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REACTIONS OF BIS(ISOPROPYLXANTHATO)NICKEL(II) WITH NITROGEN-DONOR LIGANDS—II

ZDENĚK TRÁVNÍČEK,* RICHARD PASTOREK, ZDENĚK ŠINDELÁŘ
and ROMAN KLIČKA

Department of Inorganic and Physical Chemistry, Palacký University,
Křížkovského 10, 771 47 Olomouc, Czech Republic

and

JAROMÍR MAREK

Department of Inorganic Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno,
Czech Republic

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Abstract—New complexes of bivalent nickel with isopropylxanthates and nitrogen-donor ligands of composition $[Ni(Pr^ixa)_2(L)]$, $[Ni(Pr^ixa)_2(L^1)_2]$, $[Ni(L^2)_2](Pr^ixa)_2$, and $[Ni(L^3)_3](Pr^ixa)_2$ have been synthesized, where $Pr^ixa = i\text{-}C_3H_7OCS_2^-$, L = 1,2-diaminopropane (1,2-pn), *N,N,N′,N′*-tetramethylethylenediamine (tmen) or 4,4′-bipyridine (4,4′-bipy), L^1 = pyridine (py), L^2 = diethylenetriamine (dien) and L^3 = ethylenediamine (en), 1,2-diaminopropane or 1,10-phenanthroline (phen). The compounds have been characterized by elemental analysis, IR and UV–vis spectroscopy, magnetochemical measurements, molar conductivity and thermal analysis. The compounds containing the complex cation have been one-electron irreversibly oxidized using cyclic voltammetry. The crystal and molecular structures of $[Ni(Pr^ixa)_2(tmen)]$ and $[Ni(phen)_3](Pr^ixa)_2$ have been elucidated.

It is known from the literature that diamagnetic square-planar complexes of composition $[Ni(Rxa)_2]$ (R = alkyl, aryl; xa = xanthate) react easily with monodentate (in the molar ratio 1 : 2) or bidentate nitrogen-donor ligands (in the molar ratio 1 : 1) and afford octahedral nickel(II) complexes.[1–5] Xanthate ligands are coordinated to the nickel atom as monodentate sulphur ligands or bidentate S,S′-ligands for all the above-mentioned compounds. This fact follows from results of X-ray analyses.[6] Nickel(II) complexes containing xanthate anions outside the coordination sphere of nickel have not yet been synthesized. Preparation and physicochemical study of compounds of this type is the subject of this work. This paper also reports the continuation of the systematic study of the reactions of bis(isopropylxanthato)nickel(II) with nitrogen-, phosphorus- or sulphur-donor ligands at our department.[5,7]

EXPERIMENTAL

Preparation of $[Ni(Pr^ixa)_2]$

The starting $[Ni(Pr^ixa)_2]$ complex was prepared according to the method reported in the literature.[8]

Preparation of $[Ni(Pr^ixa)_2(py)_2]$

Pyridine (2.5 mmol) was added to a solution of $[Ni(Pr^ixa)_2]$ (1 mmol) in $CHCl_3$ (10 cm^3). The solution was left standing at room temperature until green microcrystals were obtained. They were

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*Author to whom correspondence should be addressed.

filtered off, washed with petroleum ether and dried in a vacuum desiccator.

Preparation of $[Ni(Pr^ixa)_2(4,4'\text{-bipy})]_n$

This green compound was obtained through an analogous procedure to that described in the literature[9] for $[Ni(Bu^nxa)_2(4,4'\text{-bipy})\cdot 2CCl_4]_n$ (where $Bu^nxa = n\text{-}C_4H_9OCS_2^-$).

Preparation of $[Ni(Pr^ixa)_2(1,2\text{-pn})]$ *and* $[Ni(Pr^ixa)_2(tmen)]$

Ligand (2 mmol) was added while stirring to a mixture of $[Ni(Pr^ixa)_2]$ (2 mmol) in EtOH (10 cm^3) and in both cases a green powder was immediately formed. The powder was separated by filtration, washed with EtOH and Et_2O and dried under an IR lamp at 40°C. Green crystals suitable for X-ray analysis were obtained from the filtrate by standing overnight.

Preparation of $[Ni(dien)_2](Pr^ixa)_2$

Diethylenetriamine (2.2 mmol) was added to a solution of the starting complex (1 mmol) in EtOH (20 cm^3). The reaction solution was stirred until a pale violet powder was formed. This was filtered off, washed with EtOH and Et_2O and dried under an IR lamp.

Preparation of $[Ni(en)_3](Pr^ixa)_2$ *and* $[Ni(1,2\text{-pn})_3](Pr^ixa)_2$

A solution of $[Ni(Pr^ixa)_2]$ (1 mmol) in $CHCl_3$ (5 cm^3) was added to a solution of ligand (3 mmol) in EtOH (5 cm^3). After stirring for a few minutes a pale violet powder was obtained. The reaction mixture was further stirred for 2 h. The powder was collected by filtration, washed with small amounts of EtOH and Et_2O and dried under an IR lamp.

Preparation of $[Ni(phen)_3](Pr^ixa)_2$

A solution of $[Ni(Pr^ixa)_2]$ (2 mmol) in acetone (5 cm^3) was added to a solution of 1,10-phenanthroline (6.2 mmol) in the same solvent (10 cm^3). The reaction mixture was stirred for 1 h and a small amount of yellow–brown substance was obtained. This was filtered off and orange crystals were formed by spontaneous evaporation of solvent from the filtrate. They were collected by filtration, washed with a small amount of Et_2O and dried under an IR lamp.

General methods

All the chemicals used were of p.a. purity and were supplied by Lachema Brno Co. or Fluka Co.

The carbon, hydrogen, nitrogen and sulphur analyses were determined on an EA1108 instrument (Fisons). IR spectra were measured on a Specord M80 (Carl Zeiss, Jena) using Nujol mulls within the region $v = 4000\text{–}400\ cm^{-1}$. Diffuse reflectance spectra in the solid state (in the 40,000–11,100 cm^{-1} range) were recorded on a Specord M40 (Carl Zeiss, Jena). Magnetic susceptibilities were measured at laboratory temperature using the Faraday method with $Hg[Co(NCS)_4]$ as a calibrant. The correction for diamagnetism of the constituent atoms was calculated using Pascal's constants.[10] The molar conductivities Λ_m were measured on a Conductivity Meter OK 102/1 (Radelkis, Budapest) at 25°C in DMFA. Thermal decomposition was studied with a Q 1500 D Derivatograph (MOM Budapest) with a sample weight of 100–120 mg over the temperature range 20–900°C and temperature increase of 2.5°C min^{-1}.

The electrochemical measurements were carried out on a Polarographic Analyser PA4 (Laboratorní přístroje, Praha) in a three-electrode arrangement with platinum as working electrode (surface area 0.32 cm^2), platinum foil with a large surface area and the potentials referenced to the saturated calomel electrode (SCE). The measurements were performed in the polarization range 0.0 to +1.2 V in DMFA in the presence of $KClO_4$ (0.05 mol dm^{-3}) as supporting electrolyte and with concentration of the complexes 8×10^{-5} mol dm^{-3}. The polarization scan rate varied from 0.01 to 0.1 V s^{-1}.

Determination of the structures of $[Ni(Pr^ixa)_2(tmen)]$ *and* $[Ni(phen)_3](Pr^ixa)_2$

The diffraction experiments were performed on a KUMA KM-4 diffractometer at laboratory temperature using graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystals suitable for X-ray analyses of both compounds were obtained directly from the reaction mixture. The structures were solved by the heavy-atom method. The hydrogen atoms of both structures were positioned theoretically and all their parameters were left free for refinement. Refinements of both structures were based on F^2. The weighted R-factor, R_w, and all goodnesses-of-fit S were based on F^2. The conventional R-factor, R, was based on F. The

Table 1. Crystal data and structure refinement for [Ni(Pr^{i}xa)$_2$(tmen)] (**A**) and [Ni(phen)$_3$] (Pr^{i}xa)$_2$ (**B**)

	A	**B**
Empirical formula	$C_{14}H_{30}N_2NiO_2S_4$	$C_{44}H_{38}N_6NiO_2S_4$
Formula weight	445.35	869.75
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$C2/c$
Unit cell dimensions (Å, °)	$a = 9.342(2)$, $\alpha = 90$ $b = 15.098(3)$, $\beta = 90$ $c = 15.996(3)$, $\gamma = 90$	$a = 23.423(5)$, $\alpha = 90$ $b = 11.852(2)$, $\beta = 128.55(3)$ $c = 18.667(4)$, $\gamma = 90$
Volume (Å^3)	2256.2(8)	4052.8(14)
Z	4	4
Density ($D_{X\text{-ray}}/D_m$), (Mg m^{-3})	1.311/1.32	1.425/1.44
Absorption coefficient (mm^{-1})	1.238	0.731
$F(000)$	944	1808
Reflections collected	3844	3590
Independent reflections	3418 ($R_{int} = 0.0339$)	3481 ($R_{int} = 0.0400$)
Data/parameters	3418/329	3481/334
$S_{obs/all}$	1.033/1.006	1.090/1.005
R_{obs} [$I > 2\sigma(I)$]	$R = 0.0332$, $R_w = 0.0862$	$R = 0.0330$, $R_w = 0.0901$
R_{all}	$R = 0.0488$, $R_w = 0.0915$	$R = 0.0737$, $R_w = 0.1049$

calculations were performed using the programs SHELXS-86[11] and SHELXL-93[12] on PC AT 486 and IBM RS/6000 980F.

The experimental density of crystals of [Ni (Pr^{i}xa)$_2$(tmen)] was estimated by the flotation method under an aqueous solution of KI at 20°C. The dimensions of the crystal for data collection were $0.60 \times 0.50 \times 0.20$ mm^3. The unit-cell parameters were obtained from 50 reflections in the range of $24.6 < 2\theta < 32.8°$. Data were measured using ω–2θ scan techniques within the $5.4 < 2\theta < 50.5°$ region. A total of 3844 reflections were measured, of which 2924 [on the basis of the condition $I > 2\sigma(I)$] were retained for structure determination and refinement. Index ranges: $0 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 9$. Three standard reflections (4 4 −3, 2 −7 −5, −2 1 8) were checked after every 70 measurements; no significant change of their intensities was detected. The data were corrected for absorption effects. We applied an empirical absorption procedure DIFABS ($T_{min} = 0.293$; $T_{max} = 1.000$). The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure with weight $w = 1/[\sigma^2(F_0{}^2)+(0.0504P)^2+0.6107P]$, where $P = (F_0{}^2+2F_c{}^2)/3$. The maximum and minimum electron densities on the final differential Fourier map were 0.284 and −0.398 e Å^{-3}. The structure was solved as an absolute structure with the Flack absolute structure parameter[13] 0.36(2).

The experimental density of the crystals of [Ni(phen)$_3$](Pr^{i}xa)$_2$ was determined pycnometrically in a $CHCl_3$–CH_2Cl_2 mixture. A crystal of dimensions $0.50 \times 0.20 \times 0.10$ mm^3 was used for data collection. Final values of the lattice parameters were determined from 50 reflections in the $25.1 < 2\theta < 36.8°$ region. Intensities were measured within the $4.1 < 2\theta < 50.6°$ region, using ω–2θ scans. Index ranges: $-25 \leqslant h \leqslant 22$, $-8 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 20$. The crystal stability during the data collection was checked by measuring three standard reflections (3 5 −3, 3 1 5, −12 2 7) after every 70 measurements. Extinction and absorption effects were ignored. The structure was anisotropically refined by the full-matrix least-squares procedure with weight $w = 1/[\sigma^2(F_0{}^2)^2+(0.0560P)^2+0.0673P]$, where $P = (F_0{}^2+2F_c{}^2)/3$. Largest differences in the peak and hole were 0.264 and −0.427 e Å^{-3}.

Crystal data and refinement parameters are given in Table 1. The structures are shown in Figs 1 and 2.

RESULTS AND DISCUSSION

Chemical composition of the newly prepared compounds and results of physicochemical study are given in Tables 2 and 3.

The magnetic moments of these nickel(II) complexes are characteristic for octahedral coordination.[10] The μ_{eff} values vary in the range of 3.12–3.46 B.M. The assignment of octahedral geometries is also supported by the electronic absorption spectra,[14] where absorption maxima of *d*–*d* transitions are observed at 15,400–16,100 cm^{-1} [$^3A_{2g} \rightarrow {}^3T_{1g}(F)$], at 20,400–20,800 cm^{-1} ($^3A_{2g} \rightarrow {}^1T_{1g}$) and 23,200–23,800 cm^{-1} [$^3A_{2g} \rightarrow {}^3T_{1g}(P)$] for complexes **I**–**IV**. The maxima at 18,900–20,400 cm^{-1} and 23,200–25,600 cm^{-1} were assigned to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions for complexes **V**–**VIII**. The very intense bands in the range of 30,300–32,200 cm^1 are ascribed to charge-transfer transitions[15] (the same authors claim that they can be connected with the $\pi \rightarrow \pi^*$ transition[16]).

The IR spectra of the compounds contain bands characteristic for nickel(II) xanthates. Their assignment is obvious from Table 2. Bands attributed to the ν_{as}(C—O—C) vibration appear in the region 1204–1264 cm^{-1} for complexes **I**–**IV**, while the same vibration was observed at 1180–1184 cm^{-1} for complexes **V**–**VIII**. This shift may be due to a change of coordination of the isopropylxanthate anion.[17]

Complexes **I**–**IV** behave as non-electrolytes in DMFA. The values of molar conductivity for complexes **V**–**VIII** (85.2–112.4 S cm^2 mol^{-1}) are considerably lower than the values corresponding to electrolytes of the 1 : 2 type (130–170 S cm^2 mol^{-1})

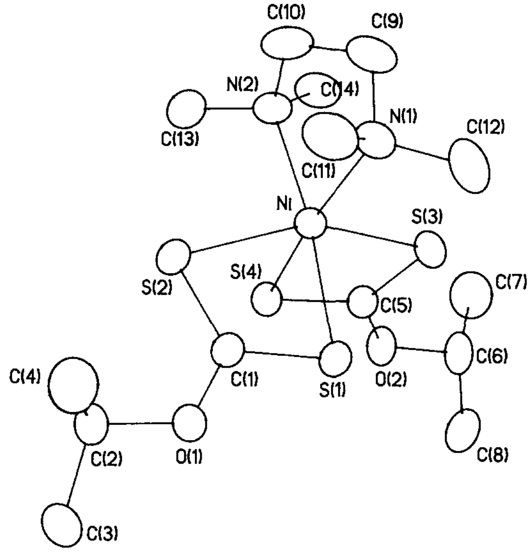

Fig. 1. A view of the molecule of $[\mathrm{Ni(Pr^ixa)_2(tmen)}]$. The non-hydrogen atoms are shown as thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for the sake of clarity.

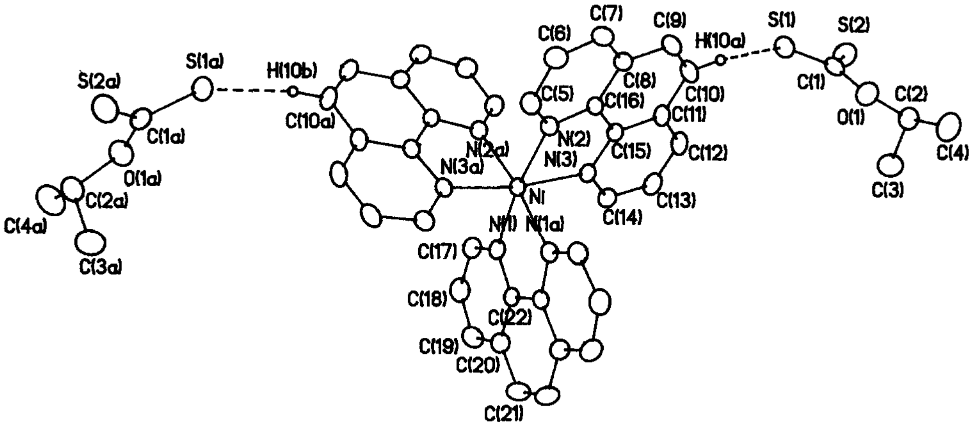

Fig. 2. Representation of $[\mathrm{Ni(phen)_3}](\mathrm{Pr^ixa})_2$ with thermal ellipsoids drawn at the 30% probability level. Most of the H atoms are omitted for clarity. Dashed lines indicate the hydrogen bonding.

Table 2. Chemical composition of the complexes

		Found (Calc.) (%)			
Compound		C	H	N	S
I	$[\mathrm{Ni(Pr^ixa)_2(py)_2}]$	44.9 (44.4)	4.9 (5.0)	6.0 (5.7)	25.6 (26.3)
II	$[\mathrm{Ni(Pr^ixa)_2(4,4'\text{-}bipy)}]_n$	43.9 (44.6)	4.4 (4.6)	5.5 (5.8)	25.8 (26.4)
III	$[\mathrm{Ni(Pr^ixa)_2(1,2\text{-}pn)}]$	32.1 (32.8)	5.7 (6.0)	6.4 (6.9)	31.2 (31.8)
IV	$[\mathrm{Ni(Pr^ixa)_2(tmen)}]$	37.8 (37.8)	6.8 (6.8)	6.4 (6.3)	27.9 (28.8)
V	$[\mathrm{Ni(dien)_2}](\mathrm{Pr^ixa})_2$	35.4 (35.9)	7.5 (7.5)	15.7 (15.7)	23.4 (23.9)
VI	$[\mathrm{Ni(en)_3}](\mathrm{Pr^ixa})_2$	33.1 (33.0)	7.6 (7.5)	16.9 (16.5)	24.8 (25.2)
VII	$[\mathrm{Ni(1,2\text{-}pn)_3}](\mathrm{Pr^ixa})_2$	37.0 (37.0)	8.1 (8.0)	15.2 (15.2)	23.1 (23.2)
VIII	$[\mathrm{Ni(phen)_3}](\mathrm{Pr^ixa})_2$	60.3 (60.8)	4.3 (3.7)	9.6 (9.7)	14.1 (14.7)

Table 3. The physicochemical properties of the complexes

Compound	μ_{eff}/μ_B	Λ_m[a] (S cm^2 mol^{-1})	IR (cm^{-1}) ν_{as}(C—O—C)	ν_s(C—O—C)	ν(C—S)	UV–vis[b] ($\times 10^3$ cm^{-1})	E_p^a (V)	T_s[c]	Thermal analysis (°C) plateau
I	3.13	17.9	1264s	1140m	630m 1036s	15.5 20.6 23.8 30.3	—	80	480–680
II	3.23	16.1	1260s	1144s	632s 1044s	15.4 20.4 23.8 31.2	—	80	470–670
III	3.46	14.4	1204s	1142s	630w 1040s	16.1 20.8 23.2 31.2	—	100	460–640
IV	3.12	4.7	1208s sh	1144m	655w 1034s	15.4 20.8 23.2 31.2	—	130	510–670
V	3.15	89.2	1184s	1144s	634m 1036s	20.4 23.8 32.2	0.35	130	520–695
VI	3.14	85.2	1182m	1146m	664w 1040s	20.4 25.3 31.2	0.31	130	520–705
VII	3.16	78.6	1184m	1146m	650m 1026s	18.9 25.6 31.5	0.33	120	515–690
VIII	3.24	112.4	1180m	1144m	644w 1030	23.8 31.2	0.36	160	500–780

[a] Measured in DMFA.

[b] Measured using the Nujol technique.

[c] The beginning of thermal decomposition.

E_p^a, potentials of anodic peaks corresponding to one-electron irreversible oxidation.

Table 4. Bond lengths (Å) and selected angles (°) for $[\mathrm{Ni(Pr^ixa)_2(tmen)}]$

Ni—N(1)	2.189(4)	N(2)—Ni—N(1)	83.9(2)
Ni—N(2)	2.183(4)	S(1)—Ni—S(2)	72.82(4)
Ni—S(1)	2.4525(12)	S(4)—Ni—S(3)	72.86(4)
Ni—S(2)	2.4932(12)	C(1)—S(1)—Ni	84.07(14)
Ni—S(3)	2.4917(13)	C(1)—S(2)—Ni	83.01(14)
Ni—S(4)	2.4554(12)	C(5)—S(3)—Ni	83.0(2)
S(1)—C(1)	1.702(4)	C(5)—S(4)—Ni	84.3(2)
S(2)—C(1)	1.691(4)	C(11)—N(1)—C(12)	108.0(6)
S(3)—C(5)	1.708(4)	C(9)—N(1)—Ni	104.0(3)
S(4)—C(5)	1.697(4)	C(13)—N(2)—C(14)	106.8(5)
N(1)—C(11)	1.479(8)	C(10)—N(2)—Ni	104.6(3)
N(1)—C(12)	1.495(8)	C(1)—O(1)—C(2)	120.8(3)
N(1)—C(9)	1.505(8)	C(5)—O(2)—C(6)	121.7(3)
N(2)—C(10)	1.480(7)	O(1)—C(1)—S(2)	124.4(3)
N(2)—C(13)	1.485(8)	O(1)—C(1)—S(1)	115.8(3)
N(2)—C(14)	1.496(7)	S(2)—C(1)—S(1)	119.8(2)
O(1)—C(1)	1.346(5)	O(1)—C(2)—C(4)	109.2(5)
O(1)—C(2)	1.480(5)	O(1)—C(2)—C(3)	104.8(4)
O(2)—C(5)	1.338(5)	C(4)—C(2)—C(3)	113.6(5)
O(2)—C(6)	1.483(5)	O(2)—C(5)—S(4)	116.5(3)
C(2)—C(4)	1.499(8)	O(2)—C(5)—S(3)	124.1(3)
C(2)—C(3)	1.533(7)	S(4)—C(5)—S(3)	119.3(2)
C(6)—C(7)	1.481(10)	O(2)—C(6)—C(7)	109.7(6)
C(6)—C(8)	1.522(9)	O(2)—C(6)—C(8)	104.9(5)
C(9)—C(10)	1.507(10)	C(7)—C(6)—C(8)	114.0(6)
		N(1)—C(9)—C(10)	110.8(5)
		N(2)—C(10)—C(9)	111.2(5)

in the same solvent.[18] Lowering of the values of Λ_m can be explained as a consequence of the existence of very weak hydrogen bonds. This assumption is supported by the results of X-ray analysis of $[\mathrm{Ni(phen)_3}](\mathrm{Pr^ixa})_2$ as the model complex, where the following hydrogen bonds were observed: C(10)—H(10a)···S(1) 3.785(3) Å [the S···H distance is equal to 2.85(3) Å] and C(10a)—H(10b)···S(1a) 3.785(3) Å [the S···H distance is equal to 2.85(3) Å] (see Fig. 2). Similar intermolecular hydrogen contacts between the sulphur and hydrogen atoms were also found by Newman *et al.*[19]

Anodic peaks occurring on the cyclic voltammograms of all the complexes in the 0.20–0.25 V region are connected with oxidation of the xanthate ligand.[20] One-electron irreversible oxidation of the central atom was observed at 0.31–0.36 V for complexes **V**–**VIII**. No anodic peak was observed in the above-mentioned region for the remaining complexes (**I**–**IV**). Other anodic peaks at the potentials of 0.85 and 0.90 V were found for compounds **V** and **VII**, but their current densities attained only 40% of the value corresponding to a one-electron oxidation.

It was found from thermograms that the thermal decomposition of all compounds occurs in a few steps to about 480°C without thermally stable intermediates. Plateaux occur in the interval of 460–780°C (see Table 2) and are connected with the formation of a mixture of NiO and $\mathrm{NiSO_4}$ as intermediates. The existence of these by-products was proved using X-ray powder diffraction. The decomposition was not complete, even at 900°C.

Crystallographic discussion

The X-ray structural analyses of both $[\mathrm{Ni(Pr^ixa)_2(tmen)}]$ (**A**) and $[\mathrm{Ni(phen)_3}](\mathrm{Pr^ixa})_2$ (**B**) reveal an octahedral environment of ligands around the nickel (see Tables 4 and 5). A degree of deformation of the coordination sphere of the *cis*-octahedral complex $[\mathrm{Ni(Pr^ixa)_2(tmen)}]$ is greater than in $[\mathrm{Ni(phen)_3}](\mathrm{Pr^ixa})_2$, where the presence of the $\mathrm{NiN_6}$ chromophore was proved. This results from the difference of the Ni—N bond lengths owing to the Ni—S bond lengths (Table 4). We observed a similar phenomenon in our previous work[5] on *cis*-$[\mathrm{Ni(Pr^ixa)_2(phen)}]$ and *trans*-$[\mathrm{Ni(Pr^ixa)_2(btz)_2}]$ complexes (btz = benzothiazole). In both structures a typical shortening of the C(1)—O(1) bonds in relation to the C(2)—O(1) bonds was observed.[5–7,21]

Table 5. Selected bond lengths (Å) and angles (°) for $[Ni(phen)_3](Pr^ixa)_2$

Vicinity of the central atom			
Ni—N(1)	2.089(2)	N(1)—Ni—N(1)[a]	79.55(12)
Ni—N(2)	2.107(2)	N(3)—Ni—N(2)	79.52(8)
Ni—N(3)	2.091(2)	N(1)—Ni—N(2)	172.96(8)
		N(3)[a]—Ni—N(3)	170.14(11)
Isopropylxanthate anion			
S(1)—C(1)	1.699(3)	C(1)—O(1)—C(2)	121.0(2)
S(2)—C(1)	1.666(3)	O(1)—C(1)—S(2)	121.5(2)
O(1)—C(1)	1.363(4)	O(1)—C(1)—S(1)	112.5(2)
O(1)—C(2)	1.460(4)	S(1)—C(1)—S(2)	126.0(2)
C(2)—C(3)	1.496(5)	O(1)—C(2)—C(3)	109.4(3)
C(2)—C(4)	1.502(6)	O(1)—C(2)—C(4)	105.7(3)
		C(3)—C(2)—C(4)	113.1(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x+1, y, -z+1/2$.

In the $[Ni(phen)_3](Pr^ixa)_2$ complex the xanthate anions are not coordinated to the nickel and are thus considered to be ionic. This has not been observed in xanthate complexes of nickel before.

REFERENCES

1. D. Coucouvanis and J. P. Fackler Jr, *Inorg. Chem.* 1967, **6**, 2047.
2. A. G. Krüger and G. Winter, *Aust. J. Chem.* 1971, **24**, 161.
3. A. I. Prisyazhnyuk, I. I. Seifulina and A. P. Martinenko, *Koord. Khim.* 1989, **15**, 1359.
4. R. L. Ballester, M. E. C. Gonzales, A. A. Guttierrez and M. F. V. Perpinan, *An. Quim.* 1991, **87**, 1016.
5. Z. Trávníček, R. Pastorek, Z. Šindelář and J. Marek, *Transition Met. Chem.* 1994, **19**, in press.
6. E. R. T. Tiekink and G. Winter, *Rev. Inorg. Chem.* 1992, **12**, 211.
7. R. Pastorek, Z. Trávniček, Z. Šindelář, R. Klička, F. Březina and J. Marek, *Polyhedron* 1995, in press.
8. *Gmelins Handbuch der Anorganischen Chemie, Nickel*, Teil C, Lief. 2, p. 985. Verlag Chemie, Weinheim (1969).
9. R. W. Gable, B. F. Hoskins and G. Winter, *Inorg. Chim. Acta* 1985, **96**, 151.
10. E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds.* Springer, Berlin (1966).
11. G. M. Sheldrick, SHELXS-86, *Acta Cryst.* 1990, **A46**, 467.
12. G. M. Sheldrick, SHELXL-93, *J. Appl. Cryst.* 1994, in preparation.
13. H. D. Flack, *Acta Cryst.* 1983, **A39**, 876.
14. A. B. P. Lever, *Inorganic Electron Spectroscopy*, p. 334. Elsevier, Amsterdam (1968).
15. A. A. M. Aly, M. S. El-Meligy, A. S. A. Zidan and M. El-Shabasy, *Synth. React. Inorg. Met.-Org. Chem.* 1987, **17**, 257 and refs therein.
16. A. A. M. Aly, M. M. Kamal, M. S. El-Meligy and A. I. El-Said, *Croat. Chim. Acta* 1988, **61**, 155.
17. J. Zagal and J. A. Costamagna, *J. Inorg. Nucl. Chem. Lett.* 1977, **13**, 411 and refs therein.
18. W. J. Geary, *Coord. Chem. Rev.* 1971, **7**, 81.
19. P. W. G. Newman, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.* 1973, 1332.
20. S. B. Choudhury, D. Ray and A. Charkavorty, *Inorg. Chem.* 1990, **29**, 4603.
21. Z. Trávníček, R. Pastorek and J. Marek, *Collect. Czech. Chem. Commun.* 1994, **59**, 616.