Reactions between Bis(*O*-alkyl dithiocarbonato)nickel(II) Complexes and Phosphines. Formation of a Dithiocarbonate Complex of Nickel(II): [Ni(S_2CO)($Ph_2PCH_2CH_2PPh_2$)]

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The behaviour of *O*-alkyl dithiocarbonato complexes, [Ni(S_2COR)$_2$], towards several phosphines has been studied. Depending on the S_2COR derivative and phosphine (L) used, octahedral complexes [Ni(S_2COR)$_2L_2$] [R = cyclo-C_6H_{11}, L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe); R = Et, L = $PMePh_2$], paramagnetic five-co-ordinate complexes [Ni(S_2COR)$_2$(dppe)], and square-planar [Ni(S_2COR)$_2$(PMe_2Ph)$_2$] (R = Et or cyclo-C_6H_{11}) and [Ni($S_2COC_6H_{11}$)$_2$($PMePh_2$)] complexes have been obtained. The reaction of [Ni(S_2COR)$_2$] (R = Me, Et, or cyclo-C_6H_{11}) with an excess of dppe gives [Ni(S_2CO)(dppe)] which is the first Ni^{II}–dithiocarbonate complex described. This compound reacts with MeI and C_3H_5Br to give [NiX_2(dppe)] (X = I or Br). There is no reaction with Lewis-base N donors or with carbon monoxide.

O-Alkyl dithiocarbonate (xanthate) complexes, [M(S_2COR)$_2$] (M = Ni, Pd, or Pt) react with N-donor nucleophiles giving rise frequently to an increase of the co-ordination number.[1,2] However tertiary phosphines (L) give complexes [M(S_2COR)$_2$L], [M(S_2COR)L_2][S_2COR], and [M(S_2COR)$_2L_2$] (M = Pd or Pt) with square-planar geometry. On the other hand, an excess of phosphine leads to C–O and P–O cleavage in [M(S_2COR)$_2$] and [M{$S_2P(OR)_2$}] to form the complexes [M(S_2CO)L_2], [M{$S_2P(O)OR$}L_2] (M = Pd or Pt) and [Ni{$S_2P(O)OMe$}($Ph_2PCH_2CH_2AsPh_2$)].[3–10] To date, the formation of dithiocarbonates of Ni^{II} has not been described in the literature.

Compounds [Ni(S_2COR)$_2L_2$] (L = trialkylphosphine) are square planar with the xanthates as monodentate ligands.[11] Adducts of [Ni{$S_2P(OR)_2$}$_2$] with phosphine and arsine ligands are known.[10,12–14] Adducts of [Ni(S_2COR)$_2$] with triarylphosphines have not been isolated.

We report here the reactions of [Ni(S_2COR)$_2$] (R = Me, Et, or cyclo-C_6H_{11}) with several mono- or bi-dentate mixed phosphines of different basicity, 1,2-bis(diphenylphosphino)ethane (dppe), $PMePh_2$, and PMe_2Ph, and with tris(2-cyanoethyl)phosphine (tcep).

Results and Discussion

The spectroscopic and magnetic data for the isolated new complexes are given in the Table.

Formation of [Ni(S_2CO)(dppe)] (**1**).—The reaction of [Ni(S_2COR)$_2$] (R = Me, Et, or cyclo-C_6H_{11}) with an excess of dppe and with long reaction times leads to formation of the dithiocarbonate complex (**1**), structure **III** (Scheme), as a crystalline orange-red solid; it is diamagnetic, a non-electrolyte in dimethylformamide, and stable to air and atmospheric moisture. The i.r. spectrum shows two ν(C=O) bands of the S_2CO ligand at *ca.* 1 600 and 1 680 cm^{-1}. The electronic spectra indicate a square-planar environment. Reaction yields and the formation rate depend on the xanthate used, reaction conditions, amount of dppe, solvent used, and reaction temperature. The formation of (**1**) occurs when an excess of dppe and an acetone–chloroform mixture are used. The reaction rate varies in the following order: Et > Me > cyclo-C_6H_{11}.

Complex (**1**) does not react with 2,2′-bipyridine, pyridine, or CO; however, when it is heated with the RX derivatives (R = allyl, X = Br; R = Me, X = I) it yields [NiX_2(dppe)] complexes.[15]

Co-ordination Reactions of Tertiary Phosphines to [Ni(S_2COR)$_2$] (R = Et *or* cyclo-C_6H_{11}).—The reaction of [Ni(S_2COR)$_2$] with dppe (1:1 mol ratio) in chloroform leads immediately to paramagnetic reddish-brown solids [Ni(S_2COR)$_2$(dppe)] [R = Et, (**2**); R = cyclo-C_6H_{11}, (**3**)], structure **V** (Scheme). When R = cyclo-C_6H_{11}, a crystalline green isomer (**4**), structure **IV** (Scheme), can be isolated from the filtrate also. Complexes (**2**) and (**3**) are unstable to temperature, decomposing to give (**1**). The green isomer (**4**) changes into the reddish-brown complex (**3**) under pressure (*ca.* 10^9 Pa). Complex (**3**) is very unstable in solution; in chloroform it gives complex (**1**).

The green derivative (**4**) presents all the characteristics of the Ni^{II} six-co-ordinate adducts, with $\mu_{eff.}$ = 3.15 and a ν(C–O–R) i.r. band (Table), attributable to a bidentate xanthate ligand.[16] From the magnetic data for the reddish-brown complexes (**2**) and (**3**) having $\mu_{eff.}$ values of *ca.* 2 and Weiss constants of 7.2 K, we deduce that these complexes could be five-co-ordinated species with an equilibrium between a high-spin and a low-spin form.[17] The ν(C–O–R) frequencies for (**2**) and (**3**) are lower than those found for bidentate xanthates in the square-planar complexes,[18] indicating a higher co-ordination number for Ni^{II}.

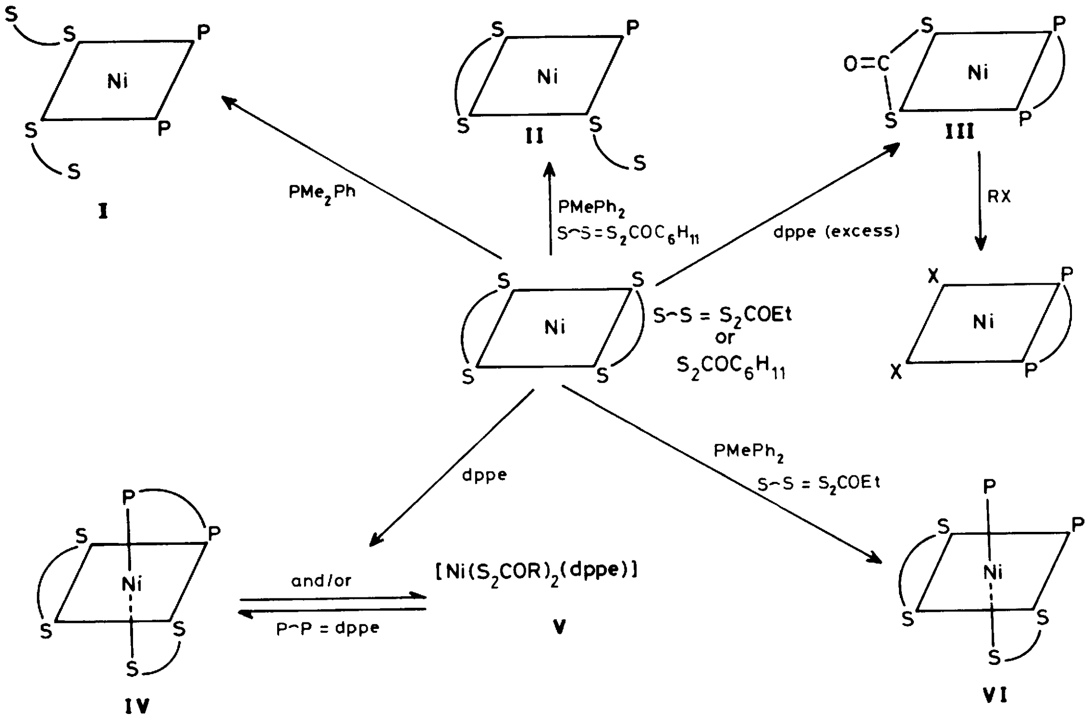
Ionic species with dppe were not isolated when KPF_6 was added to a reaction medium. The addition of dppe in acetone to [Ni(S_2COR)$_2$] with different mol ratios and reaction times did not cause an increase in the electrolytic conductivity.

The reaction of [Ni(S_2COR)$_2$] with $PMePh_2$ (1:2 mol ratio) gives a green paramagnetic solid, [Ni(S_2COEt)$_2$($PMePh_2$)$_2$] (**5**), structure **VI** (Scheme), with spectroscopic and magnetic properties similar to those found for complex (**4**), and a dark brown diamagnetic compound, [Ni($S_2COC_6H_{11}$)$_2$($PMePh_2$)] (**6**), structure **II**. The i.r. spectrum of (**6**) shows two ν(C–O–R) bands which are consistent with the presence of mono- and bi-dentate xanthate groups. To date, this type of complex has been

Table. Physical, spectroscopic, and magnetic data for the compounds

	I.r.[a] (cm^{-1})					Electronic spectra			
						Solid	Solution[b]		
Complex	ν(C^1–O–R)	ν(C^2–O)	ν(C=S)	ν(Ni–S)	ν(C=O)	$\lambda_{max.}$/nm	$\lambda_{max.}$/nm	ε[c]	$\mu_{eff.}$[d]
(**1**) [Ni(S$_2$CO)(dppe)]					1 680 1 600	480 415 340 265	480 415	97 345	diamag.
(**2**) [Ni(S$_2$COEt)$_2$(dppe)]	1 190 1 160	1 143	1 085	340					2.13
(**3**) [Ni(S$_2$COC$_6$H$_{11}$)$_2$(dppe)]	1 195 1 180	1 145	1 030	340 325		630 500 415 325 270			2.12
(**4**) [Ni(S$_2$COC$_6$H$_{11}$)$_2$(dppe)]	1 197 1 180	1 143	1 040	337 320		825 575 415 325 270			3.01
(**5**) [Ni(S$_2$COEt)$_2$(PMePh$_2$)$_2$]	1 200	1 150	1 055	330		*ca.* 900 660 585 445 380			
(**6**) [Ni(S$_2$COC$_6$H$_{11}$)$_2$(PMePh$_2$)]	1 275 1 190	1 145	1 040	340 325		675 525 470 364 262			diamag.
(**7**) [Ni(S$_2$COEt)$_2$(PMe$_2$Ph)$_2$]	1 195	1 120	1 040	320					diamag.
(**8**) [Ni(S$_2$COC$_6$H$_{11}$)$_2$(PMe$_2$Ph)$_2$]	1 175	1 145	1 060	340					diamag.

[a] In KBr discs; (**4**) in Nujol mulls. [b] 1.1 × 10^{-3} mol dm^{-3} in acetone. [c] Values in dm^3 mol^{-1} cm^{-1}. [d] diamag. = diamagnetic.



Scheme. Reactions and probable geometry of the complexes obtained isolated only for Pd and Pt. Complex (**5**) is unstable to air and room temperature and must be stored under N_2 at 0 °C.

The complexes $[Ni(S_2COR)_2]$ react with PMe_2Ph to give red solids, $[Ni(S_2COR)_2(PMe_2Ph)_2]$ [R = Et, (**7**); R = cyclo-C_6H_{11}, (**8**)]. These new derivatives are unstable to room temperature and their properties are analogous to those of *cis*-$[Ni(S_2COR)_2(PBu_3)_2]$,[11] structure **I** (Scheme). The behaviour of $[Ni(S_2COR)_2]$ towards this phosphine, with a higher alkyl character than dppe and $PMePh_2$, is similar to that towards a trialkylphosphine.

Electronic spectra of the complexes are indicative of a very low stability of these compounds in solution. The diffuse reflectance spectra of the solids are completely different from those of solutions, except for complex (**1**). The $PMePh_2$ and PMe_2Ph derivatives decompose in acetone or chloroform solution according to the equilibrium (1). Addition of an excess

$$[Ni(S_2COR)_2L_x] \rightleftharpoons [Ni(S_2COR)_2] + xL \quad (1)$$

of phosphine causes formation of the new species, probably of structure **I**.

Both isomers of $[Ni(S_2COC_6H_{11})_2(dppe)]$, (**3**) and (**4**), show the same electronic spectrum in acetone or chloroform solution with the $\lambda_{max.}$ and ε values very similar to those reported for the square-planar complex of structure **I**.[11] The ^1H n.m.r. spectra show clearly that the species present in solution are diamagnetic, consistent with square-planar geometry.

The complexes (**4**) and (**5**) (structures **IV** and **VI**, Scheme) have absorption maxima at 800—900 and *ca.* 570 nm, which can be attributed to the *d–d* transitions $^3T_{2g} \leftarrow {}^3A_{1g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$.[19] These transitions are shifted to lower wavelength with respect to those of the $[Ni(S_2COR)_3]^-$ complexes.[16] This fact is consistent with the higher ligand-field strength of the phosphine with respect to the xanthate ligand. The absorption maxima which appear to lower wavelength include probably the $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ transition and charge-transfer transitions.

Complexes of structure types **II** and **III** show diffuse reflectance spectra which correspond to four-co-ordinate planar species.[19] Thus, the two maxima which appear to higher wavelength in the complexes (**1**) and (**6**) can be assigned to the ν_1 and ν_2 transitions. The spectra of the complexes of structure **V** in the solid state are consistent with the proposed geometry.

No reaction between $[Ni(S_2COC_6H_{11})_2]$ and tcep (1:2 mol ratio) under mild reaction conditions was observed. If the reaction was carried out under ethanol reflux for 5 h the starting compounds and a decomposition product were recovered. This fact is due to the very low basicity of the phosphine tcep.

Experimental

All starting materials and solvents were reagent grade. Electronic spectra were recorded using a Kontron Uvikon 820 spectrophotometer equipped with a reflectance attachment and i.r. spectra on a 325 Perkin-Elmer spectrophotometer. The magnetic susceptibilities were measured by the Faraday method. Analysis (C, H, N) was carried out by Elemental Micro-analysis Laboratories Ltd. (Devon), England.

Nickel *O*-alkyl dithiocarbonates were prepared according to methods reported in the literature.[1]

Preparation of the Complexes.—$[Ni(S_2CO)(dppe)]$ (**1**). In a typical experiment $[Ni(S_2COR)_2]$ (R = Me) (1 mmol) and dppe (2 mmol) in acetone–chloroform (2:1) were stirred for 24 h. The solvent was removed to one-fifth of the volume at reduced pressure and the red solid formed was recrystallized from acetone to give (**1**) as red crystals, m.p. 201 °C (decomp.) (Found: C, 58.70; H, 4.45. $C_{27}H_{24}NiOP_2S_2$ requires C, 59.0; H, 4.35%).

$[Ni(S_2COEt)_2(dppe)]$ (**2**). When $[Ni(S_2COEt)_2]$ (0.1 mmol) and dppe (1 mmol) in $CHCl_3$ (5 cm^3) were stirred for 3 min, a solution was formed from which a red-brown solid was precipitated with light petroleum (b.p. 40—60 °C). The precipitate was filtered off, washed with light petroleum and dried under vacuum, m.p. 64 °C (decomp.) (Found: C, 54.05; H, 4.50. $C_{32}H_{34}NiO_2P_2S_4$ requires C, 54.95; H, 4.85%).

$[Ni(S_2COC_6H_{11})_2(dppe)]$, (**3**) *and* (**4**). $[Ni(S_2COC_6H_{11})_2]$ (0.1 mmol) was added to a stirred $CHCl_3$ solution of dppe (0.1 mmol). After 3 min a reddish-brown solid precipitated on addition of light petroleum which was filtered off, washed with light petroleum, and dried. After some hours a green solid was recovered from the solution, which was washed with ethanol and dried under vacuum; m.p. for (**3**) 98 °C (decomp.), m.p. for (**4**) 110 °C (decomp.) [Found for (**3**): C, 59.05; H, 5.65. $C_{40}H_{46}NiO_2P_2S_4$ requires C, 59.5; H, 5.70%. Found for (**4**): C, 59.35; H, 6.20. $C_{40}H_{46}NiO_2P_2S_4$ requires C, 59.35; H, 5.05%).

$[Ni(S_2COEt)_2(PMePh_2)_2]$ (**5**). $[Ni(S_2COEt)_2]$ and $PMePh_2$ (1:2 mol ratio) were stirred in $CHCl_3$ for 2 h. Removal of solvent and addition of EtOH with stirring for 3 or 4 min afforded a crystalline green solid, which was filtered off, washed with EtOH, dried under vacuum, and kept under N_2 at 0 °C, m.p. 58 °C (decomp.) (Found: C, 53.95; H, 5.0. $C_{32}H_{36}NiO_2P_2S_4$ requires C, 54.8; H, 5.15%).

$[Ni(S_2COC_6H_{11})_2(PMePh_2)]$ (**6**). $PMePh_2$(0.2 mmol) was added to a solution of $[Ni(S_2COC_6H_{11})_2]$ (0.1 mmol) in $CHCl_3$ (5 cm^3). After stirring for 4 min, light petroleum (b.p. 40—60 °C, 100 cm^3) was added. On standing at room temperature a dark brown solid crystallized which was filtered off, washed with light petroleum, and dried under vacuum, m.p. 60 °C (decomp.) (Found: 52.95; H, 5.55. $C_{27}H_{35}NiO_2PS_4$ requires C, 53.25; H, 5.75%).

$[Ni(S_2COEt)_2(PMe_2Ph)_2]$ (**7**). PMe_2Ph (0.2 mmol) and $[Ni(S_2COEt)_2]$ (0.1 mmol) in $CHCl_3$ were stirred for a few minutes and the solvent was removed to dryness. An ethanol–light petroleum (1:1) mixture was added to precipitate a red solid, which after filtration was washed with the same mixture and dried under vacuum. The compound was kept at 0 °C under N_2, m.p. 40 °C (Found: C, 44.9; H, 5.05. $C_{22}H_{32}NiO_2P_2S_4$ requires C, 45.8; H, 5.55%).

$[Ni(S_2COC_6H_{11})_2(PMe_2Ph)_2]$ (**8**). PMe_2Ph and $[Ni(S_2COC_6H_{11})_2]$ (2:1 mol ratio) were stirred in the minimum amount of acetone. After a few minutes the solvent was removed to dryness. The red solid obtained was treated with EtOH, filtered off, washed with EtOH, and dried. The product was kept at 0 °C under N_2, m.p. 96 °C (decomp.) (Found: C, 51.6; H, 6.15. $C_{30}H_{44}NiO_2P_2S_4$ requires C, 52.6; H, 6.4%).

Reaction of $[Ni(S_2CO)(dppe)]$ *with Allyl Bromide and Methyl Iodide.*—To a solution of $[Ni(S_2CO)(dppe)]$ (0.1 mmol) in $CHCl_3$ under N_2 an excess (3 cm^3) of alkyl halide was added. After reflux (1.5 h for allyl bromide and 10 min for methyl iodide), the solvent was removed to dryness. By addition of acetone a red solid was formed which after filtration was washed with acetone, dried under vacuum, and identified by elemental analysis and spectroscopic data as $[NiX_2(dppe)]$ (X = Br or I).

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