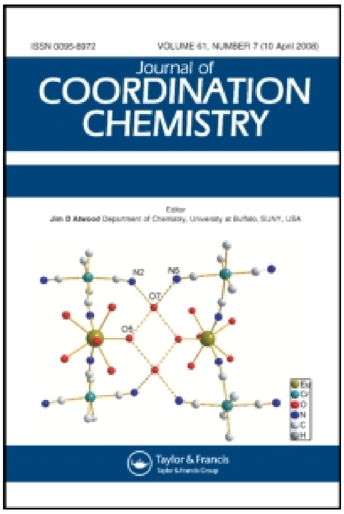

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REACTION OF *BIS*(ISOPROPYLXANTHATO)NICKEL(II) WITH NITROGEN DONOR LIGANDS IV

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The coordination compounds [Ni(*i*-prxa)(L$_1$)] (*i*-prxa) and [Ni(*i*-prxa)$_2$(L$_2$)] (*i*-pr = *i*-C_3H_7, xa = S_2CO^-, L$_1$ = *tris*(2-aminoethyl)amine (*taa*), L$_2$ = N-(2-aminoethyl)-1,3-diaminopropane (*apa*), *bis*(3-aminopropyl)amine (*baa*), 2-(aminomethyl)pyridine (*amp*), 2,2′-dipyridylamine (*dpa*) or 2,2′:6′,2″-terpyridine (*tpy*)) have been synthesized by reaction of *bis*(isopropylxanthato)nickel(II) with the corresponding nitrogen donor ligands. The complexes have been characterized on the basis of analytical data, magnetochemical and conductivity measurements, electronic and infrared spectroscopies as octahedral nickel(II) compounds. The structures of [Ni(*i*-prxa)$_2$(dpa)]•dmso (*1*) and [Ni(*i*-prxa)$_2$(amp)] (*2*) have been determined by a single-crystal X-ray analysis. In both structures nickel is coordinated by four sulfur atoms of two isopropylxanthato ligands and by two nitrogen atoms of the other N-donor ligand. The coordination of donor atoms around nickel in (*1*) and (*2*) is distorted *cis*-octahedral with an S_4N_2 donor set. For (*1*): $C_{20}H_{29}N_3NiO_3S_5$, monoclinic, $P2_1/c$, $a = 11.330(2)$, $b = 14.890(3)$, $c = 16.940(3)$ Å, $\beta = 104.65(3)°$, $V = 2764.9(9)$ Å^3, $Z = 4$, $M_r = 578.5$, $D_{calc} = 1.390$ g/cm^3, $\lambda = 0.71073$ Å, $\mu = 1.104$ mm^{-1}, $F(000) = 1208$, $R = 0.053$, $R_w = 0.131$. For (*2*): $C_{14}H_{22}N_2NiO_2S_4$, monoclinic, $P2_1/c$, $a = 19.395(4)$, $b = 9.977(2)$, $c = 20.305(4)$ Å, $\beta = 98.14(3)°$, $V = 3889.5(14)$ Å^3, $Z = 8$, $M_r = 473.3$, $D_{calc} = 1.494$ g/cm^3, $\lambda = 0.71073$ Å, $\mu = 1.435$ mm^{-1}, $F(000) = 1820$, $R = 0.0527$, $R_w = 0.1432$.

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

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INTRODUCTION

Although nickel(II) xanthate complexes have been known since the early 1800s they are still extensively studied for their possible applications in several branches of industry,[1] as fungicides, insecticides, antioxidants, *etc*. In previous papers we have described and discussed the preparation and a physicochemical study of a number of nickel(II) xanthates with homo- or heteroueneous coordination spheres.[2–7] These compounds were studied mainly by single-crystal X-ray structure analysis and were characterized as square planar or octahedral nickel(II) complexes. This paper represents the continuation of our systematic study of nickel complexes with heterogeneous coordination spheres containing a combination of sulfur and nitrogen ligands. The work is focussed on the study of the reaction products of *bis*(isopropylxanthato)nickel(II) with aliphatic and aromatic amines.

EXPERIMENTAL

The elemental analyses were performed on an EA1108 instrument (Fisons). IR spectra were measured on a Specord M80 (Carl Zeiss, Jena) using the Nujol mull technique in the region 4000–400 cm^{-1}. Solid-state electronic absorption spectra (diffuse-reflectance) of the complexes were recorded on a Specord M40 (Carl Zeiss, Jena) in the region 33 000–11 000 cm^{-1}. The magnetic susceptibilities of the complexes were measured by the Faraday method with $Hg[Co(NCS)_4]$ as calibrant. Corrections for diamagnetism were made using Pascal's constants.[8] Conductivities were measured on an OK 102/1 instrument (Radelkis, Budapest) at 25°C and the concentration of solutions was 1×10^{-3} mol dm^{-3}.

X-ray Crystallographic Analyses

Data were collected on a KUMA KM-4 diffractometer with graphite-monochromated MoK_α radiation (0.71073 Å) using the $\varpi/2\theta$ scan mode. Crystals of $[Ni(i\text{-prxa})_2(dpa)]\cdot dmso$ (*1*) suitable for a single-crystal X-ray analysis were obtained by recrystallization of the substance from dimethyl sulfoxide. Unit cell dimensions were determined from 24 reflections in the range $15.1° < 2\theta < 24.4°$. Three standard reflections (0 0 −2, 0 −2 0, 1 0 0) were monitored after every 300 measurements; no significant changes of intensities were detected. The phase problem was solved by the heavy-atom method (SHELXS-97).[8] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure (SHELXL-97)[9] with weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0654P)^2 + 2.5406P]$, where

$P = (F_o^2 + 2F_c^2)/3$. The H atoms bonded to C7, C8 and C16 were positioned theoretically. Hydrogen atoms of dimethyl sulfoxide were not located. The other hydrogen atom positions were found from difference Fourier maps and all their parameters were refined. Crystals of [Ni(*i*-prxa)$_2$(amp)] (*2*) applicable to X-ray study were obtained by recrystallization from ethanol. Unit cell parameters were obtained from 32 reflections in the range $16.30° < 2\theta < 25.8°$. Three standard reflections (0 0 2, 2 0 0, 0 −4 0) were checked after every 400 measurements; no significant changes of intensities were detected. The data were corrected for absorption effects using an empirical absorption correction involving DIFABS[11] ($T_{min} = 0.301$, $T_{max} = 1.000$). The structure was solved by direct methods (SHELXS-97).[9] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares procedure (SHELXL-97)[10] with weight $w = 1/[\sigma^2(F_o^2) + (0.0995P)^2 + 7.3034P]$, where $P = (F_o^2 + 2F_c^2)/3$. All hydrogen atoms were found from difference Fourier maps. Hydrogen atoms bonded to C7, C8, C17 and C18 were refined using AFIX 137 and their U values were held at 1.5 times the equivalent isotropic U of the above mentioned carbon atoms.

Refinements of both structures were based on F^2. The weighted R factors, R_w, and all goodnesses-of-fit S were based on F^2. The conventional R factor, R, was based on F. The calculations were performed on a PC AT Pentium. Crystal data and structure refinement parameters for both structures are summarized in Table I. Atomic coordinates of non-hydrogen atoms and equivalent isotropic displacement parameters for [Ni(*i*-prxa)$_2$(dpa)]·dmso (*1*) and [Ni(*i*-prxa)$_2$(amp)] (*2*) are given in Tables II and III, respectively. Selected bond lengths and angles are listed in Tables VI and VII. The structures are shown in Figures 1 and 2. Preliminary data for [Ni(*i*-prxa)$_2$(dpa)·dmso were previously published in the literature.[12]

Syntheses

Preparation of [Ni(i-prxa)$_2$]

The complex was obtained according to the procedure described in the literature.[13] Nitrogen donor ligands were supplied from Aldrich Chemical Co. or Fluka Co. and were used without further purification.

Preparation of [Ni(i-prxa)(taa)](i-prxa), [Ni(i-prxa)$_2$(apa)] and [Ni(i-prxa)$_2$(amp)]

An amine (*taa*, *apa* or *amp*) (2 mmol) was added to imperfectly dissolved [Ni(*i*-prxa)$_2$] (2 mmol) in EtOH (15 cm^3). After a few minutes a solid formed.

TABLE I Crystal data and structure refinement details for [Ni(*i*-prxa)$_2$(dpa)]•dmso (*1*) and [Ni(*i*-prxa)$_2$(amp)] (*2*)

	(*1*)	(*2*)
Empirical formula	$C_{20}H_{29}N_3NiO_3S_5$	$C_{14}H_{22}N_2NiO_2S_4$
Formula weight	578.47	437.29
Temperature (K)	293(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)	$a = 11.330(2)$, $\alpha = 90$	$a = 19.395(4)$, $\alpha = 90$
	$b = 14.890(3)$, $\beta = 104.65(3)$	$b = 9.977(2)$, $\beta = 98.14(3)$
	$c = 16.940(3)$, $\gamma = 90$	$c = 20.305(4)$, $\gamma = 90$
Volume (Å)	2764.9(9)	3889.5(14)
Z, Calculated density (Mg m^{-3})	4, 1.390	8, 1.494
Absorption coefficient (mm^{-1})	1.104	1.435
$F(000)$	1208	1824
Crystal size (mm)	0.60 × 0.60 × 0.10	0.80 × 0.80 × 0.60
θ range for data collection (°)	$1.85 \rightarrow 25.06$	$1.06 \rightarrow 25.10$
Index ranges	$0 \leq h \leq 13$	$0 \leq h \leq 23$
	$-17 \leq k \leq 0$	$-11 \leq k \leq 0$
	$-20 \leq l \leq 19$	$-24 \leq l \leq 23$
Reflections collected/unique	5194/4902 [R(int) = 0.0473]	7094/6876 [R(int) = 0.0836]
Data/restraints/parameters	4902/0/365	6876/0/535
Goodness-of-fit on F^2	1.041	1.038
Final R indices [$I > 2\sigma(I)$]	$R = 0.0533$, $R_w = 0.1305$	$R = 0.0527$, $R_w = 0.1432$
R indices (all data)	$R = 0.2018$, $R_w = 0.1723$	$R = 0.0996$, $R_w = 0.1734$
Largest diff. peak and hole (e Å^{-3})	0.530 and −0.500	1.093 and −0.775

The mixture was stirred at room temperature for 3 h. The product was filtered off, washed with EtOH and Et_2O and dried under an infrared lamp at 40°C.

Preparation of [Ni(i-prxa)$_2$(baa)]

The complex was prepared by a similar procedure as described above but with petroleum ether (20 cm^3) added to the reaction mixture. This led to formation of the solid which was filtered off, washed with petroleum ether and dried under an infrared lamp at 40°C.

Preparation of [Ni(i-prxa)$_2$(dpa)]

2,2′-Dipyridylamine (*dpa*) (2 mmol) in acetone (5 cm^3) was added with stirring at room temperature to a solution of [Ni(*i*-prxa)$_2$] (2 mmol) in acetone (10 cm^3). The color of solution changed to green immediately. Green microcrystals formed after a few minutes. Then, the reaction mixture was stirred for 2 h. The green solid was filtered off, washed with petroleum ether and dried under an infrared lamp at 40°C.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Ni(*i*-prxa)$_2$(dpa)]·dmso (*I*). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni (1)	1412 (1)	523 (1)	2307 (1)	46 (1)
S (1)	2171 (2)	−803 (2)	3186 (1)	68 (1)
S (2)	3623 (2)	584 (1)	2669 (1)	55 (1)
S (3)	−717 (2)	373 (1)	2361 (1)	57 (1)
S (4)	1216 (2)	1304 (2)	3532 (1)	66 (1)
N (1)	1158 (4)	1638 (4)	1553 (3)	43 (1)
N (2)	2169 (5)	927 (4)	670 (3)	49 (1)
N (3)	1281 (5)	−216 (4)	1267 (3)	48 (1)
C (1)	3536 (6)	−359 (5)	3213 (4)	49 (2)
O (1)	4583 (4)	−660 (4)	3665 (3)	68 (2)
C (2)	4615 (8)	−1453 (7)	4187 (6)	76 (2)
C (3)	4842 (16)	−2235 (9)	3744 (8)	116 (4)
C (4)	5646 (11)	−1280 (9)	4932 (6)	94 (3)
O (2)	−906 (4)	1095 (4)	3771 (3)	65 (1)
C (5)	−215 (6)	926 (5)	3250 (4)	52 (2)
C (6)	−2177 (9)	822 (7)	3572 (6)	79 (3)
C (7)	−2907 (8)	1501 (8)	3048 (7)	114 (4)
C (8)	−2483 (10)	751 (8)	4386 (7)	119 (4)
C (9)	590 (7)	2393 (6)	1717 (5)	59 (2)
C (10)	559 (8)	3172 (6)	1318 (5)	67 (2)
C (11)	1165 (8)	3225 (6)	698 (5)	63 (2)
C (12)	1702 (7)	2490 (5)	496 (4)	53 (2)
C (13)	1675 (5)	1693 (5)	924 (3)	44 (2)
C (14)	1759 (6)	74 (5)	669 (4)	48 (2)
C (15)	1912 (9)	−527 (7)	52 (5)	70 (2)
C (16)	1496 (9)	−1376 (6)	40 (6)	81 (3)
C (17)	954 (9)	−1655 (7)	633 (7)	81 (3)
C (18)	862 (7)	−1064 (6)	1223 (5)	63 (2)
S (5)	4355 (7)	1250 (5)	8996 (4)	98 (3)
S (5)	3637 (18)	925 (8)	8680 (8)	111 (5)
C (19)	4491 (17)	145 (12)	8671 (10)	208 (9)
C (20)	3401 (16)	1649 (11)	8034 (7)	179 (7)
O (3)	3562 (7)	1253 (5)	9528 (4)	112 (2)

Preparation of [Ni(i-prxa)$_2$(tpy)]

2,2′:6′,2″-Terpyridine (*tpy*) (1 mmol) in EtOH (5 cm^3) was added to a solution of [Ni(*i*-prxa)$_2$] (1 mmol) in $CHCl_3$ (5 cm^3). The reaction mixture was stirred at room temperature for 2 h. Then, it was allowed to stand overnight and microcrystals of the complex were separated by filtration, washed with Et_2O and dried under an infrared lamp at 40°C.

RESULTS AND DISCUSSION

The reactions of *bis*(isopropylxanthato)nickel(II) with neutral nitrogen donor ligands give compounds which can be readily isolated as octahedrally

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [Ni(i-prxa)$_2$(amp)] (*2*). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni (1)	1639 (1)	7146 (1)	4478 (1)	25 (1)
S (1)	1547 (1)	9599 (1)	4354 (1)	29 (1)
S (2)	917 (1)	7556 (2)	3440 (1)	35 (1)
S (3)	2673 (1)	7105 (1)	3915 (1)	31 (1)
S (4)	1863 (1)	4791 (1)	4227 (1)	28 (1)
O (1)	940 (2)	10022 (4)	3101 (2)	36 (1)
O (2)	2939 (2)	4552 (4)	3639 (2)	32 (1)
N (1)	869 (2)	6792 (4)	5062 (2)	29 (1)
N (2)	2226 (2)	7061 (5)	5413 (2)	27 (1)
C (1)	1123 (2)	9177 (6)	3593 (3)	30 (1)
C (2)	1180 (3)	11418 (6)	3146 (3)	36 (1)
C (3)	1881 (3)	11460 (9)	2919 (4)	51 (2)
C (4)	637 (4)	12197 (8)	2714 (4)	49 (2)
C (5)	2539 (3)	5458 (5)	3899 (2)	27 (1)
C (6)	3510 (3)	4997 (6)	3297 (3)	38 (1)
C (7)	4161 (3)	4797 (9)	3729 (4)	70 (2)
C (8)	3460 (5)	4133 (17)	2695 (4)	151 (7)
C (9)	1859 (3)	6263 (6)	5862 (3)	35 (1)
C (10)	1088 (3)	6376 (5)	5671 (3)	32 (1)
C (11)	628 (3)	6031 (7)	6112 (3)	41 (1)
C (12)	−78 (3)	6158 (7)	5907 (3)	45 (2)
C (13)	−306 (3)	6598 (6)	5275 (3)	40 (1)
C (14)	175 (3)	6912 (6)	4865 (3)	33 (1)
Ni (2)	6652 (1)	7655 (1)	4491 (1)	27 (1)
S (5)	6514 (1)	5252 (1)	4621 (1)	28 (1)
S (6)	6112 (1)	6769 (2)	3410 (1)	50 (1)
S (7)	6880 (1)	9916 (2)	4143 (1)	36 (1)
S (8)	7805 (1)	7626 (1)	4117 (1)	31 (1)
O (3)	6101 (2)	4092 (5)	3516 (2)	47 (1)
O (4)	8054 (2)	10122 (4)	3726 (2)	36 (1)
N (3)	5753 (2)	8072 (4)	4893 (2)	33 (1)
N (4)	7077 (2)	8107 (4)	5458 (2)	27 (1)
C (15)	6222 (3)	5284 (6)	3804 (3)	38 (1)
C (16)	5943 (4)	4004 (11)	2796 (3)	71 (3)
C (17)	6626 (4)	3979 (10)	2517 (4)	77 (3)
C (18)	5550 (5)	2698 (12)	2673 (4)	103 (4)
C (19)	7638 (3)	9250 (6)	3972 (3)	30 (1)
C (20)	8715 (3)	9684 (6)	3521 (3)	39 (1)
C (21)	9284 (4)	9871 (8)	4087 (4)	46 (2)
C (22)	8795 (4)	10507 (8)	2917 (4)	52 (2)
C (23)	6594 (3)	8997 (6)	5749 (3)	35 (1)
C (24)	5861 (3)	8629 (5)	5497 (3)	33 (1)
C (25)	5319 (3)	8835 (6)	5856 (4)	48 (2)
C (26)	4654 (4)	8440 (7)	5595 (5)	57 (2)
C (27)	4547 (3)	7880 (7)	4981 (5)	54 (2)
C (28)	5102 (3)	7689 (6)	4636 (4)	40 (2)

coordinated complexes. Analytical data and some properties of the compounds are given in Tables IV and V. The magnetic moments of the nickel complexes indicate two unpaired electrons and thus confirm an octahedral arrangement around Ni(II).

TABLE IV Colors and analytical data for the complexes

Compound	*Found* (*Calcd.*) (%)					
	Color	M_r	*C*	*H*	*N*	*S*
[Ni(*i*-prxa)(taa)](*i*-prxa)	light-violet	475.4	35.8(35.4)	7.0(6.8)	11.4(11.7)	27.0(26.0)
[Ni(*i*-prxa)$_2$(apa)]	green-gray	446.3	33.9(35.0)	6.5(6.5)	9.0(9.4)	28.2(28.7)
[Ni(*i*-prxa)$_2$(baa)]	green-gray	460.3	36.2(36.5)	7.1(6.8)	8.9(9.1)	27.6(27.9)
[Ni(*i*-prxa)$_2$(amp)]	green	437.3	38.6(38.4)	5.2(5.1)	6.4(6.4)	29.3(29.3)
[Ni(*i*-prxa)$_2$(dpa)]	green	500.4	42.9(43.2)	4.8(4.6)	8.1(8.4)	25.5(25.6)
[Ni(*i*-prxa)$_2$(tpy)]	dark-green	562.4	49.1(49.1)	4.5(4.5)	6.8(7.5)	22.6(22.8)

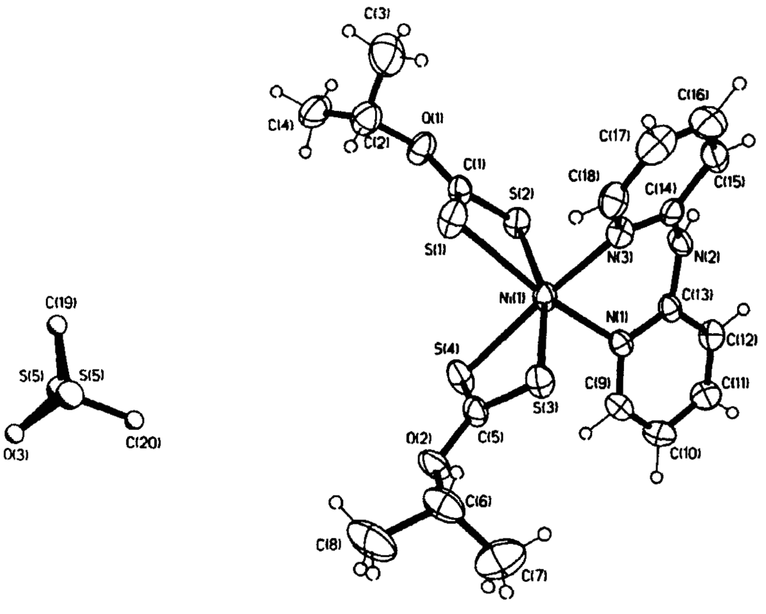

FIGURE 1 Perspective view of the structure of (*1*).

Electronic absorption spectra of the complexes are similar. The absorbance at 15800–18000 cm^{-1} can be related to the $^3A_{2g} \rightarrow {}^3T_{1g}$(F) transition, while the maxima observed in the 20400–21000 cm^{-1} region are probably connected with spin forbidden $^3A_{2g} \rightarrow {}^1T_{1g}$ transitions. The absorbance maximum at 27400 cm^{-1} in the spectrum of [Ni(*i*-prxa)(taa)](*i*-prxa) is attributable to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition.[14] The bands with wavenumber over 29000 cm^{-1} are probably caused by the charge transfer or $\pi \rightarrow \pi^*$ transitions.

IR spectra of the complexes show characteristic bands for xanthate anions (see Table V).[15] The ν(C–O–C) stretching bands are near 1260, 1210 and 1150 cm^{-1}, while the bands belonging to ν(C–S) are in the 1026–1038 and

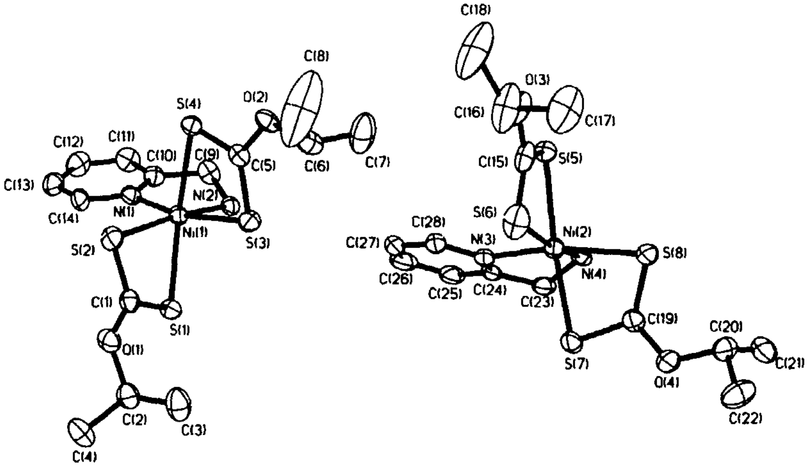

FIGURE 2 Perspective view of the structure of (*2*).

TABLE V Magnetic, diffuse-reflectance, IR and conductance data for the complexes

Compound	μ_{eff}/μ_B	*Diff.-reflect. spectra* [$\times 10^3$; cm^{-1}]	*IR data* [cm^{-1}]			Λ_M [S cm^2 mol^{-1}]	*Donor atom sets*
			ν(C-O-C)$_{as}$	ν(C-O-C)$_s$	ν(C-S)		
[Ni(*i*-prxa)(taa)](*i*-prxa)	3.07	18.0 27.4	1260m	1148m	1030w 620m	59.2[a]	N_4S_2
[Ni(*i*-prxa)$_2$(apa)]	3.35	17.4 20.8 31.6	1276s 1206vs	1140s	1026m 612s	3.7[b]	N_3S_3
[Ni(*i*-prxa)$_2$(baa)]	3.20	16.8 20.4 32.0	1260m 1202w	1144m	1038m 630w	11.5[b]	N_3S_3
[Ni(*i*-prxa)$_2$(amp)]	3.14	16.0 21.0 31.0	1264s 1214w	1140s	1030s 638s	4.9[b]	N_2S_4
[Ni(*i*-prxa)$_2$(dpa)]	3.19	15.8 32.0	1262m 1202s	1140s	1038s 626s	5.4[b]	N_2S_4
[Ni(*i*-prxa)$_2$(tpy)]	3.28	17.4 29.0	1260w 1216s	1152s	1036s 636m	10.6[b]	N_3S_3

[a] Measured in DMFA.
[b] Measured in acetone.

612–638 cm^{-1} regions. The ν(N–H) modes in complexes containing primary amines are observed at 3250–3325 cm^{-1} and between 910–770 cm^{-1}. Bands found at 1065 cm^{-1} confirm the presence of ν(C–N).[16] The maximum at 1310 cm^{-1} can be attributed to the aromatic C–N stretch and it was observed in complexes with the *amp*, *dpa* or *tpy* ligand.

Molar conductance values given in Table V indicate that the complexes, except for [Ni(*i*-prxa)(taa)](*i*-prxa), have non-ionic character.[17] The molar conductivity of the above complex was studied in DMFA solution owing to its poor solubility in acetone. Its molar conductance ($\lambda_M = 59.2\,\mathrm{S\,cm^2\,mol^{-1}}$) corresponds to a 1 : 1 electrolyte, even if the obtained value is somewhat lower than the value interval given in the literature ($65\text{–}90\,\mathrm{S\,cm^2\,mol^{-1}}$).[17] This means that one of two xanthate anions is situated outside of coordination sphere.

The metal configurations in complexes of (*1*) and (*2*) are *cis*-octahedral with NiS_4N_2 cores. Bond lengths and S–Ni–S angles in the coordination spheres of (*1*) and (*2*) (see Tables VI and VII) show small differences and are comparable with those found for the other *cis*-octahedral nickel(II) xanthates containing the abovementioned chromphore.[4] However, the N–Ni–N angles in (*1*) and (*2*) differ significantly, being 86.1(2), and 79.36(17) and 80.01(18)°, respectively. The structure of (*1*) is composed of discrete molecules (Figure 1)

TABLE VI Selected bond lengths [Å] and angles [°] for [Ni(*i*-prxa)$_2$(dpa)]•dmso (*1*)

Ni (1)–N (1)	2.071 (5)	C (9)–N (1)–Ni (1)	122.4 (5)
Ni (1)–N (3)	2.051 (6)	C (13)–N (1)–Ni (1)	121.2 (5)
Ni (1)–S (1)	2.491 (2)	C (14)–N (3)–Ni (1)	121.5 (5)
Ni (1)–S (2)	2.4254 (19)	C (18)–N (3)–Ni (1)	120.0 (5)
Ni (1)–S (3)	2.4468 (19)	C (13)–N (1)–C (9)	116.0 (6)
Ni (1)–S (4)	2.437 (2)	C (14)–N (2)–C (13)	127.4 (6)
S (1)–C (1)	1.671 (7)	C (14)–N (3)–C (18)	117.8 (6)
S (2)–C (1)	1.695 (7)	O (1)–C (1)–S (1)	124.9 (5)
S (3)–C (5)	1.685 (7)	O (1)–C (1)–S (2)	115.4 (5)
S (4)–C (5)	1.667 (7)	S (1)–C (1)–S (2)	119.6 (4)
N (1)–C (13)	1.342 (7)	C (1)–O (1)–C (2)	120.2 (6)
N (1)–C (9)	1.359 (9)	C (3)–C (2)–O (1)	108.4 (8)
N (2)–C (14)	1.352 (9)	C (3)–C (2)–C (4)	111.7 (10)
N (2)–C (13)	1.386 (8)	O (1)–C (2)–C (4)	105.2 (8)
N (3)–C (14)	1.336 (8)	C (5)–O (2)–C (6)	120.2 (6)
N (3)–C (18)	1.344 (10)	O (2)–C (5)–S (4)	115.7 (5)
C (1)–O (1)	1.318 (8)	O (2)–C (5)–S (3)	123.9 (5)
O (1)–C (2)	1.470 (10)	S (4)–C (5)–S (3)	120.4 (4)
C (2)–C (3)	1.444 (15)	O (2)–C (6)–C (7)	108.9 (7)
C (2)–C (4)	1.509 (12)	O (2)–C (6)–C (8)	104.6 (8)
O (2)–C (5)	1.345 (7)	C (7)–C (6)–C (8)	112.3 (9)
O (2)–C (6)	1.451 (10)	C (10)–C (9)–N (1)	124.5 (7)
C (6)–C (7)	1.457 (13)	N (1)–C (13)–N (2)	119.2 (6)
C (6)–C (8)	1.509 (12)	N (1)–C (13)–C (12)	122.3 (7)
C (9)–C (10)	1.338 (11)	N (2)–C (13)–C (12)	118.4 (6)
N (3)–Ni (1)–N (1)	86.1 (2)	N (3)–C (14)–N (2)	120.5 (6)
S (4)–Ni (1)–S (3)	73.09 (7)	N (3)–C (14)–C (15)	120.2 (7)
S (2)–Ni (1)–S (1)	72.53 (7)	N (2)–C (14)–C (15)	119.2 (7)
N (3)–Ni (1)–S (4)	170.11 (16)	N (3)–C (18)–C (17)	124.0 (9)
N (1)–Ni (1)–S (1)	167.81 (15)	1	1
S (2)–Ni (1)–S (3)	161.53 (6)		

TABLE VII Selected bond lengths [Å] and angles [°] for [Ni(*i*-prxa)$_2$(amp)] (**2**)

Ni (1)–N (1)	2.065 (4)	Ni (2)–N (3)	2.070 (5)
Ni (1)–N (2)	2.074 (4)	Ni (2)–N (4)	2.068 (4)
Ni (1)–S (1)	2.4636 (16)	Ni (2)–S (7)	2.4230 (16)
Ni (1)–S (2)	2.3934 (16)	Ni (2)–S (5)	2.4311 (16)
Ni (1)–S (3)	2.4459 (15)	Ni (2)–S (6)	2.4583 (18)
Ni (1)–S (4)	2.4559 (15)	Ni (2)–S (8)	2.4602 (15)
S (1)–C (1)	1.697 (5)	S (5)–C (15)	1.676 (6)
S (2)–C (1)	1.684 (6)	S (6)–C (15)	1.683 (7)
S (3)–C (5)	1.663 (6)	S (7)–C (19)	1.694 (5)
S (4)–C (5)	1.690 (5)	S (8)–C (19)	1.670 (6)
O (1)–C (1)	1.317 (6)	O (3)–C (15)	1.331 (7)
O (1)–C (2)	1.467 (7)	O (3)–C (16)	1.452 (8)
O (2)–C (5)	1.347 (6)	O (4)–C (19)	1.331 (6)
O (2)–C (6)	1.458 (6)	O (4)–C (20)	1.469 (6)
N (1)–C (10)	1.318 (7)	N (3)–C (24)	1.335 (7)
N (1)–C (14)	1.353 (6)	N (3)–C (28)	1.351 (7)
N (2)–C (9)	1.468 (7)	N (4)–C (23)	1.473 (7)
C (2)–C (4)	1.491 (8)	C (16)–C (17)	1.514 (9)
C (2)–C (3)	1.497 (8)	C (16)–C (18)	1.512 (12)
C (6)–C (7)	1.446 (9)	C (20)–C (21)	1.488 (10)
C (6)–C (8)	1.486 (10)	C (20)–C (22)	1.502 (9)
C (9)–C (10)	1.494 (7)	C (23)–C (24)	1.488 (8)
N (1)–Ni (1)–N (2)	79.36 (17)	N (3)–Ni (2)–N (4)	80.01 (18)
S (3)–Ni (1)–S (4)	72.91 (5)	S (7)–Ni (2)–S (8)	73.14 (5)
S (2)–Ni (1)–S (1)	73.49 (5)	S (5)–Ni (2)–S (6)	72.71 (6)
N (2)–Ni (1)–S (2)	171.98 (14)	S (7)–Ni (2)–S (5)	167.77 (6)
N (1)–Ni (1)–S (3)	166.75 (13)	N (4)–Ni (2)–S (6)	171.05 (13)
S (4)–Ni (1)–S (1)	160.31 (5)	N (3)–Ni (2)–S (8)	167.70 (14)
C (1)–S (1)–Ni (1)	82.3 (2)	C (15)–S (5)–Ni (2)	84.3 (2)
C (1)–S (2)–Ni (1)	84.72 (18)	C (15)–S (6)–Ni (2)	83.3 (2)
C (5)–S (3)–Ni (1)	83.67 (18)	C (19)–S (7)–Ni (2)	83.91 (19)
C (5)–S (4)–Ni (1)	82.82 (18)	C (19)–S (8)–Ni (2)	83.22 (18)
C (1)–O (1)–C (2)	120.8 (4)	C (15)–O (3)–C (16)	119.7 (6)
C (5)–O (2)–C (6)	120.1 (4)	C (19)–O (4)–C (20)	120.7 (4)
C (10)–N (1)–C (14)	118.8 (5)	C (24)–N (3)–C (28)	119.3 (5)
C (10)–N (1)–Ni (1)	115.4 (3)	C (24)–N (3)–Ni (2)	114.5 (3)
C (14)–N (1)–Ni (1)	125.8 (4)	C (28)–N (3)–Ni (2)	125.7 (5)
C (9)–N (2)–Ni (1)	109.8 (3)	C (23)–N (4)–Ni (2)	108.7 (3)
O (1)–C (1)–S (2)	116.4 (4)	O (3)–C (15)–S (5)	115.6 (5)
O (1)–C (1)–S (1)	125.1 (4)	O (3)–C (15)–S (6)	125.1 (4)
S (2)–C (1)–S (1)	118.5 (3)	S (5)–C (15)–S (6)	119.3 (4)
O (1)–C (2)–C (4)	105.5 (5)	O (3)–C (16)–C (17)	107.9 (6)
O (1)–C (2)–C (3)	107.5 (5)	O (3)–C (16)–C (18)	104.3 (7)
C (4)–C (2)–C (3)	113.6 (6)	C (17)–C (16)–C (18)	111.8 (8)
O (2)–C (5)–S (3)	125.0 (4)	O (4)–C (19)–S (8)	126.1 (4)
O (2)–C (5)–S (4)	114.4 (4)	O (4)–C (19)–S (7)	114.2 (4)
S (3)–C (5)–S (4)	120.6 (3)	S (8)–C (19)–S (7)	119.7 (3)
C (7)–C (6)–O (2)	109.0 (5)	O (4)–C (20)–C (21)	109.0 (5)
C (7)–C (6)–C (8)	111.7 (7)	O (4)–C (20)–C (22)	105.2 (5)
O (2)–C (6)–C (8)	104.4 (6)	C (21)–C (20)–C (22)	114.2 (6)
N (2)–C (9)–C (10)	110.7 (5)	N (4)–C (23)–C (24)	110.2 (5)
N (1)–C (10)–C (11)	121.9 (5)	N (3)–C (24)–C (25)	121.1 (6)
N (1)–C (10)–C (9)	116.5 (5)	N (3)–C (24)–C (23)	115.9 (5)
C (11)–C (10)–C (9)	121.6 (5)	C (25)–C (24)–C (23)	123.1 (6)

separated by dimethyl sulfoxide units. While the Ni–S bond lengths differ significantly and their values vary from 2.4254(19) to 2.491(2) Å, the Ni–N distances are similar and are equal to 2.071(5), and 2.051(6) Å, respectively. The structure of (*2*) consists of two crystallographically independent molecules in the asymmetric unit (Figure 2). The ranges of Ni–S and Ni–N lengths are 2.3934(16)–2.4636(16) Å and 2.065(4)–2.074(4) Å, respectively.

In the complexes [Ni(*i*-prxa)$_2$(apa)], [Ni(*i*-prxa)$_2$(baa)] and [Ni(*i*-prxa)$_2$(tpy)] it is difficult to define unambiguously the coordination mode of the ligand due to the lack of crystallographic data. However, on the basis of our results, mainly through conductance data, we assume that the complexes containing *apa*, *baa* or *tpy* ligands in combination with isopropylxanthate anions also have NiN_3S_3 cores. This means that one of the two xanthates is coordinated as a bidentate while the second is a monodentate ligand.

Supplementary Material

A complete list of bond distances and angles, anisotropic displacement parameters, hydrogen coordinates, and observed and calculated structure factors is available from Zdeněk Trávníček upon request.

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References

[1] Coucouvanis, D. *Progress in Inorganic Chemistry*, Edited by Lippard S.J. (John Wiley & Sons, New York, 1970), Vol. 11, pp. 235, 298, and references therein.
[2] Z. Trávníček, R. Pastorek, Z. Šindelář and J. Marek, *Transition Met. Chem.*, **20**, 67 (1995).
[3] Z. Trávníček, R. Pastorek, Z. Šindelář, R. Klička and J. Marek, *Polyhedron*, **14**, 3627 (1995).
[4] Z. Trávníček, J. Marek and R. Pastorek, *Polish J. Chem.*, **69**, 1239 (1995).
[5] Z. Trávníček, R. Pastorek, Z. Šindelář, J. Kameníček and J. Marek, *Polyhedron*, **15**, 2975 (1996).
[6] Z. Trávníček, M. Drncová, Z. Šindelář and J. Marek, *Acta Univ. Palacki. Olomuc., Fac. Rer. Nat.*, **35**, 55 (1996).
[7] Z. Trávníček, R. Pastorek, Z. Šindelář, F. Kašpárek and J. Marek, *Polyhedron*, **16**, 2573 (1997).
[8] E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds* (Springer, Berlin, 1966).
[9] G.M. Sheldrick, SHELXS-97, *Acta Crystallogr.*, **A46**, 467 (1990).
[10] G.M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement* (University of Göttingen, Germany, 1997).
[11] N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
[12] 17th European Crystallographic Meeting, Lisbon, Portugal, 24/28 August 1997, *Abstracts*, p. 120.

[13] *Gmelins Handbuch der Anorganische Chemie, Nickel*, Part C, Vol. 2, p. 982 (Verlag Chemie, Weinheim, 1969).

[14] A.B.P. Lever, *Inorganic Electron Spectroscopy* (Elsevier, Amsterdam, 1968).

[15] J. Zagal and J.A. Costamagna, *Inorg. Nucl. Chem. Letters*, **13**, 411 (1977), and references therein.

[16] C.J. Pouchert, *The Aldrich Library of Infrared Spectra* (Edition III) (Aldrich Chemical Company, Milwaukee, Wisconsin, 1981).

[17] W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).