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Nickel(II) isopropylxanthate complexes containing phosphorus donor ligands in the coordination sphere—II†

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Abstract—Nickel(II) isopropylxanthate complexes, $[Ni(Pr^ixa)_2(PPh_3)]$, $[NiX(Pr^ixa)(TCEP)]$, $[Ni(Pr^ixa)_2(TRIPHOS)]\cdot H_2O$ and $[Ni(Pr^ixa)(TRIPHOS)][Ni(Pr^ixa)_3]$ {Pr^i = i-C_3H_7, xa = S_2CO^-, X = Cl^- or Br^-, PPh_3 = triphenylphosphine, TCEP = tris(2-cyanoethyl)phosphine and TRIPHOS = 1,1,1-tris-(diphenylphosphino-methyl)ethane}, have been synthesized. The compounds have been characterized by elemental analysis, magnetochemical and conductivity measurements and IR and electron spectroscopies. The structure of $[Ni(Pr^ixa)_2(PPh_3)]$ has been determined by single-crystal X-ray diffraction. The nickel atom is four-coordinated by three sulfur atoms from two non-equivalently bonded isopropylxanthato anions and by one phosphorus atom from PPh_3 [Ni—S = 2.2282(13), 2.2588(14), and 2.2382(13), respectively, and Ni—P = 2.2023(13) Å], in a distorted square-planar geometry. One of the two xanthate ligands is coordinated as a monodentate ligand. The distance between nickel and non-coordinated sulfur atom is 2.816(2) Å. © 1997 Elsevier Science Ltd

Keywords: nickel(II) xanthates; syntheses; X-ray structure.

The chemistry of transition metal *O*-alkyldithiocarbonates, named xanthates, has developed rapidly and many complexes have been prepared and studied during the last several decades. In general, it is known, that the above complexes and their various amine, imine or phosphine adducts are still extensively investigated not only for their wide applications in industry [1], but also for coordination variability of xanthate anions, which can act as mono- or bidentate ligands, or may lie out of coordination sphere of central atom.

We have previously synthesized and characterized the complexes of the composition $[NiX(Rxa)(PPh_3)]$ (X = Cl, Br, I, NCS; R = Et, Pr^i [2]. Reactions of bis(alkylxanthato) nickel(II) with various mono-, bi- or tridentate phosphines have been systematically studied by Ballester and Perpiñán [3–6]. They prepared and characterized the compounds of the following compositions: $[Ni(Rxa)_2(PMePh_2)]$ and $[Ni(Rxa)_2(dppe)]$ [R = Et, *c*-Hex; dppe = 1,2-bis(diphenylphosphino)ethane], $[Ni(Rxa)(TRIPH)]PF_6$ [R = Et, *c*-Hex; TRIPH = bis(2-diphenylphosphinoethyl)phenylphosphine], $[Ni(Hex^cxa)(TRIPH)]X$ (X = Cl, Hex^cxa) and $[Ni(Rxa)(TRIPH)][Ni(Rxa)_3]$ (R = Et, *c*-Hex). Zagal *et al.* [7] synthesized square-planar $[Ni(Rxa)_2(PBu_3)_2]$ (R = Et or Bu^n) complexes, in which both the xanthate anions act as monodentate ligands. Aly *et al.* [8] prepared complexes of the composition $[Ni(Rxa)_2(dppe)_2]$, which have been described as square-planar compounds with both xanthate and dppe ligands monodentately coordinated. The nickel(II) xanthate compounds of the type $[Ni(Rxa)(NO)(PPh_3)]$ (R = Me, Et, Pr^n, Pr^i, Bu^t, Hex^c or phenyl) have been also studied and characterized by Kessissoglou *et al.* [9] as square-planar complexes. Some Ni^{II}-xanthates have been investigated by single-crystal X-ray diffraction and their significant

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structural features compared and discussed by Tiekink and Winter [10].

Only a few Ni^{II} xanthate complexes containing a phosphine ligand in the coordination sphere of the central atom have been structurally characterized to date: $[NiCl(Pr^ixa)(PPh_3)]$ [2], $[Ni(Hex^cxa)_2(P\text{-}MePH_2)]$ [4], $[Ni(Hex^cxa)(TRIPH)][Ni(Hex^cxa)_3]$ [6], $[Ni(\eta^5\text{-}C_5H_5)(Etxa)(PPh_3)]$ [11], $[Ni(\eta^5\text{-}C_5H_5)(Mexa)(PPh_3)]$ [12] and $[Ni(Etxa)_2(PPh_3)]$ [13]. The purpose of this present study was to synthesize and to characterize hitherto unknown nickel complexes formed by reactions between the bis(isopropylxanthato) nickel(II) and various phosphines.

EXPERIMENTAL

The general techniques and instrumentation, except IR spectra which were recorded on an ATI Mattson Genesis Series FTIR spectrometer using the KBr technique in the range 4000–400 cm^{-1}, are as described previously [2]. The starting $[Ni(pr^ixa)_2]$ complex was synthesized according to the procedure published in the literature [14], such as for tris(2-cyanoethyl)phosphine [15]. Previously described methods [16] were also used to prepare the complexes $[NiX_2(TCEP)_2]$ (X = Cl or Br). 1,1,1-Tris-(diphenylphosphino-methyl)ethane was supplied by Fluka Co.

Synthesis of $[Ni(Pr^ixa)_2(PPh_3)]$

Triphenylphosphine (PPh_3; 2 mmol) was added to a solution of $[Ni(Pr^ixa)_2]$ (2 mmol) in $CHCl_3$ (10 cm^3). The reaction mixture was stirred for 2 h at room temperature and then petroleum ether (50 cm^3) was added. Dark crystals were formed by spontaneous evaporation of solvents. They were separated by filtration, washed with a petroleum ether (2 × 5 cm^3) and dried under an IR lamp at 40°C.

Synthesis of $[NiX(Pr^ixa)(TCEP)]$, *where* $X = Cl^-$ *or* Br^-

$[NiX_2(TCEP)_2]$ (1 mmol) was added to an acetone solution (20 cm^3) of $[Ni(Pr^ixa)_2]$ (1 mmol). After 2 h stirring the reaction mixture was filtered and then evaporated to dryness. The violet solid formed was several times decanted by *n*-hexane and dried under an IR lamp at 40°C.

Synthesis of $[Ni(Pr^ixa)_2(TRIPHOS)] \cdot H_2O$

1,1,1-Tris(diphenylphosphino-methyl)ethane (TRIPHOS; 0.5 mmol) was added to a CH_2Cl_2 solution (10 cm^3) of $[Ni(Pr^ixa)_2]$ (0.5 mmol). The reaction mixture was stirred for 15 min. After adding Et_2O (100 cm^3) the light-brown solid was formed. It was filtered off, washed with Et_2O (2 × 5 cm^3) and dried in a vacuum desiccator.

Synthesis of $[Ni(Pr^ixa)(TRIPHOS)][Ni(Pr^ixa)_3]$

$[Ni(Pr^ixa)_2]$ (1 mmol) was added to a suspension of TRIPHOS (0.5 mmol) in MeOH (30 cm^3). The colour of the reaction mixture turned to brown–red immediately. It was stirred for 30 min. The solid formed was filtered off, washed with a small amount of MeOH and Et_2O solution and dried under an IR lamp at 40°C.

X-ray crystallography

Crystals of $[Ni(Pr^ixa)_2(PPh_3)]$ suitable for a X-ray analysis were obtained directly from the reaction mixture by slow evaporation of the solvents. Experimental density [$D_{exp}(20°C) = 1.36\ Mg\ m^{-3}$] was estimated by the flotation method in aqueous solution of KI.

Data were collected using a KUMA KM-4 diffractometer at 293(2) K with graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. Unit-cell dimensions were refined by using 50 centred reflections within $20.4 < 2\theta < 29.1°$ region. Diffraction intensities were measured by the ω-2θ scan technique. No absorption correction was applied. The structure was solved by the direct methods (SHELXS-86) [17] and refined on F^2 by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-93) [18]. Weight scheme: $w = 1/[\sigma^2(F_0)^2 + (0.057P)^2 + 0.800P]$, where $P = (F_0^2 + 2F_0^2)/3$. The hydrogen atom positions of phenyl rings were found from the differential Fourier maps and all their parameters were free to refinement, while the hydrogen atoms bonded to carbons of *iso*-propyl groups were positioned theoretically and refined using "rigid" refinement (i.e. AFIX 137). Calculations were carried out on a Pentium/133 personal computer and on an IBM RS/6000 98F computer. Crystal data and structure refinement for $[Ni(Pr^ixa)_2(PPh_3)]$ are given in Table 1. The structure is shown in Fig. 1 together with the atomic numbering scheme.

The atomic coordinates, thermal parameters, full lists of bond lengths and angles, and structure factor tables have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

In this study we have used the $[Ni(Pr^ixa)_2]$ complex as a starting compound for syntheses of its phosphine adducts. The analytical data for the new compounds described in this work are given in Table 2. Some results of the physico-chemical studies are presented in Table 3.

The X-ray structure, as shown in Fig. 1, reveals a

Table 1. Crystal data and structure refinement for $[Ni(Pr^ixa)_2(PPh_3)]$

Empirical formula	$C_{26}H_{29}NiO_2PS_4$
Formula weight	591.41
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P*1
Unit-cell dimensions	$a =$ 9.288(3) Å $\alpha = 81.64$ (4)°
	$b =$ 11.195 (4) Å $\beta = 80.12$ (4)°
	$c =$ 14.593 (6) Å $\gamma = 78.73$ (3)°
Volume (Å^3)	1456.2 (9)
Z	2
Density (calcd./measd.; Mg m^{-3})	1.349/1.36
Absorption coefficient (mm^{-1})	1.029
F(000)	616
Crystal size (mm)	0.50 × 0.25 × 0.10
θ range for data collection (°)	2.2–25.7
Index ranges	$-10 \leqslant h \leqslant 11$
	$0 \leqslant k \leqslant 13$
	$-17 \leqslant l \leqslant 17$
Reflections collected	5556
Independent reflections	5519 ($R_{int} = 0.0807$)
Data/restraints/parameters	5491/0/383
Goodness-of-fit on F^2	0.930
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0358$, $wR_2 = 0.0967$
R indices (all data)	$R_1 = 0.0907$, $wR_2 = 0.2309$
Largest difference peak and hole (e Å^{-3})	0.455 and −0.412

distorted square-planar environment of donor atoms around the nickel(II) cation. The structure of $[Ni(Pr^ixa)_2(PPh_3)]$ is built up of discrete molecules without any intermolecular interactions. Selected interatomic parameters are listed in Table 4. From the structure determination it is obvious that one of the two isopropylxanthate groups is bonded to the nickel cation through the S(3) atom as a monodentate ligand. The distances of atoms bonded to the nickel are: Ni—S(1) 2.2082(13), Ni(1)—S(2) 2.2588(14), Ni(1)—S(3) 2.2382(13) and Ni(1)—P(1) 2.2023(13). The distance between the Ni(1) and S(4) atoms is 2.816(2) Å. This distance is significantly longer than the typical nickel–sulfur bond length which lies in the 2.20–2.52 Å interval for nickel(II) xanthates. For this reason we cannot consider the Ni—S(4) distance to constitute a typical bond, but only for an intramolecular interaction. The distinction in coordination modes of isopropylxanthate ligands is obvious not only from the differences in the Ni—S lengths, but also from the difference in the S(1)—Ni(1)—S(2) and S(3)—Ni(1)—S(4) angles. The values of these angles differ significantly and were found to be 78.18(4) and 70.49(4)°, respectively.

The Ni(1)—S(4) interatomic length is also significantly longer than the corresponding distances found in $[Ni(Hex^cxa)_2(PMePh_2)]$ [4] and $[Ni(Etxa)_2(PPh_3)]$ [13], where the distances are 2.7223(43) and 2.654(2) Å, respectively. Thus, in the structure of $[Ni(Pr^ixa)_2(PPh_3)]$ the S(1), S(2), S(3) and P(1) atoms are directly bonded to the nickel in a distorted square-planar geometry. A degree of deformation in this arrangement is evident from non-equivalent bond lengths and angles in the vicinity of the central atom. We fitted a least-squares plane through the Ni(1), S(1), S(2), S(3) and P(1) atoms. The group of these atoms deviates significantly from planarity [the value of $\Sigma((d/s)^2) = 4976$; the value of χ^2 at 95% probability level for 2 degrees of freedom is 5.99]. The deviations are as follows: −0.113(3), −0.063(3), 0.118(3), −0.045(3) and 0.110(3) Å, respectively. The remaining interatomic parameters found for xanthate anions and triphenylphosphine, respectively, are in agreement with those reported for other related complexes [2,10].

IR spectra of all these complexes (see Table 5) show the characteristic bands for both xanthate anions and phosphine ligands. The observed IR spectra also allow the determination of the coordination modes of the S_2COPr^i group. The strong bands of the C—O—C asymmetric stretching for bidentate coordinated xanthates appeared at 1260–1280 cm^{-1}, while the same vibration is shifted to 1180–1186 cm^{-1} for the monodentate chelated ligand [7]. The last mentioned band was observed for complexes **1**, **2**, **3** and **4**, respectively, which suggests monodentate coordination by the xanthates. The C—O—C symmetric vibrations are observed around 1140 cm^{-1}. The ν(C—S) bands appeared at 620 and 1030 cm^{-1}, respectively. The maxima displayed in the IR spectra of the complexes **2** and **3** at 2240 and 2244 cm^{-1}, respectively, belong to the stretching band of the C≡N group [19]. These

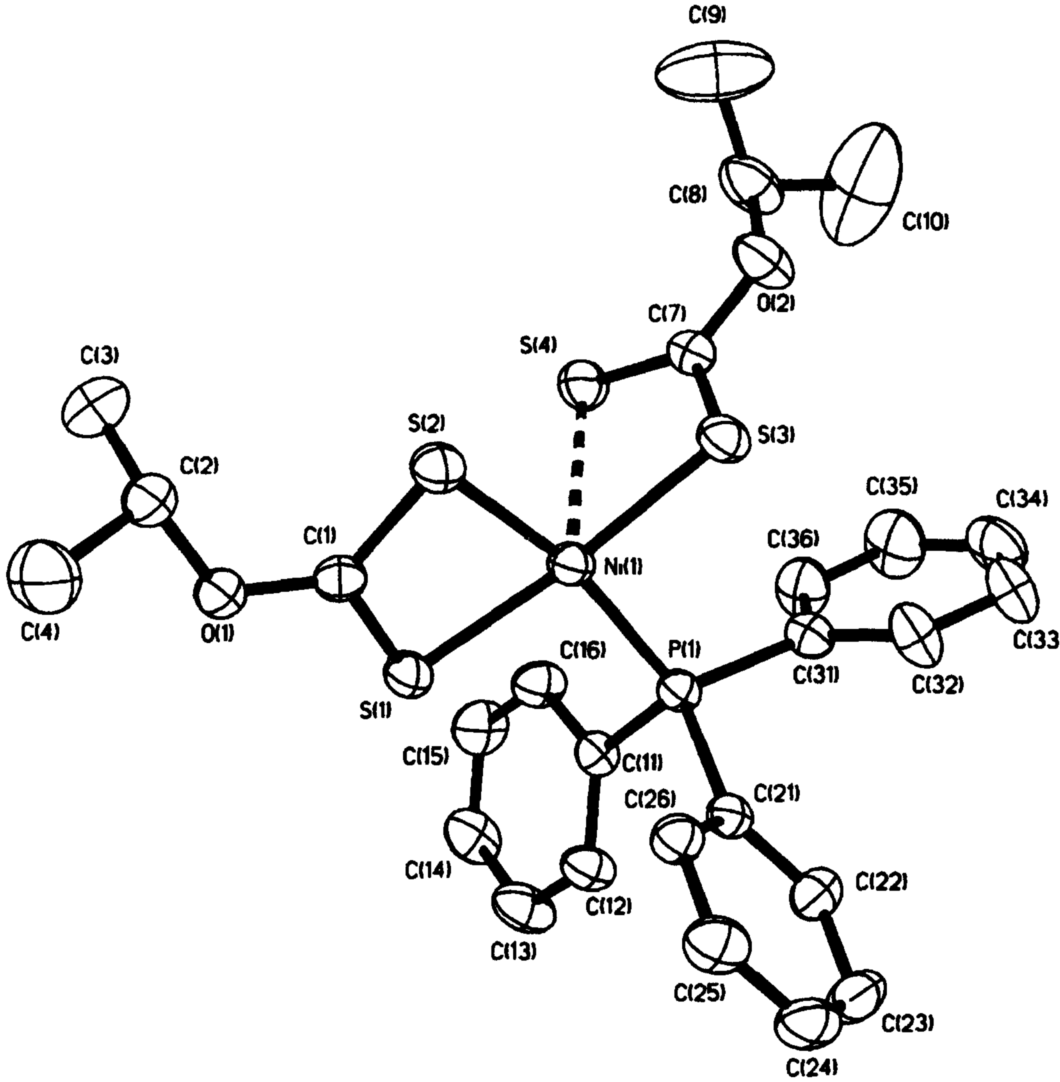

Fig. 1. Molecular structure of $[\mathrm{Ni(Pr^ixa)_2(PPh_3)}]$, showing thermal ellipsoids at the 30% probability level.

Table 2. Colour and analytical data for the new compounds

Compound	Colour	Analysis [Found/(Calcd.)]				
		%C	%H	%S	%N	%X[a]
1, $[\mathrm{Ni(Pr^ixa)_2(PPh_3)}]$	Black	53.2 (52.8)	4.9 (4.9)	21.9 (21.7)	—	—
2, $[\mathrm{NiCl(Pr^ixa)(TCEP)}]$	Violet	36.8 (36.9)	4.6 (4.5)	—	10.2 (9.9)	8.5 (8.4)
3, $[\mathrm{NiBr(Pr^ixa)(TCEP)}]$	Violet	33.5 (33.4)	4.2 (4.1)	—	9.6 (9.0)	17.6 (17.1)
4, $[\mathrm{Ni(Pr^ixa)_2(TRIPHOS)}] \cdot \mathrm{H_2O}$	Light brown	59.8 (60.5)	5.2 (5.7)	13.0 (13.2)	—	—
5, $[\mathrm{Ni(Pr^ixa)(TRIPHOS)}][\mathrm{Ni(Pr^ixa)_3}]$	Brown–red	53.2 (53.4)	5.3 (5.3)	19.2 (20.0)	—	—

[a] $\mathrm{X = Cl^-, Br^-}$.

Table 3. Magnetic, spectroscopic and conductance data for the complexes

Compound	μ_{eff}/μ_B	UV–vis (x 10^3 cm^{-1}) reflections[a]	λ_M^b (S cm^2 mol^{-1})
1, $[Ni(Pr^ixa)_2(PPh_3)]$	dia	20.8 23.8 31.2	11
2, $[NiCl(Pr^ixa)(TCEP)]$	dia	20.6 23.8 31.2	12
3, $[NiBr(Pr^ixa)(TCEP)]$	dia	20.4 23.6 31.2	17
4, $[Ni(Pr^ixa)_2(TRIPHOS)] \cdot H_2O$	dia	22.5 30.2	16
5, $[Ni(Pr^ixa)(TRIPHOS)][Ni(Pr^ixa)_3]$	3.40	12.1 21.3 30.8	117

[a] Measured using the Nujol technique.

[b] Measured in acetonitrile.

Table 4. Selected bond lengths (Å) and angles (°) for $[Ni(Pr^ixa)_2(PPh_3)]$

Ni(1)—P(1)	2.2023 (13)	O(1)—C(1)	1.321 (4)
Ni(1)—S(1)	2.2282 (13)	O(1)—C(2)	1.490 (4)
Ni(1)—S(2)	2.2588 (14)	C(2)—C(4)	1.505 (5)
Ni(1)—S(3)	2.2382 (13)	C(2)—C(3)	1.505 (6)
Ni(1)—S(4)	2.816 (2)	S(3)—C(7)	1.713 (3)
S(1)—C(1)	1.699 (3)	S(4)—C(7)	1.673 (3)
S(2)—C(1)	1.697 (3)	O(2)—C(7)	1.339 (4)
P(1)—C(21)	1.835 (3)	O(2)—C(8)	1.481 (5)
P(1)—C(11)	1.844 (3)	C(8)—C(9)	1.451 (9)
P(1)—C(31)	1.845 (3)	C(8)—C(10)	1.477 (9)
P(1)—Ni(1)—S(1)	92.83 (4)	O(1)—C(1)—S(1)	119.7 (2)
P(1)—Ni(1)—S(3)	95.25 (5)	S(2)—C(1)—S(1)	112.8 (2)
S(1)—Ni(1)—S(3)	171.05 (4)	O(1)—C(2)—O(4)	105.8 (3)
P(1)—Ni(1)—S(2)	165.41 (3)	O(1)—C(2)—C(3)	107.1 (3)
S(1)—Ni(1)—S(2)	78.18 (4)	C(4)—C(2)—C(3)	112.8 (4)
S(3)—Ni(1)—S(2)	93.12 (5)	C(7)—S(3)—Ni(1)	92.81 (11)
P(1)—Ni(1)—S(4)	97.78 (5)	C(7)—S(4)—Ni(1)	75.20 (11)
S(1)—Ni(1)—S(4)	112.21 (4)	C(7)—O(2)—C(8)	121.1 (3)
S(3)—Ni(1)—S(4)	70.49 (4)	O(2)—C(7)—S(4)	125.7 (2)
S(2)—Ni(1)—S(4)	96.27 (5)	O(2)—C(7)—S(3)	112.8 (2)
C(1)—S(1)—Ni(1)	84.94 (11)	S(4)—C(7)—S(3)	121.5 (2)
C(1)—S(2)—Ni(1)	84.04 (11)	C(9)—C(8)—C(10)	114.1 (7)
C(1)—O(1)—C(2)	120.4 (3)	C(9)—C(8)—O(2)	107.5 (5)
O(1)—C(1)—S(2)	127.5 (2)	C(10)—C(8)—O(2)	106.6 (4)

values indicate that the cyanoethyl groups do not interact with the central nickel ion and the nickel centres of adjacent molecules, respectively. Thus, tris(2-cyanoethyl)phosphine is bonded to the nickel only through the phosphorus atom. The bands exhibited at 740, 690 and 660 cm^{-1} are assigned to P—C stretching modes of the same ligand [19]. The strong absorption bands of **1**, **4** and **5** at 1434–1436 cm^{-1}

Table 5. Selected IR spectral data (cm^{-1}; in KBr discs) for the complexes

Compound	ν_{as}(C—O—C)	ν_s(C—O—C)	ν(C—O)	ν(C—S)	ν(C≡N)	ν(P—C$_{Phenyl}$)	ν(P—C)[a]
1, [Ni(Pr^{i}xa)$_2$(PPh$_3$)]	1278vs 1183m sh	1143w	1087vs	1025s 639m	—	1436s	—
2, [NiCl(Pr^{i}xa)(TCEP)]	1280s 1180m sh	1142s	1084s	1026m 620m	2240s	—	740s sh 690w 654w
3, [NiBr(Pr^{i}xa)(TCEP)]	1278s 1180m	1152s	1084s	1032s 620m	2244s	—	736s sh 690w 660w
4, [Ni(Pr^{i}xa)$_2$(TRIPHOS)] · H$_2$O	1186m	—	1094vs	1030s 622w	—	1434s	—
5, [Ni(Pr^{i}xa)(TRIPHOS)][Ni(pr^{i}xa)$_3$]	1262vs	1140m	1094vs	1045s 622w	—	1434s	—

[a] Stretching modes in TCEP.

are assignable to ν(P—C$_{Phenyl}$). The IR spectra of the complexes **2**, **3**, **4** and **5** exhibit weak shoulders at 2810–2820 cm^{-1}, which are connected with the CH$_2$ stretch band observed in the case of the phosphorus attached to the CH$_2$ group [20]. The presence of a water molecule in the complex **4** is supported by the existence of bending vibration at 1688 cm^{-1} and stretching vibrations in the 3540–3480 cm^{-1} region.

All complexes, except **5**, are diamagnetic and behave as non-electrolytes in acetonitrile solutions ([Ni^{2+}] = 1×10^{-3} mol dm^{-3}). The magnetic moment of the [Ni(Pr^{i}xa)(TRIPHOS)][[Ni(Pr^{i}xa)$_3$] complex is 3.40 BM. The value of its molar conductance in acetonitrile indicates that the complex behaves as an electrolyte of the 1 : 1 type. From the literature it is known that for this type of electrolyte the λ_M value should lie in the 120–160 S cm^2 mol^{-1} interval [21]. The somewhat lower molar conductance found for complex **5** (λ_M = 117 S cm^2 mol^{-1}) can be explained as a consequence of the incomplete dissociation of this compound in the solvent used. An arrangement of donor atoms in the vicinity of the nickel atom in the [Ni(Pr^{i}xa)(TRIPHOS)][Ni(Pr^{i}xa)$_3$] complex can be derived not only from the above-mentioned results, but also on the basis of similarity with the structure of [Ni(Hex^{c}xa)(TRIPH)][Ni(Hex^{c}xa)$_3$]. Thus, we suppose that the structure consists of five coordinated [Ni(Pr^{i}xa)(TRIPHOS)]$^+$ cations, in which the nickel atom is surrounded by two sulfur atoms from xanthate and by three phosphorus's from the TRIPHOS, together with six coordinated [Ni(Pr^{i}xa)$_3$]$^-$ anion.

The maxima observed in the electronic diffuse-reflectance spectra of all complexes are given in Table 3. The intense absorption bands appearing in the UV region can be assigned to the CT or $\pi \rightarrow \pi^*$ transitions, while the maxima displayed in the visible region are connected with the *d*–*d* transitions [22]. On the basis of the similarity of the IR and diffuse reflectance spectra, magnetic and conductivity data for the complexes with TCEP we assume that the structure of these complexes is very close to that determined for [Ni(Pr^{i}xa)$_2$(PPh$_3$)], i.e. square-planar. The absorption bands observed in electronic spectra of these complexes in the 20,800–20,400 and 23,800–23,600 cm^{-1} ranges may probably be attributed to the $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively [22]. In the diffuse-reflectance spectrum of [Ni(Pr^{i}xa)$_2$(TRIPHOS)] · H$_2$O only one *d*–*d* band was recorded at 22,500 cm^{-1}. We suppose that the nickel atom in complex **4** is five-coordinated by three phosphorus atoms from TRIPHOS and by two sulfur atoms from two monodentately coordinated isopropylxanthate ligands and thus the central atom has distorted trigonal bipyramidal geometry. Conclusions about coordination geometry in [Ni(Pr^{i}xa)$_2$(TRIPHOS)] · H$_2$O are also supported by the IR spectrum, which exhibits bands characteristic of monodentate xanthates (see Table 5). The presence of a non-coordinated water molecule in this complex was also proved by means of thermal analysis. The compound starts to decompose at 70°C. The first step of the decay is connected with the loss of a water molecule showing on the TG curve by a decrease in sample weight [1.9%/(1.8%); found/(calc.)]. The sample is further decomposed in the three stages without the formation of thermally stable intermediates. A plateau occurred in the 500–740° region. An intermediate in this temperature interval was not identified but we suppose that it is connected with the formation of a NiO/NiSO$_4$ mixture likely in the case of bis(isopropylxanthato)nickel(II) nitrogen base adducts [23]. The decomposition is not finished even at 900°C.

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