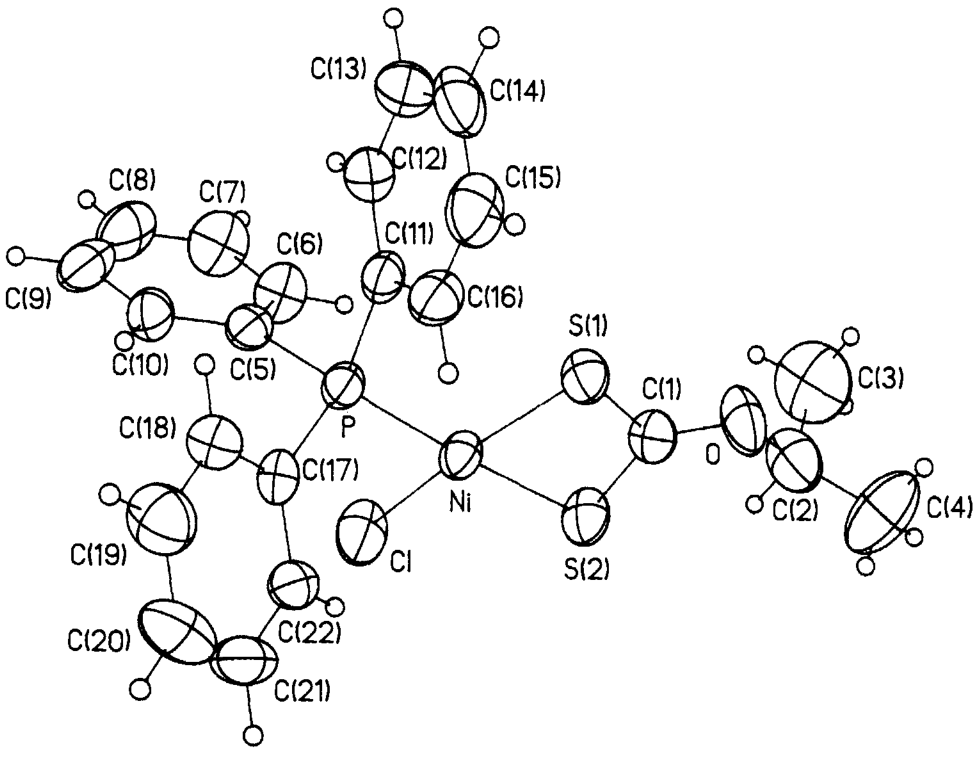

Fig. 1. The molecular structure of [NiCl(i-PrXa)(PPh$_3$)] showing 50% probability displacement ellipsoids.

Table 2. The results of elemental analysis[a]

	Compound	Analysis (%) Ni	C	H	N	X[b]	P
I	$[NiCl(EtXa)(PPh_3)]$	12.0(12.3)	52.3(52.8)	4.1(4.2)	—	6.9(7.4)	6.0(6.5)
II	$[NiBr(EtXa)(PPh_3)]$	11.4(11.2)	48.4(48.3)	3.4(3.9)	—	14.7(15.3)	5.3(5.9)
III	$[NiI(EtXa)(PPh_3)]$	10.7(10.3)	44.1(44.3)	3.9(3.5)	—	—	5.9(5.4)
IV	$[Ni(NCS)(EtXa)(PPh_3)]$	11.3(11.7)	52.6(52.8)	4.3(4.0)	3.1(2.8)	—	5.8(6.2)
V	$[NiCl(i\text{-}PrXa)(PPh_3)]$	12.0(11.9)	54.0(53.7)	4.6(4.5)	—	7.8(7.2)	6.8(6.3)
VI	$[NiBr(i\text{-}PrXa)(PPh_3)]$	10.8(11.0)	48.6(49.3)	4.1(4.1)	—	15.0(14.9)	6.3(5.8)
VII	$[NiI(i\text{-}PrXa)(PPh_3)]$	10.0(10.1)	44.9(45.3)	3.8(3.8)	—	—	6.0(5.3)
VIII	$[Ni(NCS)(i\text{-}PrXa)(PPh_3)]$	11.1(11.4)	53.7(53.7)	4.2(4.3)	2.4(2.7)	—	5.6(6.0)

[a] Calculated values are given in parentheses.
[b] X = Cl, Br.

Table 3. The results of physico-chemical study

Compound	μ_{eff}^{cor}/μ_B	λ_M (S cm^2 mol^{-1})	IR (cm^{-1}) ν (C—S)	ν_s (C—O—C)	ν_{as} (C—O—C)	Diffuse refl. spectra ($\nu \times 10^3$ cm^{-1})		TA (°C) Θ[b]
I	dia	0	638m 1026m	1094m	1180w	20.5 23.7 31.5	39.4	50
II	dia	8.9	636m 1030w	1100m	1156m	19.1 23.8 31.7	39.7 43.8	50
III	dia	12.6	618m 1025m	1098m	1180m	18.4 24.4 31.6	39.4 43.9	50
IV	dia	3.0[a]	616w 1025w	1095w	1170m	19.8 23.9 31.6	39.4 44.0	60
V	dia	0	638w 1020m	1084m	1168m	19.4 30.9 39.7	46.8	105
VI	dia	2.1	635w 1020m	1088s	1182w	20.5 23.8 31.3	39.4	120
VII	dia	15.8	634w 1020m	1088m	1180w	18.6 31.5 39.6		60
VIII	dia	2.5	616w 1026m	1085w	1172w	19.0 24.0 31.4	42.6 46.4	80

[a] [Ni] = 5×10^{-4} mol dm^{-3}.
[b] Initial temperature of decomposition.

atom to the nickel atom. For these complexes absorption maxima of the NCS^- group have been found and assigned to ν(C≡N) at 2095–2100 cm^{-1} and ν(C—S) at 825–840 cm^{-1}.[19] This conclusion is in good accordance with the result of the X-ray structural analysis of the $[Ni(NCS)(n\text{-}Bu_2Dtc)(PPh_3)]$ complex ($Dtc^- = S_2CN^-$), where the Ni—N bond was proved.[20]

On the basis of the comparison of the beginnings of thermal decomposition, isopropylxanthate complexes seem to be more stable than ethylxanthate complexes. Their decomposition started at 60–120°C, while the ethylxanthate complexes started to decompose in the region of 50–60°C. All complexes decompose without formation of thermally stable intermediates and their decomposition was not terminated even at 900 C (working temperature of the device used).

Anodic peaks occurred in the region of 0.55–0.70 V only on the cyclic voltammograms of the [NiI(EtXa)(PPh$_3$)] and [NiI(i-PrXa)(PPh$_3$)] complexes. Its height depends linearly on the square root of the polarization rate and agrees with the Faraday current value of a one-electron irreversible diffusion-controlled process.[21] For the remaining complexes (except for [Ni(NCS)(i-PrXa)(PPh$_3$)], where no suggestion of oxidation was observed) an oxidation in the same potential region as described above was observed, but the current densities attained only 20% of the value corresponding to a one-electron oxidation.

Chemical oxidations by bromine, iodine, NOClO$_4$ and FeCl$_3$ were unsuccessful.

Crystallographic discussion

The results of the X-ray structural analysis of the model [NiCl(i-PrXa)(PPh$_3$)] complex confirmed the distorted square-planar arrangement around the central nickel(II) atom (see Tables 1, 4 and Fig. 1). This fact is evident from the different values of the bond lengths and angles between the nickel and donor atoms of ligands as well as from deviations of the Ni, P, Cl, S(1) and S(2) atoms from a least-squares plane fitted through the Ni—P—Cl—S(1)—S(2) atoms (Plane 1). The deviations are: Ni (−0.013 Å), P (−0.038 Å), Cl (0.045 Å), S(1) (0.050 Å) and S(2) (−0.044 Å). For xanthates a typical shortening of the O—C(1) bond [1.280(8) Å] in comparison with the O—C(2) bond [1.476(9) Å] was found. This difference is probably due to a larger proportion of π-bonding on the O—C(1) bond owing to the O—C(2) bond. This fact was already observed by the other authors.[16,17,22] The three phenyl rings are situated in three different planes. The dihedral angles formed by least-squares planes are as follows: 71.6(2) [Plane 1—Plane 2 C(5)—C(10)], 73.2(2) [Plane 1—Plane 3 C(11)—C(16)], 112.2(2) [Plane 1—Plane 4 C(17)—C(22)], 90.1(2) (Plane 2—Plane 3), 59.7(3) (Plane 2—Plane 4) and 63.5(3) (Plane 3—Plane 4), respectively.

Table 4. Selected bond lengths (Å) and angles ( ) for [NiCl(i-PrXa)(PPh$_3$)]

Ni—Cl	2.167(2)
Ni—P	2.177(2)
Ni—S(1)	2.185(2)
Ni—S(2)	2.228(2)
S(1)—C(1)	1.686(7)
S(2)—C(1)	1.695(7)
O—C(1)	1.280(8)
O—C(2)	1.476(9)
C(2)—C(3)	1.440(12)
C(2)—C(4)	1.482(13)
Cl—Ni—P	93.34(8)
Cl—Ni—S(1)	170.73(8)
P—Ni—S(1)	95.39(7)
Cl—Ni—S(2)	92.61(8)
P—Ni—S(2)	173.91(8)
S(1)—Ni—S(2)	78.74(7)
C(1)—S(1)—Ni	85.3(2)
C(1)—S(2)—Ni	83.7(2)
C(1)—O—C(2)	121.9(6)
O—C(1)—S(1)	121.5(5)
O—C(1)—S(2)	126.7(5)
S(1)—C(1)—S(2)	111.8(4)
C(3)—C(2)—O	106.9(8)
C(3)—C(2)—C(4)	113.7(9)
O—C(2)—C(4)	107.4(8)

Supplementary material

Atomic coordinates of all atoms, thermal parameters, complete bond distances, bond angles and a list of structure factors are available from the authors on request.

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