

INTERACTION OF DITERTIARY PHOSPHINES WITH PHENYL- AND 1-NAPHTHYLDITHIOCARBAMATONICKEL(II)

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The synthesis of the following mixed ligand complexes is reported: $[\text{Ni}(\text{phdtc})_2(\text{dpm})_2]$, $[\text{Ni}(\text{phdtc})_2(\text{dpe})_2]$, $[\text{Ni}(\text{phdtc})_2(\text{dpp})_3]$, $[\text{Ni}(1\text{-naphdtc})_2(\text{dpm})_2]$, $[\text{Ni}(1\text{-naphdtc})_2]$, and $[\text{Ni}(1\text{-naphdtc})_2(\text{dpp})_2]$, where $\text{phdtc} = \text{PhNHCSS}^-$, $1\text{-naphdtc} = 1\text{-NaphNHCSS}^-$, $\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\text{dpe} = \text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, and $\text{dpp} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$. The complexes are characterised by microanalysis, IR and UV-Vis spectra, magnetic measurements, conductivity, X-ray powder diffraction, and thermal analysis. All the mixed ligand complexes are diamagnetic, and thus a square-planar or square-pyramidal (low-spin) structure was proposed for the present complexes.

Our interest on the interaction of phosphines with 1,1-dithiolates¹ has prompted us to investigate the interaction of phosphines with bis(aryldithiocarbamato)nickel(II).

For quite some years have been dithiocarbamato metal complexes extensively studied². The ability of bis(dithiocarbamato)nickel(II) to interact with Lewis bases in order to expand their coordination is intermediate to the behaviour of nickel(II) xanthate complexes which interact strongly with Lewis bases and other 1,1- or 1,2-dithiolato complexes which are particularly unaffected with them².

Various mixed ligand complexes were obtained from the interaction of phosphines and $[\text{M}(1,1\text{-dithiolato})_2]$ ($\text{M} = \text{Ni}(\text{II}), \text{Pd}(\text{II}), \text{or Pt}(\text{II})$). Thus the reaction of xanthato, dithiophosphato, dithiocarbonato, and dithiophosphine complexes with phosphines gave rise to the following complexes: $[\text{M}(\text{S}_2\text{CO})(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{III}), \text{R} = \text{alkyl or aryl}$), $[\text{Ni}(\text{S}_2\text{COR})_2(\text{P}(\text{n-Bu}_3)_2)]$ ($\text{R} = \text{ethyl, isobutyl}$), $[\text{Pd}(\text{S}_2\text{P}(\text{O})\text{OEt})(\text{PR}_3)_2]$, $[\text{Pt}(\text{S}_2\text{CNR}_2)_2(\text{PR}_3)_2]$, and $[\text{M}(\text{S}_2\text{PR}_2)_2(\text{PR}_3)_2]$ ($\text{M} = \text{Pd}(\text{II}), \text{Pt}(\text{II}); \text{R} = \text{alkyl or aryl}$)^{3,4}. A complex of the formula $[\text{Pt}(\text{S}_2\text{CO})\text{-(diphos)}] \cdot 1/4 \text{CHCl}_3$ (diphos = 1,2-bis(diphenylphosphine)ethene) was isolated; its X-ray structure was analogous to the structure of $[\text{Pt}(\text{S}_2\text{CO})(\text{PPh}_3)_2]$ which had a *cis*- PtS_2P_2 chromophore^{3,4}.

In this paper we report the preparation and characterisation of some mixed ligand-complexes of bis(dithiocarbamato)nickel(II) with a series of diphosphines

in order to obtain more informations about the type of interaction between phosphines and 1,1-dithiolato metal(II) complexes.

RESULTS AND DISCUSSION

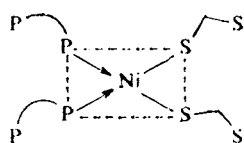
Bis(phenyldithiocarbamato)nickel(II) and bis(1-naphthyldithiocarbamato)nickel(II) interact with some ditertiary phosphines, namely bis(diphenylphosphine)methane (dpm), 1,2-bis(diphenylphosphine)ethane (dpe), and 1,3-bis(diphenylphosphine)propane (dpp) to give the corresponding mixed ligand complexes according to the reaction $2 \text{ Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2 + [\text{Ni}(\text{RNHCSS})_2] \rightarrow [\text{Ni}(\text{RNHCSS})_2(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]$ ($\text{R} = \text{Ph}$ or 1-Naph; $n = 1, 2, 3$).

It is of interest to note that mixing a 1 : 1 molar ratio of acetone solutions of bis(dithiocarbamato)nickel(II) and chloroform solutions of phosphines led to the formation of mixed ligand complexes in which two phosphine molecules were bound to the nickel(II) instead of one molecule. The change of the green colour of bis(dithiocarbamato)nickel(II) to an orange colour upon addition of phosphine took place immediately in all the complexes, except with dpm, where the colour has been changed after 24 h. The isolated complexes were orange or yellow in colour; they were moderately soluble in chloroform and acetone, soluble in nitrobenzene and DMSO. They were found to be quite stable in air. The analytical data and colour are shown in Table I.

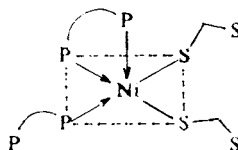
The new complexes present characteristics of both dithiocarbamates and phosphines. The IR spectra of the parent bis(dithiocarbamato)nickel(II) complexes exhibited the $\text{C}\equiv\text{N}$ band at $1\,375\text{--}1\,390\text{ cm}^{-1}$, while $\text{C}\equiv\text{S}$ at $995\text{--}1\,000\text{ cm}^{-1}$ (ref. ^{2,5}). The isolated mixed ligand complexes showed some changes in IR spectra concerning $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{S}$ bands, which may suggest that the dithiocarbamate ligand has changed its coordination mode upon interaction with phosphines. This was manifested by the apparent reduction of the intensity of the $\text{C}\equiv\text{N}$ band, though the position of this band in the mixed ligand complexes remained almost at the same position as in the parent dithiocarbamate complexes. Moreover, the band at $c. 1\,000\text{ cm}^{-1}$ corresponding to $\text{C}\equiv\text{S}$ vibration is splitted up in two bands with a difference of $c. 30\text{ cm}^{-1}$ indicating the presence of two different $\text{C}\equiv\text{S}$ moieties (Table II). Consequently, we have concluded that the dithiocarbamate anion acts in these complexes as a monodentate ligand. This type of coordination was known in related complexes. In complexes of the formula $[\text{Ni}(\text{S}_2\text{COR})_2(\text{PR}_3)_2]$ and $[\text{Pt}(\text{S}_2\text{CNR}_2)_2(\text{PR}_3)_2]$ the dithiolate anions act as unidentate ligands; this conclusion came from the X-ray analysis of these complexes^{3,4}. The new bands which appeared in the range $720\text{--}790\text{ cm}^{-1}$ in all complexes were indicative of a phosphine coordination. These absorptions lie in the region of $\text{—CH}_2\text{—}$ (rocking) and PPh_2 -frequencies.

Magnetic susceptibility measurements in the temperature range $80\text{--}340\text{ K}$ indicated the diamagnetic nature of these compounds; a square-planar or low spin square-pyramidal stereochemistry can therefore be suggested.

The low conductivity values for these complexes in nitrobenzene at 25°C showed that they behave as non-electrolytes. In fact, accepting the general formula $[\text{Ni} \cdot (\text{S}_2\text{CNHR})_2 (\text{dpph})_2]$ of the isolated complexes and the diamagnetic behaviour of them, it is not possible to formulate the structures without assuming that either both phosphine molecules are monodentate in case of square planar structure (I) or one of the phosphine ligands is monodentate while the remaining one is bidentate in case of square-pyramidal structure (II)



I



II

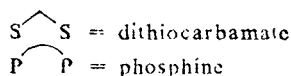


TABLE I

Analytical results and colour for complexes prepared

No	Complex	Colour	% C	% H	% S
			calc. found	calc. found	calc. found
1	[Ni(phdte) ₂ (dpm) ₂]	yellow	66.03	4.84	11.01
			65.71	5.03	11.41
2	[Ni(phdte) ₂ (dpe) ₂]	orange	66.50	5.07	10.70
			66.01	4.90	11.11
3	[Ni(phdte) ₂ (dpp) ₂]	orange	66.90	5.28	10.51
			66.20	4.92	11.01
4	[Ni(1-naphdte) ₂ (dpm) ₂]	yellow	68.40	4.78	10.14
			67.80	4.31	10.66
5	[Ni(1-naphdte) ₂ (dpe) ₂]	orange	68.78	4.95	9.92
			68.11	4.35	10.40
6	[Ni(1-naphdte) ₂ (dpp) ₂]	orange	69.14	5.19	9.71
			68.72	5.01	10.11

Monodentate, mixed bidentate and monodentate, and mixed bidentate and bridging phosphines were suggested for some nickel(II) phosphine complexes⁶.

The electronic spectra in chloroform solutions for all the complexes were not different from those obtained in the solid state (nujol mull) which may indicate no change in the coordination geometry of the complexes upon dissolution in chloroform (Table II). Only a slight shift of some of the bands was observed which may be due to solvent effect. Moreover, no colour change was noticed in chloroform solutions.

Assuming a square-planar structure around the nickel(II) we could assign the bands in the range 21 920–23 360 cm^{-1} and in the range 18 860–20 400 cm^{-1} as $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ transitions, respectively⁷.

In all complexes investigated the band at *c.* 29 000 cm^{-1} can be assigned to nickel–phosphorous charge transfer⁶. This was shifted to higher energy from phenyldithiocarbamato to 1-naphthyldithiocarbamato complexes (Table III). It is to be noted that the relatively high intensity of the *d*–*d* bands in the electronic spectra of these complexes are ascribed to the strong π -interaction of nickel–phosphorous and/or nickel–sulphur linkage^{4,7}.

The bands occurring in the range 33 000–38 000 cm^{-1} are tentatively assigned to π – π^* transition. A charge transfer origin for some of them is also a possible⁸.

We have attempted to prepare the corresponding complexes with triphenylphosphine (tpp) from the interaction of 1 : 2 acetone solutions of the bis(dithiocarbamato) nickel(II) and a chloroform solution of tpp. After a period of about two days a red colouration was developed indicating the formation of a new compound, but it was not possible to isolate the products. A similar situation was reported on the reaction between bis(ethylxanthato)nickel(II) and triphenylphosphine in 1 : 2 molar ratio, where a red colour appeared and the reaction product could not be isolated⁴. Evaporating the solution till dryness gave impure products, which are diamagnetic,

TABLE II
Main IR absorption bands (cm^{-1}) of the complexes

Compound						Assignment
1	2	3	4	5	6	
990	990, 1 000	990, 1 020	990, 1 010	990, 1 020	990, 1 010	$\nu(\text{C}=\text{S})$
1 380	1 390	1 390	1 390	1 385	1 390	$\nu(\text{C}=\text{N})$
770, 780	710, 760	740, 750 780	740	770, 780	770, 790	$\nu(\text{Ph}_2\text{P}^+)$ $\rho(-\text{CH}_2-)$
—	380	380, 420	—	380, 410	380, 410	$\nu(\text{Ni}-\text{S})$

having splitted C=S bands at about $1\,000\text{ cm}^{-1}$ and in the visible region having characteristic bands of square-planar complexes.

Table IV gives the X-ray powder diffraction spectra of compounds 2, 3, 5 and 6. The X-ray powder patterns of bis(diphenylphosphine)ethanenickel(II) chloride, bis(phenyldithiocarbamato)nickel(II), and bis(2-naphthyldithiocarbamato)nickel(II) were also included in the Table IV for comparison. Consideration of the d values suggests that the compounds 2, 3, 6 are nearly isomorphous with the parent complexes for which on the basis of spectroscopic data a square-planar structure were assumed^{5,9}. The X-ray powder pattern for 5 was considerably different from the others and had a different pattern. This may suggest that compound 5 (and may be others) has a square-pyramidal structure.

TABLE III

Electronic spectral maxima of the complexes prepared and their assignments (in cm^{-1})

Compound	λ_{max} (solution)	λ_{max} (mull)	Tentative assignment
1	23 360	22 220	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	30 670	29 230	charge transfer
	32 890	—	$\pi \rightarrow \pi^*$
	39 060	—	$\pi \rightarrow \pi^*$
2	20 400	20 740	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	23 250	22 720	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	31 840	29 230	charge transfer
	36 490	—	$\pi \rightarrow \pi^*$
3	19 840	—	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	22 220	23 250	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	—	31 060	charge transfer
	34 480	33 110	$\pi \rightarrow \pi^*$
	37 590	—	$\pi \rightarrow \pi^*$
4	17 540	17 540	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	18 860	18 860	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	35 970	—	$\pi \rightarrow \pi^*$
	37 030	—	$\pi \rightarrow \pi^*$
5	19 840	19 600	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	32 050	30 300	charge transfer
	37 030	35 970	$\pi \rightarrow \pi^*$
6	19 600	—	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	21 920	—	${}^1A_{1g} \rightarrow {}^1B_{1g}$
	35 970	—	$\pi \rightarrow \pi^*$

TABLE IV
X-Ray powder patterns (*s*-spacings, pm)^a

[Ni(phdte) ₂ (dpe) ₂]	[Ni(phdte) ₂ · (dpp) ₂]	[Ni(1-naphdte) ₂ · dpe] ₂	[Ni(1-naphdte) ₂ · dpp] ₂	[Ni(phdte) ₂]	[Ni(1-naphdte) ₂]	[Ni(dpe)Cl ₂] ^b
982 w	1 105 vs	1 105 vs	1 105 vs	1 105 vs	1 606 S	982 m
737 m	737 w	88 vw	88 vw	—	881 w	804 w
680	680 m	680 w	680 w	680 w	737 w	—
632 w	553 m	632 w	632 w	632 s	680 w	632 s
553 w	467 m	590 w	590 w	553 w	590 m	590 w
467 s	443 w	443 m	443 m	443 m	—	553 w
443 m	423 s	423 s	423 s	—	467 w	467 w
423 w	342 s	370 w	370 w	271 w	388 w	404 m
404 w	271 w	250 w	250 w	249 w	330 w	—
		diffused pattern				

^a Intensities were estimated visually. ^b Prepared according to reference⁹.

The ^1H NMR spectra of the complexes in deuterated chloroform showed a multiplet at $\delta = 6.7\text{--}7.8$ ppm attributed to the phenyl groups in both phosphine and dithiocarbamates. The multiplet at $\delta = 1.4\text{--}2.4$ ppm is related to $-(\text{CH}_2)_n-$ of phosphines in the mixed ligand complexes.

Thermogravimetric and differential thermal analysis were performed on two of the compounds, *i.e.* compounds 2, 3 as representative. A weight loss occurring in the range $150\text{--}170^\circ\text{C}$ corresponds to about 10% loss as PhNHCSSH . The corresponding DTA peak occurred as a strong endothermic peak in the temperature range $130\text{--}180^\circ\text{C}$. Dithiocarbamic acid might be formed from a proton loss of one of the phosphine molecules in the complexes and a dithiocarbamate anion; an organometallic compound is thus assumed to be formed in this temperature range. Further, three exothermic peaks in the DTA curves were recorded in the temperature range 200 to 220, 400–430, and $530\text{--}550^\circ\text{C}$. The corresponding temperature ranges in TGA curves were characterised by a continuous weight loss without giving any conclusive informations.

EXPERIMENTAL

All chemicals were of analytical grade. Magnetic susceptibilities were determined in the temperature range $80\text{--}340$ K by the Gouy method. The calibrant used was $\text{Hg}[\text{Co}(\text{CNS})_4]$. IR spectra ($4000\text{--}200\text{ cm}^{-1}$) were obtained using KBr pellets with a Perkin-Elmer 599B recording spectrophotometer. Electronic spectra in chloroform solutions were obtained with a Shimadzu UV-200S and matched 1.0 cm quartz cells. Nujol mull spectra were recorded on a Cary Model 219 spectrophotometer. Conductance measurements were done on fresh solutions (10^{-3} M) at 25°C using nitrobenzene as solvent in a YSI 31 conductivity bridge. ^1H NMR spectra were recorded on a Varian EM-360 60 MHz spectrometer with tetramethylsilane as an external standard. Thermal gravimetric analysis and differential thermal analysis were determined with a Shimadzu TGA-30H and DTA-30H recording thermobalance. Powder diffraction patterns were recorded on Riga-Ku X-ray Diffractometer using the Cu K_α radiation.

The parent complexes, namely bis(phenyldithiocarbamato)nickel(II) and bis(1-naphthyldithiocarbamato)nickel(II) were prepared as previously reported in the literature^{2,5}.

All the mixed ligand complexes were obtained by reaction of the parent phenyl- and 1-naphthyldithiocarbamato complexes dissolved in acetone with the phosphine ligands dissolved in chloroform in the stoichiometric ratio 1 : 1. An orange colour were developed immediately except with the two mixed ligand complexes of bis(diphenylphosphine)methane, where the orange colour were observed after 24 h. The complexes were precipitated by adding diethyl ether to the reaction mixtures, filtered off, washed with acetone and dried over P_2O_5 .

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