Pergamon

Polyhedron Vol. 15, No. 7, pp. 1103–1112, 1996
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0277–5387/96 $15.00+0.00

0277-5387(95)00358-4

FIVE-COORDINATE NICKEL(II) XANTHATE DERIVATIVES WITH TRIPHOS. CRYSTAL STRUCTURE OF TRIS(O-CYCLOHEXYLDITHIOCARBONATO)NICKELATE(II) OF BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE-O-CYCLOHEXYLDITHIOCARBONATONICKEL(II)

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(*Received* 30 *March* 1995; *accepted* 27 *July* 1995)

Abstract—Five-coordinate complexes, $[Ni(S_2COR)(TRIPHOS)]X$ ($R = cyclo\text{-}C_6H_{11}$, $X = Cl, PF_6, [Ni(S_2COC_6H_{11})_3]$; $R = Et$, $X = PF_6, [Ni(S_2COEt)_3]$), have been obtained by the reaction of O-alkyldithiocarbonato complexes, $[Ni(S_2COR)_2]$, with bis(2-diphenylphosphinoethyl)phenylphosphine (TRIPHOS). The structure of $[Ni(S_2COC_6H_{11})(TRIPHOS)][Ni(S_2COC_6H_{11})_3]$ was determined by X-ray crystallography. The compound contains a five-coordinate cation and a hexa-coordinate anion. The geometry about the nickel atom in the $[Ni(S_2COC_6H_{11})(TRIPHOS)]^+$ is distorted trigonal bipyramidal with the axial positions occupied by one sulfur atom of the bidentate O-cyclohexyldithiocarbonate and the central phosphorus atom of the TRIPHOS. In the $[Ni(S_2COC_6H_{11})_3]^-$ anion, the nickel atom is bonded to six sulfur atoms of three O-cyclohexyldithiocarbonate ligands. Formation of the dithiocarbonato complexes in the reactions of $[Ni(S_2COEt)_2]$ with TRIPHOS has also been observed.

We have previously studied the behaviour of the $[Ni(S_2COR)_2]$ complexes towards several mono- and bidentate phosphine ligands.[1–3] Depending on the $ROCS_2^-$ derivative, the phosphine used and the reaction conditions, different types of compounds have been obtained. Thus, octahedral, diamagnetic and paramagnetic five-coordinate or square-planar complexes are formed, with mono- or bidentate coordination of the O-alkyldithiocarbonate, $ROCS_2^-$ ligand (xanthate). It is to be noted that decomposition of the coordinated xanthate ligands, which occur when an excess phosphine is used, produces either a dithiocarbonato complex, $[Ni(S_2CO)(dppe)]$,[1] or an intramolecular carbonylation with formation of $[Ni(CO)_2(PR_3)_2]$.[3]

We have now extended our studies to the reactions of $[Ni(S_2COR)_2]$ ($R = Et$, $cyclo\text{-}C_6H_{11}$) complexes with the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine ($Ph_2PCH_2CH_2P\{Ph\}CH_2CH_2PPh_2$, TRIPHOS). Several possible coordination modes may be available for this tridentate phosphine ligand,[4–6] but actually only a few modes are observed. Polydentate phosphine ligands

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can be used to modify the coordination stereochemistry of phosphine metal complexes by carefully selecting parameters such as the number of phosphorus donor atoms, the length of the connecting chains between phosphorus atoms and the sterically demanding substituent groups.[4] So, the chelating polyphosphine ligands are useful to stabilize unusual coordination numbers and geometries in transition metal complexes. We describe here the synthesis and characterization of the five-coordinate species $[Ni(S_2COR)(TRIPHOS)]^+$, a less frequent coordination in the nickel chemistry with sulphur donors. We also report the formation of dithiocarbonato complexes from xanthate derivatives.

RESULTS AND DISCUSSION

Crystal structure of $[Ni(S_2COC_6H_{11})(TRIPHOS)]$ $[Ni(S_2COC_6H_{11})_3]$ (**4**)

The structure of complex **4** is illustrated in Fig. 1. Crystal data are given in Table 1, and selected bond lengths and angles in Table 2. The solid-state structure consists of five-coordinate $[Ni(S_2COC_6H_{11})(TRIPHOS)]^+$ cations and hexacoordinate $[Ni(S_2COC_6H_{11})_3]^-$ anions. In the cation the metal atom is surrounded by three phosphorus atoms of the TRIPHOS ligand and by two sulfur atoms of the xanthate group. The geometry may be described in terms of a highly distorted trigonal bipyramid due to the small bite of the xanthate ligand. The two axial positions are occupied by the S(2) atom from the bidentate xanthate and the central phosphorus atom from the tridentate phosphine ligand. The Ni atom lies on a plane with the atoms S(1), P(1) and P(3) approximately occupying the centre of the equatorial triangle. The Ni—P distances lie in the range 2.16–2.25 Å, similar to those found in related systems.[2,7–10]

The characteristic feature of the tris(O-cyclohexyldithiocarbonato)nickelate(II) anion is that the central Ni atom is surrounded by six S atoms at the vertices of a distorted octahedron. The three xanthate ligands are bidentate with the cyclohexyl rings in the chair form. The general features of this anion are similar to those found in $[Me_4N]$ $[Ni(S_2COC_6H_{11})_3]$.[11]

As expected from other xanthate structures, the S_2CO groups are planar to a very good approximation. The mean values for S—C and C—O in these S_2CO groups of the xanthate ligands in the cation and anion complex are 1.68 and 1.33 Å,

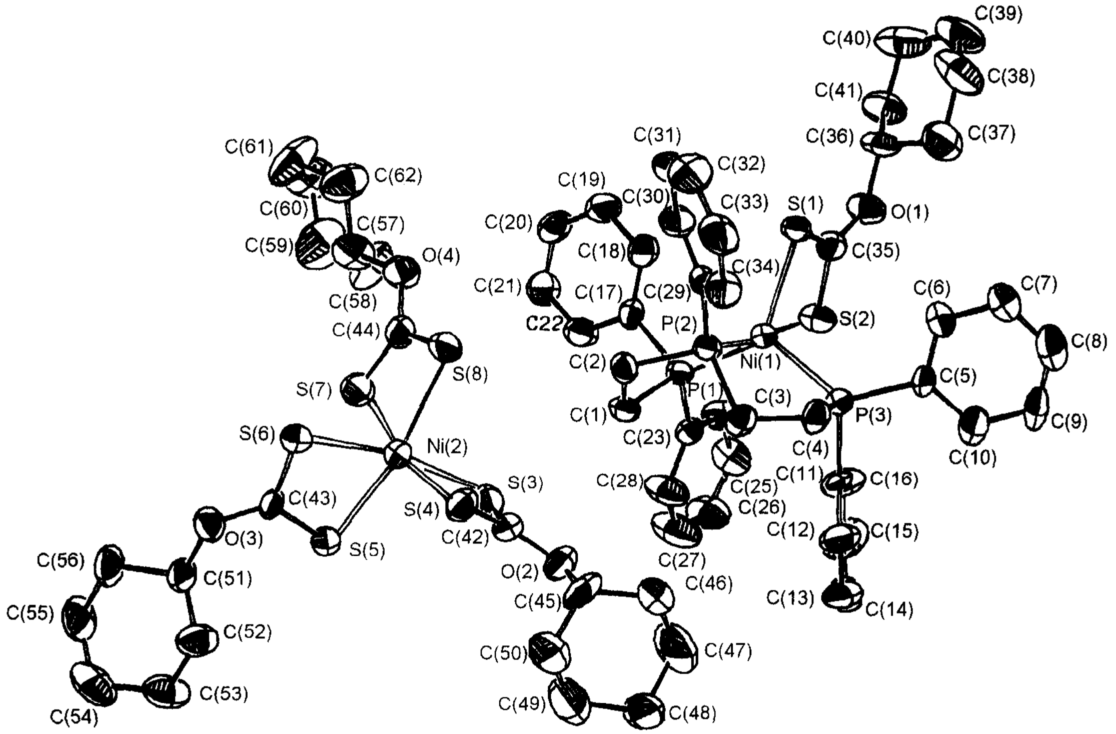
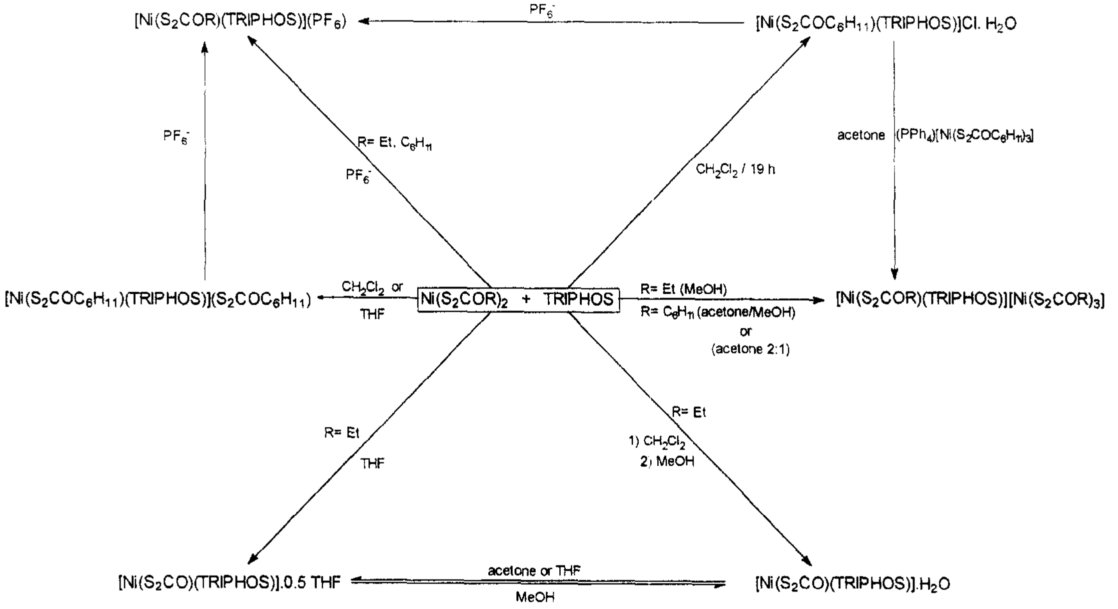


Fig. 1. ORTEP perspective of $[Ni(S_2COC_6H_{11})(TRIPHOS)]$ $[Ni(S_2COC_6H_{11})_3]$ showing the atom numbering scheme.

respectively, and compare well with the corresponding values of the previously reported xanthate complexes.[11,12] These values indicate partial double-bond character in the S_2CO groups, and therefore a certain contribution of the resonance structure **I** for the xanthate ligands.



Scheme 1.

On the other hand, the Ni—S distances range from 2.400 to 2.463 Å in the $[Ni(S_2COC_6H_{11})_3]^-$ anion, which is in very good agreement with the corresponding distances found in other $[Ni(S_2COR)_3]^-$ anions.[11,12] The five-coordinate $[Ni(S_2COC_6H_{11})(TRIPHOS)]^+$ cation shows shorter Ni—S distances (2.237 and 2.358 Å) than the hexa-coordinate $[Ni(S_2COC_6H_{11})_3]^-$ anion, and longer than those found in $[Ni(S_2COC_6H_{11})_2]$ (2.23–2.24 Å), where the geometry about the nickel atom is square-planar.[13]

$[Ni(S_2COR)(TRIPHOS)]X$ (R = *cyclo*-C_6H_{11}, X = Cl^-, PF_6^-, $C_6H_{11}COS_2^-$, $[Ni(S_2COC_6H_{11})_3]^-$; R = Et, X = PF_6^-, $[Ni(S_2COEt)_3]^-$) *and* $[Ni(S_2CO)(TRIPHOS)]$ *complexes*

The reactions leading to the new compounds are shown in Scheme 1. Analytical, conductance and spectroscopic data are collected in Tables 3 and 4. The reaction of $[Ni(S_2COR)_2]$ (R = Et, cyclo-C_6H_{11}) with TRIPHOS gives rise to the formation of several compounds depending on the starting nickel(II) complex and on the reaction conditions. So, the reaction of $[Ni(S_2COR)_2]$ with TRIPHOS generally leads to five-coordinate ionic species, $[Ni(S_2COR)(TRIPHOS)]X$ (**1**–**6**), which is indicative of a stepwise cleavage of nickel–sulfur bonds by the phosphine ligand. This series of complexes exhibits conductance values (Table 4) typical of uni-univalent electrolytes in acetonitrile solution. The low conductance values can be attributed to the relatively low specific conductance of the large cation $[Ni(S_2COR)(TRIPHOS)]^+$, and the presence of the large anions ($C_6H_{11}OCS_2^-$, $[Ni(S_2COR)_3]^-$) in some derivatives. All the ionic complexes are soluble in polar organic solvents and in some non-polar solvents such as benzene.

In $[Ni(S_2COC_6H_{11})(TRIPHOS)]Cl \cdot H_2O$ (**1**), obtained by prolonged reaction of $[Ni(S_2COR)_2]$ with TRIPHOS in CH_2Cl_2, the presence of chlorine was confirmed by direct analysis. This chloride ion can only arise from the CH_2Cl_2 used in this reaction. This reaction type had already been described in dithiocarbamato platinum(II) complexes.[14] Evidence for the water molecule is based on the appearance of the OH stretching and bending modes in the IR spectrum.

The IR spectra of complexes **1**–**6** present the characteristic bands (Table 3) of a bidentate xanthate ligand. The ν(C—O—R) frequencies are lower than those found for bidentate xanthate in square-planar nickel(II) complexes[15,16] and higher than in octahedral nickel(II) complexes.[16] This fact agrees with an intermediate coordination number according to the proposed five-coordination. The presence of additional IR bands can be observed in $[Ni(S_2COC_6H_{11})(TRIPHOS)](S_2COC_6H_{11})$ (**3**) and $[Ni(S_2COR)(TRIPHOS)][Ni(S_2COR)_3]$ (**4**). These bands correspond to those found in $NaS_2COC_6H_{11}$ and $[PPh_4][Ni(S_2COR)_3]$,[16] respectively. On the other hand, the ν(C—O—R) region of the IR spec-

Table 1. Crystal and refinement data

Formula	$Ni_2S_8P_3O_4C_{62}H_{77}$
Mr	1353.1
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	11.324(7)
b (Å)	15.954(4)
c (Å)	18.559(3)
α (°)	84.08(2)
β (°)	103.19(3)
γ (°)	92.16(5)
V (Å^3)	3247.(2)
Z	2
F(000)	1420
ρ (calc) (g cm^{-3})	1.38
Temperature (°C)	22
μ (cm^{-1})	9.5
Crystal dimensions (mm)	0.32 × 0.02 × 0.10
Diffractometer	Enraf–Nonius CAD-4
Radiation	Graphite-monochromated Mo-K_α (λ = 0.71069 Å)
Scan technique	$\omega/2\theta$
Data collected	(−13, −19,0) to (13,19,22)
Reflections collected	12 221
Unique data	11 446
Unique data (I) $\geq 2\sigma(I)$	4806
R_{int} (%)	1.8
Standard reflections	3
R_F (%)	5.2
R_wF (%)	6.0
Average shift/error	0.35

tra in solutions of polar (CH_3CN) or non-polar (CS_2) solvents are similar to those in the solid state, indicating a maintenance of the metal coordination environment in solution.

The ionic character of all these complexes can be confirmed by the conductance values in acetonitrile, the IR data, the determination of the crystal structure of [Ni($S_2COC_6H_{11}$)(TRIPHOS)] [Ni($S_2COC_6H_{11}$)$_3$] and the ready synthesis of any of these complexes from the others by anion exchange.

The [Ni(S_2COEt)(TRIPHOS)]X (X = Cl, EtCOS$_2$) derivatives cannot be isolated in a pure state because of the formation of the dithiocarbonato complexes. Thus, two dithiocarbonato complexes, [Ni(S_2CO)(TRIPHOS)] · H_2O (**7**) and [Ni(S_2CO)(TRIPHOS)] · 1/2THF (**8**) are obtained when [Ni(S_2COEt)$_2$] reacted with the TRIPHOS ligand in certain solvents. This fact shows that once the initial product, [Ni(S_2COEt)(TRIPHOS)] (S_2COEt), is formed it rapidly suffers a nucleophilic attack from the free EtCOS$_2^-$ to the alkoxy group of the coordinated ethylxanthate with the formation of the $O{=}CS_2^{2-}$ ligand. The dithiocarbonato complex (**7**) is immediately converted to the derivative (**8**) when dissolved in acetone, THF or DMSO and the reverse reaction occurs when **8** is stirred in MeOH for several hours. The formation of these dithiocarbonato complexes is coherent with the behaviour previously reported for other tridentate phosphine ligands. Therefore, the [MP_3] fragments (M = Co, Ni, Rh, Pd, Ir and Pt) can be used to stabilize small groups of atoms that cannot exist by themselves or to activate a large variety of small molecules. In this way several complexes, [M(S_2CO){MeC(CH_2PPh_2)$_3$}]$^{n+}$ (M = Co, Rh, n = 0, 1), have been synthesized. The structures of these derivatives are normally square pyramidal or trigonal bypiramidal with the tridentate phosphine ligand occupying three facial positions, and the dithiocarbonato coordinated in an η^2-fashion.[4] A similar situation is proposed for the dithiocarbonato complexes reported in this paper. Thus, the IR spectrum of complex **8** contains two bands at 1680 (m) and 1570(vs) cm^{-1} whose position and relative intensities are typical of a η^2-S,S-dithio-

Table 2. Principal bond lengths (Å) and angles (°) in $[Ni(S_2COC_6H_{11})(TRIPHOS)][Ni(S_2COC_6H_{11})_3]$

Ni(1)—S(1)	2.358(3)	P(1)—C(1)	1.83(1)
Ni(1)—S(2)	2.237(3)	P(1)—C(17)	1.82(1)
Ni(1)—P(1)	2.204(3)	P(1)—C(23)	1.82(1)
Ni(1)—P(2)	2.163(3)	P(2)—C(2)	1.81(1)
Ni(1)—P(3)	2.251(3)	P(2)—C(3)	1.82(1)
Ni(2)—S(3)	2.445(3)	P(2)—C(29)	1.80(1)
Ni(2)—S(4)	2.406(3)	P(3)—C(4)	1.81(1)
Ni(2)—S(5)	2.435(3)	P(3)—C(5)	1.81(1)
Ni(2)—S(6)	2.463(3)	P(3)—C(11)	1.83(1)
Ni(2)—S(7)	2.400(3)	O(1)—C(35)	1.33(1)
Ni(2)—S(8)	2.429(3)	O(1)—C(36)	1.47(1)
S(1)—C(35)	1.68(1)	O(2)—C(42)	1.34(2)
S(2)—C(35)	1.68(1)	O(2)—C(45)	1.48(2)
S(3)—C(42)	1.66(1)	O(3)—C(43)	1.33(1)
S(4)—C(42)	1.68(1)	O(3)—C(51)	1.46(1)
S(5)—C(43)	1.69(1)	O(4)—C(44)	1.36(1)
S(6)—C(43)	1.68(1)	O(4)—C(57)	1.46(1)
S(7)—C(44)	1.68(1)	C(1)—C(2)	1.51(1)
S(8)—C(44)	1.66(1)	C(3)—C(4)	1.51(1)

P(1)—Ni(1)—P(3)	122.2(2)	Ni(1)—P(1)—C(1)	108.6(4)
P(1)—Ni(1)—P(2)	86.0(1)	C(17)—P(1)—C(23)	103.7(5)
S(2)—Ni(1)—P(3)	94.5(1)	C(1)—P(1)—C(23)	104.8(5)
S(2)—Ni(1)—P(2)	176.6(3)	C(1)—P(1)—C(17)	102.7(5)
S(2)—Ni(1)—P(1)	94.7(1)	Ni(1)—P(2)—C(29)	119.6(4)
S(1)—Ni(1)—P(3)	109.9(1)	Ni(1)—P(2)—C(3)	106.4(4)
S(1)—Ni(1)—P(2)	101.2(2)	Ni(1)—P(2)—C(2)	110.2(4)
S(1)—Ni(1)—P(1)	127.7(2)	C(3)—P(2)—C(29)	107.2(5)
S(1)—Ni(1)—S(2)	75.8(1)	C(2)—P(2)—C(29)	106.4(5)
S(7)—Ni(2)—S(8)	73.4(1)	C(2)—P(2)—C(3)	106.1(5)
S(6)—Ni(2)—S(8)	98.9(1)	Ni(1)—P(3)—C(11)	113.2(4)
S(6)—Ni(2)—S(7)	92.1(1)	Ni(1)—P(3)—C(5)	124.0(4)
S(5)—Ni(2)—S(8)	164.1(1)	Ni(1)—P(3)—C(4)	105.7(4)
S(5)—Ni(2)—S(7)	93.0(1)	C(5)—P(3)—C(11)	104.7(5)
S(5)—Ni(2)—S(6)	72.8(1)	C(4)—P(3)—C(11)	105.2(5)
S(4)—Ni(2)—S(8)	95.8(1)	C(4)—P(3)—C(5)	102.0(5)
S(4)—Ni(2)—S(7)	167.1(1)	C(35)—O(1)—C(36)	121.3(9)
S(4)—Ni(2)—S(6)	96.6(1)	C(42)—O(2)—C(45)	122(1)
S(4)—Ni(2)—S(5)	98.6(2)	C(43)—O(3)—C(51)	121.1(9)
S(3)—Ni(2)—S(8)	97.6(1)	C(44)—O(4)—C(57)	118.9(9)
S(3)—Ni(2)—S(7)	100.8(1)	P(1)—C(1)—C(2)	107.3(7)
S(3)—Ni(2)—S(6)	161.4(2)	P(2)—C(3)—C(4)	108.3(8)
S(3)—Ni(2)—S(5)	93.0(1)	S(1)—C(35)—S(2)	114.3(6)
S(3)—Ni(2)—S(4)	73.2(1)	S(1)—C(35)—O(1)	127.9(8)
Ni(1)—S(1)—C(35)	82.9(4)	S(2)—C(35)—O(1)	117.7(8)
Ni(1)—S(2)—C(35)	86.9(4)	S(3)—C(42)—S(4)	120.1(8)
Ni(2)—S(3)—C(42)	82.9(4)	S(3)—C(42)—O(4)	117.1(9)
Ni(2)—S(4)—C(42)	83.8(4)	S(4)—C(42)—O(2)	122.7(9)
Ni(2)—S(5)—C(43)	84.3(4)	S(5)—C(43)—S(6)	119.1(6)
Ni(2)—S(6)—C(43)	83.5(4)	S(5)—C(43)—O(3)	123.6(7)
Ni(2)—S(7)—C(44)	83.6(4)	S(6)—C(43)—O(3)	117.3(8)
Ni(2)—S(8)—C(44)	83.1(4)	S(7)—C(44)—S(8)	119.7(7)
Ni(1)—P(1)—C(23)	119.7(4)	S(7)—C(44)—O(4)	124.1(9)
Ni(1)—P(1)—C(17)	115.7(4)	S(8)—C(44)—O(4)	116.1(8)

Table 3. Analytical, conductance and IR spectroscopic data (cm^{-1} in KBr) for the new compounds

Complex	Analysis[a] (%) C	(%) H	Λ_m[b] ($S\ cm^{-1}$)	IR $\nu(C—O—R)$	$\nu(C—O)$	$\nu(C{=}S)$	Other bands	Magnetic data μ (B.M.)	T (K)
(**1**) $[Ni(S_2COC_6H_{11})(TRIPHOS)]Cl \cdot H_2O$	59.8 (59.9)	5.5 (5.7)	121	$\left.\begin{matrix}1245\\1220\end{matrix}\right\}$ vs	1110 s	1059 s 1048 s	3490 b $\nu(OH)$	diamagnetic	
(**2**) $[Ni(S_2COC_6H_{11})(TRIPHOS)]PF_6$	53.7 53.9	4.4 (4.4)	119	$\left.\begin{matrix}1242\\1229\end{matrix}\right\}$ vs	1093 s	1050 s 1037 s	824 vs (PF_6^-)	2.88 1.66	268 71
(**3**) $[Ni(S_2COC_6H_{11})(TRIPHOS)](S_2COC_6H_{11})$	60.8 (61.1)	5.8 (5.8)	96	$\left.\begin{matrix}1250\\1219\end{matrix}\right\}$ vs	1106 s 1087 s	1052 s 1038 s		diamagnetic	
(**4**) $[Ni(S_2COC_6H_{11})(TRIPHOS)][Ni(S_2COC_6H_{11})_3]$	54.8 (55.0)	5.5 (5.7)	120	$\left.\begin{matrix}1248\\1230\end{matrix}\right\}$ vs $\left.\begin{matrix}1190\\1170\end{matrix}\right\}$ vs		1050 s 1038 s		3.02 2.95	247 84
(**5**) $[Ni(S_2COEt)(TRIPHOS)]PF_6$	51.5 (51.7)	4.4 (4.4)	122	1233 vs	1103 s	1040 sh 1029 m	830 vs (PF_6^-)	diamagnetic	
(**6**) $[Ni(S_2COEt)(TRIPHOS)][Ni(S_2COEt)_3]$	48.0 (48.6)	4.5 (4.7)	82[c]	1230 vs 1170 vs	1118 vs	1035 vs		3.95 3.31	286 76
(**7**) $[Ni(S_2CO)(TRIPHOS)] \cdot H_2O$	59.8 (59.8)	5.0 (5.0)					1670 m 1575 vs $\nu(C{=}O)$ 1540 vs 3490 b $\nu(OH)$	diamagnetic	
(**8**) $[Ni(S_2CO)(TRIPHOS)] \cdot 0.5\ THF$	60.8 (61.6)	5.1 (5.1)					1680 m 1570 vs $\nu(C{=}O)$	diamagnetic	

[a] Calculated values are given in parentheses.

[b] In acetonitrile solution (10^{-3} M).

[c] In acetonitrile solution (6×10^{-4} M).

Table 4. ^{31}P NMR and electronic spectral data for new complexes

				Electronic data		
	^{31}P NMR data			Solution		Solid
Complex	δ (ppm)	^{3}J(P,P)(Hz)	^{1}J(P,F)(Hz)	λ (nm)	ε^{a}	λ (nm)
1	113.1^{b}t	36.5				
	47.9 d					
2	112.1^{b}t	37.0		530^{c}	850	570 br
	47.2 d			380	525	415
	−144.5 sept		713.0			325
						270 sh
3	112.9^{b}t	36.2				
	47.4 d					
4	117.1^{b}t	37.6		510^{c}	788	
	52.2 d			476 sh	706	
				390	826	
5	112.4^{b}t	37.9		508^{c}	1960	580
	48.4 d			382	1645	410
	−144.5 sept		713			325
						270 sh
6	117.8^{d}t	35.8		525^{c}	2105	660
	51.9 d			487 sh	1960	570 sh
				408	2149	425
						325
						270
7	98.4^{d}t	19.3		655^{e}		705
	31.7 d			512		560 sh
						380
						320 sh
						270 sh
8	98.5^{d}t	19.3		655^{e}		740
	31.8 d			512		540
						350
						320
						270 sh

[a] Values in dm^{3} mol^{-1} cm^{-1}.
[b] In CDCl$_3$ solution.
[c] In acetronitrile solution.
[d] In deuterated DMSO solution.
[e] In dimethylformamide.

carbonato.[14,17–19] The absorption at higher frequencies is assigned to the Fermi resonance between the carbon–oxygen stretching mode and the first overtone band of the carbon–sulfur stretching mode.[18] The other dithiocarbonato complex (**7**) shows an additional band at lower frequencies (1540 cm^{-1}). The nature of this complex is not obvious. It is probably dimeric: [(TRIPHOS) Ni(μ^{2}-S$_2$CO)$_2$Ni(TRIPHOS)], in which the bridges are broken by donor solvents to give the corresponding monomeric derivative (**8**).

As expected, the nature of the R group of the ROCS$_2^{-}$ ligand influences the formation of the dithiocarbonato ligand,[1,19] and indeed, in our case the dithiocarbonato complexes are only produced when the reaction is carried out with the ethylxanthate derivative. No dithiocarbonato formation is observed in the reaction of [Ni(S$_2$COC$_6$H$_{11}$)$_2$] with a large excess of TRIPHOS (1 : 4 molar ratio) over 5 days. We have previously found that the rate of the reaction between [Ni(S$_2$COR)$_2$] and dppe to give [Ni(S$_2$CO)(dppe)] varies in the following order: Et > Me > cyclo-C$_6$H$_{11}$.[1]

The NMR spectra are in accordance with all the conclusions commented above. The ^{31}P NMR spectrum ot the free phosphine consists of a doublet at $\delta - 13.5$ ppm and a triplet at $\delta - 17.0$ ppm.[20] The ^{31}P NMR spectral data (Table 4) for all complexes suggest that the TRIPHOS is acting as a tridentate ligand because only two resonance signals, which appear as a doublet for the terminal phosphorus atoms and a triplet for the central one, are observed. The coordination chemical shift of the central P atom is larger than that observed in the two terminal P atoms, according to the more basic character of the former.[21,22]

There is no indication of additional resonance signals or signals corresponding to uncoordinated phosphorus in the ^{31}P NMR spectra of $[Ni(S_2COR)(TRIPHOS)]X$ complexes. This fact, along with the characteristic IR spectra in solution, confirms the existence in solution, as in the solid state, of five-coordinate $[Ni(S_2COR)(TRIPHOS)]^+$. However, dissociation reactions in non-polar solvents of complexes of the type $[Pt(S_2COR)(PR_3)_2](S_2COR)$ to give $[Pt(S_2COR)_2(PR_3)]$ are reported.[14] The chelating nature of the TRIPHOS ligand can prevent the phosphine dissociation in contrast to the behaviour observed in complexes with monodentate phosphine ligands.

The ^{31}P NMR spectra, like the electronic spectra, show that, in solution, the two dithiocarbonato complexes give rise to the same species. The TRIPHOS acts as a tridentate ligand to form five-coordinate species with an S_2P_3 donor set as in the ionic compounds **1**–**6**. However, a larger shielding is observed in the ^{31}P NMR spectra of the dithiocarbonato complexes, according to their higher donor character compared with the xanthate ligand.

The electronic spectra of the $[Ni(S_2COR)(TRIPHOS)]X$ complexes also show that in solution (polar or non-polar solvents) and in the solid state the same species are present (Table 4). Since electronic data of five-coordinate nickel(II) derivatives with similar environments of our complexes are not reported, we have not assigned the maxima observed in the spectra of $[Ni(S_2COR)(TRIPHOS)]^+$ cations. The ionic nature of these derivatives is also confirmed by the electronic spectra, because all the complexes show the same spectrum for the same R group, although for the $[Ni(S_2COR)(TRIPHOS)][Ni(S_2COR)_3]$ compounds (**4** and **6**) additional maxima corresponding to the hexa-coordinate $[Ni(S_2COR)_3]^-$ anion are observed.[16,23] According to the above mentioned interconversion, the two dithiocarbonate complexes show the same electronic spectrum in solution.

The magnetic properties of these compounds are coherent with the proposed structures. As expected, the presence in these derivatives of soft donors gives rise to the formation of low-spin five-coordinate species, $[Ni(S_2COR)(TRIPHOS)]^+$ and $[Ni(S_2CO)(TRIPHOS)]$. Thus, complexes **1**, **3**, **5**, **7** and **8** are diamagnetic, while the $[Ni(S_2COR)(TRIPHOS)][Ni(S_2COR)_3]$ derivatives (**4** and **6**) show a paramagnetic behaviour due to the presence of nickel(II) in a hexa-coordinate environment ($[Ni(S_2COR)_3]^-$; Table 3). Complex **2**, $[Ni(S_2COC_6H_{11})(TRIPHOS)]PF_6$, is paramagnetic. This fact is not consistent with the remaining experimental data, which confirm the existence of five-coordinate species in solution and the solid state. Therefore, this complex would be a low-spin derivative as are other $[Ni(S_2COR)(TRIPHOS)]^+$ compounds.

EXPERIMENTAL

All the starting materials and solvents were reagent grade. Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. IR spectra were taken in KBr disks using a Perkin–Elmer 1300 spectrophotometer. Electronic spectra were recorded in solution or in the solid state using a Uvikon 620 spectrophotometer equipped with diffuse reflectance accessories. The ^{31}P NMR spectra were run on a Varian VXR-300 instrument, using 85% H_3PO_4 as an external reference. Conductivity measurements in solution were performed using a Phillips PR9512/00 apparatus.

Bis(O-alkyldithiocarbonato)nickel(II) complexes and $(PPh_4)[Ni(S_2COC_6H_{11})_3]$ were prepared according to methods reported in the literature.[24]

Preparation of the complexes

$[Ni(S_2COC_6H_{11})(TRIPHOS)]Cl \cdot H_2O$ (**1**). When $[Ni(S_2COC_6H_{11})]_2$ (0.25 mmol) and TRIPHOS (0.25 mmol) in CH_2Cl_2 (7 cm^3) were stirred for 19 h a dark purple solution was formed from which a dark violet solid was precipitated with diethylether (200 cm^3). The precipitate was filtered off, washed with a CH_2Cl_2/Et_2O mixture (1/10) and dried *in vacuo* (97% yield).

$[Ni(S_2COC_6H_{11})(TRIPHOS)]PF_6$(**2**). Method (A). An aqueous solution of KPF_6 (0.25 mmol) was added to a solution of **1** (0.25 mmol) in methanol. The violet precipitate formed was filtered off, washed with water and dried *in vacuo* over P_4O_{10} (95% yield).

Method (B). The same compound was also obtained when $[Ni(S_2COC_6H_{11})_2]$ in acetone/methanol was treated with a slight excess of TRIPHOS in a minimum volume of acetone, followed by the immediate addition of an aqueous solution of excess KPF_6. The resulting solution was stirred for 15 min and then filtered. The addition of a large volume of water gave a purple precipitate which was filtered off, washed with water and dried *in vacuo* over P_4O_{10} (quantitative yield).

$[Ni(S_2COC_6H_{11})(TRIPHOS)](S_2COC_6H_{11})$ (**3**). Method (A). $[Ni(S_2COC_6H_{11})_2]$ (0.25 mmol) in CH_2Cl_2 (5 cm^3) was treated with TRIPHOS (0.25 mmol) to give an immediate purple solution. Precipitation with diethylether (150 cm^3) gave a brown purple solid, which was filtered off, washed with diethylether and dried *in vacuo* over P_4O_{10} (85% yield).

Method (B). A suspension in MeOH of $[Ni(S_2COC_6H_{11})_2]$ (0.25 mmol) and TRIPHOS (0.25 mmol) was stirred for 50 min and the reaction mixture was filtered. Addition of water to the filtrate afforded a purple solid, which was washed with water and diethylether and dried *in vacuo* over P_4O_{10} (quantitative yield).

$[Ni(S_2COC_6H_{11})(TRIPHOS)][Ni(S_2COC_6H_{11})_3]$ (**4**). Method (A). $[Ni(S_2COC_6H_{11})]_2$ in acetone was treated with TRIPHOS (2 : 1 molar ratio) in a minimum volume of acetone to give a purple solution. The reaction mixture was stirred for 45 h and then a large volume of water was added. The purple solid formed was filtered off, washed with water and diethylether and dried *in vacuo* over P_4O_{10} (quantitative yield).

Method (B). $[Ni(S_2COC_6H_{11})(TRIPHOS)]Cl$ (0.25 mmol) in acetone was treated with (PPh_4) $[Ni(S_2COC_6H_{11})_3]$ (0.25 mmol) in a minimum volume of acetone. After stirring for 24 h, trituration with excess water gave a dark purple precipitate, which was washed with water and diethylether and dried *in vacuo* over P_4O_{10} (quantitative yield).

$[Ni(S_2COC_6H_{11})(TRIPHOS)]PF_6$(**2**), *method (C), and* $[Ni(S_2COC_6H_{11})(TRIPHOS)][Ni(S_2COC_6H_{11})_3]$(**4**), *method (C)*. $[Ni(S_2COC_6H_{11})_2]$ (0.25 mmol) was added to excess (0.15 g) TRIPHOS in an acetone/methanol (2/1) mixture (25 cm^3) and then an aqueous solution of KPF_6 (0.25 mmol) was added. After stirring for 15 min, the precipitation with water (150 cm^3) gave a product mixture. This was extracted with acetone, partially dissolving. The remaining solid was treated with methanol and filtered. The residue was unreacted TRIPHOS, and the methanol solution was precipitated with water. The violet solid formed was filtered off, washed with water and diethylether and dried *in vacuo* over P_4O_{10}. This compound was identified as **2**. The acetone solution mentioned above was allowed to stand at room temperature for 4 days to give rise to dark purple crystals of **4**, which were filtered off, washed with methanol and dried *in vacuo*.

$[Ni(S_2COEt)(TRIPHOS)]PF_6$(**5**). A slight excess of TRIPHOS (0.3 g) and $[Ni(S_2OEt)_2]$ (0.5 mmol) in an acetone/methanol mixture (2/1) were treated with a concentrated aqueous solution of KPF_6 (0.5 mmol). After stirring for 1 h, the reaction mixture was filtered. Addition of water to the filtrate afforded a purple solid, which was washed with water and diethylether and dried *in vacuo* over P_4O_{10} (quantitative yield).

$[Ni(S_2COEt)(TRIPHOS)][Ni(S_2COEt)_3]$ (**6**). $[Ni(S_2COEt)_2]$ (0.5 mmol) was added to a suspension of TRIPHOS (0.25 mmol) in methanol (30 cm^3). After stirring for 45 min, the dark blue–purple solid formed was filtered off, washed with methanol and diethylether and dried *in vacuo* over P_4O_{10} (65% yield).

$[Ni(S_2CO)(TRIPHOS)]\cdot H_2O$ (**7**). TRIPHOS (0.25 mmol) in a minimum volume of CH_2Cl_2 was added to a solution of $[Ni(S_2COEt)_2]$ (0.25 mmol) in a minimum volume of the same solvent. After stirring for 1 or 2 min, the solvent was removed to dryness. Methanol was added and a blue–purple solid precipitated. After filtration the solid was washed several times with methanol until the filtrate was colourless, and then was washed with diethylether and dried *in vacuo* over P_4O_{10} (60% yield).

$[Ni(S_2CO)(TRIPHOS)]\cdot 0.5THF$ (**8**). $[Ni(S_2COEt)_2]$ (0.25 mmol) was added to a stirred THF solution (50 cm^3) of TRIPHOS (0.25 mmol). The purple solution formed was allowed to stand overnight at room temperature. The brown–purple crystals formed were filtered off, washed with light petroleum and diethylether and dried *in vacuo* (80% yield).

Crystallography

A summary of the fundamental crystal data is given in Table 1. A black crystal of prismatic shape was resine epoxy coated and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, S and P were taken from the International Tables for X-ray Crystallography.[25] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[26] was applied at the end of the isotropic refinement.

A final refinement was undertaken with fixed isotropic factors and coordinates for all H atoms and unit weights. No trend in ΔF *versus* F_o or $(\sin\theta)/\lambda$ was observed. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-ray 80 system.[27]

Complete tables of distances and angles and atomic positional and thermal parameters and structure factors have been deposited as supplementary material.

Acknowledgements—We thank the D.G.Y.C.I.T. (PB91/0402) and C.A.M. (268/94) for financial support.

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