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Transition Metal Complexes of Organo-thiophosphorus Ligands. I. Nickel(II) Chelates of Some New Diphenylthiophosphinyl Thioureas

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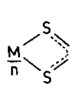
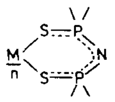
Some new diphenylthiophosphinyl thioureas $Ph_2P(S)NHC(S)NR'R''$ ($R' = H$, $R'' = \alpha$- and β-naphthyl, m-tolyl and $NR'R''$ = piperidyl) were prepared. They form nickel(II) chelates, which have been characterized by infrared and electronic spectra. Two isomeric forms of β-naphthyl derivatives were isolated, both showing anomalous magnetic behaviour. The electronic structure of the chelate ring is discussed on the basis of infrared spectral data.

Introduction

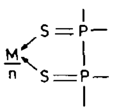
Various types of chelating ligands, attached to the metal through sulphur atoms, were extensively investigated in recent years[1–4]. The interest towards such types was stimulated by the promotion of unusual coordination at the metal and/or interesting stereochemistry of the chelate ring. Among such ligands were dithiolenes, dithioacetylacetone, dithiocarbamates, xanthates, dithiocarboxylates and related types[1,2]. An interesting feature, not enough stressed in the past, was the formation of carbon-free chelate rings, with such ligands as dithiophosphates[5] and dithiophosphinates[6] (**I**), dithiophosphoryl imides[7] (**II**) or dithiodiphosphines[8] (**III**).



I

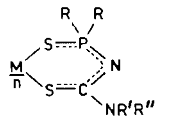


II



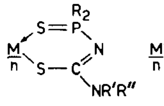
III

Thiophosphinyl thioureas, $R_2P(S)NHC(S)NR'R''$, hold an intermediate position by forming chelate rings with five different elements in the six-membered ring, only one of them being a carbon atom (**IV**).

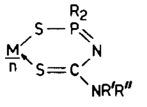


IV

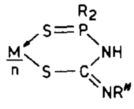
Although the chelate ring in **IV** was depicted as delocalized, the contribution of various canonical structures (**IVa–IVc**) may be rather different, depending on the nature of the substituents and, perhaps, of the metal.



IVa

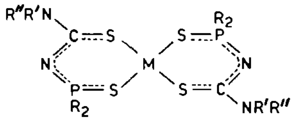


IVb



IVc

The literature of thiophosphinyl thiourea chelates is very scarce. Some nickel(II) chelates (**V**) were described recently[9–12]: R = Ph; R′, R″ = H or Me[9]; R′ = H, R″ = Ph[10,11]; R′ = R″ = Me[11], Et[10,11]; R′ = H, R″ = p-$MeOC_6H_4$[12].



V

In all these cases the nickel(II) chelates are diamagnetic; this behaviour and their electronic spectra suggest a square planar coordination.

In order to study the influence of various substituents (R′ and R″) we have prepared some new thiophosphinyl thioureas as ligands with various steric and electronic requirements, having R′ = H, R″ = α- and β-naphthyl, m-tolyl, and NR′R″ = piperidyl. For comparison the known derivative with R′ = H, R″ = Ph[11,12] was also prepared and investigated.

Experimental

Analytical grade reagents were used in the syntheses. Elemental analyses (carbon, hydrogen) were performed by the Microanalytical Laboratory of the Chemical Institute MEI, Cluj-Napoca (Romania) and phosphorus was determined by the microgravimetric method

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as ammonium molybdophosphate. Infrared spectra were recorded on a UR-20 Carl Zeiss, Jena spectrophotometer, solution electronic spectra on a Spekord UV–VIS Carl Zeiss, Jena instrument and the diffuse reflectance spectra were determined point by point and plotted manually using a VSU-2 Carl Zeiss, Jena instrument. Magnetic moments were determined with a Faraday balance. Melting points are uncorrected. Acetonitrile used as solvent was purified and dried by distillation over phosphorus(V) oxide.

Preparation of the Ligands

3-Diphenylthiophosphinyl-1-α-naphthyl-thiourea (TPTUNp-α)

Diphenylthiophosphine chloride, prepared from 10 g diphenylchlorophosphine and 1.36 g elemental sulphur, was diluted with 10 ml dry acetonitrile, treated in portions with 3.45 g NH_4SCN dissolved in acetonitrile and stirred for 2 hr. The precipitate of NH_4Cl formed was filtered and the filtrate was treated with a solution of 6.4 g α-naphthylamine, dissolved in diethyl ether. After 3 hr of stirring the precipitate formed was filtered and washed with diethyl ether. Recrystallization from ethanol gave fine white crystals, insoluble in water, scarcely soluble in ethanol, very soluble in chloroform, carbon tetrachloride and acetone. Yield 8.8 g (47%), m.p. 161–2° C. Found: C 66.1, H 4.2, P 6.7%. Calcd. for $C_{23}H_{19}N_2S_2P$: C 65.9, H 4.5, P 7.4%.

3-Diphenylthiophosphinyl-1-β-naphthyl-thiourea (TPTUNp-β)

This ligand was prepared as above, using β-naphthylamine. The yield was 12.6 g (65%), m.p. 122–4° C. Found: C 65.9, H 4.4, P 6.8%. Calcd. for $C_{23}H_{19}N_2S_2P$: C 65.9, H 4.5, P 7.4%. The compound is soluble in chloroform and carbon tetrachloride, insoluble in water and diethyl ether, slightly soluble in ethanol.

3-Diphenylthiophosphinyl-1-m-tolyl-thiourea (TPTUTol)

Diphenylchlorophosphine (5 g) was treated with 0.68 g elemental sulphur and heated on an oil bath at *ca.* 120° C until complete dissolution, then cooled and diluted with 8 ml dry acetonitrile, followed by treatment with 1.74 g NH_4SCN dissolved in 30 ml acetonitrile. The mixture was heated to reflux, then cooled and treated with 2.5 g *m*-toluidine, heated again for 30 min with stirring, filtered and concentrated to deposit white crystals, m.p. 136–7° C. The yield was 75.2%. Found: C 63.1, H 5.1, P 7.2. Calcd. for $C_{20}H_{19}N_2S_2P$: C 63.2, H 5.0, P 8.1%.

3-Diphenylthiophosphinyl-1-pentamethylene-thiourea (TPTUPip)

Addition of 2 g piperidine to $Ph_2P(S)NCS$ prepared as above from 5 g diphenylchlorophosphine, resulted in a temperature increase to 45° C. The mixture was stirred for 0.5 hr, then cooled and the solvent removed to leave a viscous residue. A small part of this was treated with butanol to separate white crystals, m.p. 181–2° C. Found: P 9.4%. Calcd. for $C_{18}H_{21}N_2S_2P$: P 9.4%. The rest of the compound was used for the preparation of the nickel(II) chelate without further purification, as described below.

3-Diphenylthiophosphinyl-1-phenylthiourea (TPTUPh)

Diphenylthiophosphine chloride, prepared from 10 g diphenylchlorophosphine and elemental sulphur, was diluted with 50 ml dry benzene, and 4.4 g KSCN was added. The mixture was refluxed with stirring for 40 hr, then 4.2 g aniline was added, and the system was refluxed for another 1.5 hr. The mixture was cooled, then poured into cold water. A viscous, heavy deposit was formed, which solidified after removal of the aqueous layer and treatment with ethanol. Recrystallization from ethanol gave a white solid, m.p. 148° C. The yield was 4.0 g (24%). Found: P 7.5%. Calcd. for $C_{19}H_{17}N_2S_2P$: P 7.6%.

Preparation of the Nickel(II) Chelates

Bis-[3-(diphenylthiophosphinyl)-1-α-naphthyl-thioureato]nickel(II), Ni(TPTUNp-α)₂

A warm ethanolic solution containing 1.5 g TPTUNp-α was treated with an ethanolic solution containing 0.44 g $Ni(OCOCH_3)_2 \cdot 4H_2O$. On cooling a peas-green crystalline precipitate was formed, which was filtered, washed with ethanol and dried. M.p. 128–30° C, yield 76.5%. Found: P 6.2%. Calcd. for $C_{46}H_{36}N_4S_4P_2Ni$: P 6.9%.

Bis-[3-(diphenylthiophosphinyl)-1-β-naphthyl-thioureato]nickel(II), Ni(TPTUNp-β)₂

An ethanolic solution containing 0.5 g $Ni(OCOCH_3)_2 \cdot 4H_2O$ was treated with a warm solution of 1.7 g TPTUNp-β in ethanol. On cooling, a dark green precipitate was formed, Ni(TPTUNp-β)$_2$, I. This was washed with ethanol and dried. Yield 0.7 g, m.p. 121–3° C. Found: C 61.6, H 4.0, P 6.6%. Calcd. for $C_{46}H_{36}N_4S_4P_2Ni$: C 61.7, H 4.3, P 6.9%.

An additional amount of solid deposited was treated with acetone, to give a light peas-green crystalline precipitate, which was washed with acetone and dried to give 0.65 g Ni(TPTUNp-β)$_2$, II, m.p. 135–40° C. Found: C 61.4, H 4.2, P 6.8%. Calcd. for $C_{46}H_{36}N_4S_4P_2Ni$: C 61.7, H 4.3, P 6.9%.

Bis-[3-(diphenylthiophosphinyl)-1-m-tolyl-thioureato]Nickel(II), Ni(TPTUTol)₂

A solution of 0.5 g TPTUTol in chloroform was stirred with an aqueous solution of $Ni(OCOCH_3)_2 \cdot 4H_2O$ (0.16 g) at room temperature. The green organic layer was separated, dried over anhydrous $CaCl_2$ and the solvent was evaporated to leave a pale green solid. This was redissolved in chloroform and reprecipitated with petroleum ether, then filtered and dried. M.p. 115° C. Found: P 7.3%. Calcd. for $C_{40}H_{56}N_4S_4P_2Ni$: P 7.5%.

Bis-[3-(diphenylthiophosphinyl)-1-pentamethylenethioureato]nickel(II), Ni(TPTUPip)$_2$

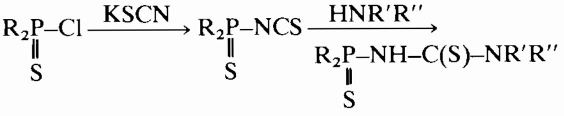
The viscous product from the synthesis of TPTUPip was dissolved in chloroform, and this solution was stirred with an excess of aqueous nickel(II) acetate solution. A yellow–brown organic layer was formed, which was separated, dried over $CaCl_2$ and precipitated with petroleum ether to give a yellow–brown solid, m.p. 90° C (dec.). Found: P 8.7%. Calcd. for $C_{36}H_{40}N_4S_4P_2Ni$: P 7.9%.

Bis-[3-(diphenylthiophosphinyl)-1-phenylthioureato]nickel(II), Ni(TPTUPh)$_2$

A warm alcoholic solution of TPTUPh was mixed with the stoichiometric amount of nickel(II) acetate in aqueous solution. On cooling, the nickel(II) chelate precipitated as long, dark green needles, m.p. 200° C, identical with the compound reported in the literature.

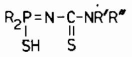
Results and Discussion

The new ligands prepared, their abbreviations and their typical infrared bands are listed in Table I. The ligands were synthesised by the addition of a primary amine or piperidine to diphenylthiophosphinyl thiocyanate in acetonitrile, according to a procedure described previously for related compounds[12] (R = Ph):



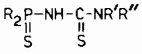
$$\underset{\underset{S}{\|}}{R_2P}\text{–Cl} \xrightarrow{KSCN} \underset{\underset{S}{\|}}{R_2P}\text{–NCS} \xrightarrow{HNR'R''} \underset{\underset{S}{\|}}{R_2P}\text{–NH–C(S)–NR'R''}$$

Three tautomeric forms (**VI–VIII**) are possible for the free ligand. The infrared spectra suggest the predominance of the tautomeric form **VII**:



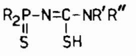
$$\underset{\underset{SH}{|}}{R_2P}\text{=N–}\underset{\underset{S}{\|}}{C}\text{–NR'R''}$$

VI



$$\underset{\underset{S}{\|}}{R_2P}\text{–NH–}\underset{\underset{S}{\|}}{C}\text{–NR'R''}$$

VII



$$\underset{\underset{S}{\|}}{R_2P}\text{–N=}\underset{\underset{SH}{|}}{C}\text{–NR'R''}$$

VIII

Thus, the lack of bands characteristic of $\nu_{P=N}$ in the region around 1300 cm^{-1} indicates the absence of P=N double bonds and insignificant contribution of structure **VI.** Also, no band characteristic of ν_{SH} was observed, which seems to eliminate both structures **VI** and **VIII** (although SH stretching vibrations are not always easily detected). The ν_{PN} frequency is shifted to lower values (975–1002 cm^{-1}) which indicates a single bond character of the P–N bond, as shown by either structures **VII** or **VIII.** Structure **VII** is supported also by the ν_{CN} bands, which are shifted to lower values (1500–1470 cm^{-1}) than those corresponding to a double bond C=N.

Alcoholic solutions of diphenylthiophosphinyl thioureas react with aqueous or alcoholic solutions of nickel(II) acetate to form green complexes, which often precipitate or are extracted in chloroform, as described in the Experimental part. With TPTUNp-β two isomeric compounds were obtained when treating an ethanolic solution of Ni(II) acetate with an ethanolic solution of the ligand: a dark green one Ni(TPTUNp-β)$_2$, I, and a light green one, Ni(TPTUNp-β)$_2$, II, differing in their melting points, but having the same composition and almost identical infrared spectra. In acetone solution the isomer I was converted into the isomer II. The nickel(II) chelates prepared in this work are listed in Table II; their infrared and electronic spectra, and their magnetic properties are discussed below.

Infrared Spectra

Only the absorption bands due to groups involved in the formation of the chelate ring are discussed.

TABLE I. Diphenylthiophosphinylthioureas Used in This Work.

Compound	Abbreviation	Typical IR Bands		
		ν_{PN}	ν_{PS}	ν_{CN}
$Ph_2P(S)NHC(S)NHC_{10}H_7$-$\alpha$	TPTUNp-α	1002s	638m 615m	1470s
$Ph_2P(S)NHC(S)NHC_{10}H_7$-$\beta$	TPTUNp-β	995s	632m 615m	1495s
$Ph_2P(S)NHC(S)NHC_6H_4Me$-*m*	TPTUTol	985s	630m 615m	1493s
$Ph_2P(S)NHC(S)NC_5H_{10}$	TPTUPip	980sh	618m 598m	1485m
$Ph_2P(S)NHC(S)NHPh$	TPTUPh	975s	630m 615m	1500s

TABLE II. Infrared Spectra of Ni(II) Diphenylthiophosphinylthioureates.

Compound	ν_{PN} cm^{-1}	ν_{PS} cm^{-1}	ν_{CN} cm^{-1}	ν_{MS}[a] cm^{-1}
Ni(TPTUNp-α)$_2$	1010s	591s	1485s	402w
Ni(TPTUNp-β)$_2$, I	1015s	590s	1492s	404w
Ni(TPTUNp-β)$_2$, II	1018s	585s	1492s	401w
Ni(TPTUTol)$_2$	1000m	590m	1502s	b
Ni(TPTUPip)$_2$	1008m	577m	1545m	405w
Ni(TPTUPh)$_2$[c]	996s	590s	1504s	420w

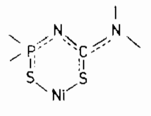
[a] Since the limit of our instrument was 400 cm^{-1} these bands cannot be assigned with full certainty. [b] Not observed.
[c] See also refs. 10, 11.

Significant changes are observed in the infrared spectra as a result of chelation and some information concerning the structure of the ring can be deduced from them. The infrared spectral data of Ni(II) chelates are listed in Table II.

The ν_{PN} bands in the Ni(II) chelates are shifted (*ca.* 20 cm^{-1}) to higher wavelengths, thus indicating an increase in the PN bond order, as compared with the free ligand. The doublet in the region between 650–600 cm^{-1}, observed in the free ligand and assigned to ν_{PS}, is shifted by complex formation to lower values, and occurs at *ca.* 590 cm^{-1} as a single band of strong or medium intensity. The metal–sulphur bond formation weakens the PS bond, reducing its bond order, which results in a lower infrared absorption frequency.

The ν_{CN} band in the region around 1500 cm^{-1} is close to the vibration frequency due to C=N (double) bond. The increase of this frequency due to coordination is not large, because the double bond character can be distributed among endocyclic and exocyclic C–N bonds, when R′ = H in the ligand, as shown by the superposition of structures **IVa** and **IVc**, perhaps involving to some extent the lone electron pair of one of the exocyclic nitrogens. In the case of Ni(TPTU Pip)$_2$, where exocyclic double bond formation is not possible and structure **IVc** is eliminated, the shift of ν_{CN} by coordination is the most dramatic (*ca.* 60 cm^{-1}) and the CN bond order within the ring is larger. For this complex the contribution of structure **IVa** is much more significant than in previous cases.

The infrared data clearly indicate that chelate ring formation results in observable bond order changes, thus suggesting a redistribution of the electron density along the S–P–N–C–S group involved in ring closure with the metal, with some π electron delocalization in the ring. The different electronegativities of the ring atoms prevent an uniform π electron distribution within the ring, and therefore describing the ring as "aromatic" would be an exaggeration. With this in mind the structure of the chelate ring can be depicted by a delocalized representation, **IX**, with a certain degree of confidence:



IX

Electronic Spectra and Magnetic Properties

Electronic spectra were recorded either in chloroform solution or in solid state (diffuse reflectance spectra (Fig. 1, 2)). The data for solution spectra (Fig. 3) are listed in Table III. These data suggest a square-planar coordination around nickel in solution and the identity of the coordination sites in the isomers I and II derived from the β-naphthylamino ligand.

The diffuse reflectance spectra for Ni(TPTUNp-β)$_2$, I and II (Figure 1), Ni(TPTUTol)$_2$ and Ni(TPTUNp-α)$_2$ (Figure 2) are poorly resolved and do not exhibit clearly defined maxima, which makes the spectrum analysis rather difficult. Some of the chelates show an "anomalous" magnetic behaviour in solid state; the observed magnetic moments at room temperature were: Ni(TPTUNp-β)$_2$, I, 1.3 B.M., Ni (TPTUNp-β)$_2$, II, 2.4 B.M. and Ni(TPTUPip)$_2$ 1.24 B.M. All other Ni(II) chelates investigated in this work were diamagnetic. For a tetrahedral Ni(II) complex the magnetic moment is in the range 3.6–4.00 B.M. The value of μ_{eff} = 1.3 B.M. would correspond to a crystal containing the tetrahedral (paramagnetic)

TABLE III. Electronic Spectra of Ni(II) Chelates in CHCl$_3$ Solution.

Compound	ν_{max} kK	ε M^{-1} cm^{-1}	Oscillator Strength M^{-1} cm^{-1}
Ni(TPTUNp-β)$_2$, I	15.7	244	3.36×10^{-6}
	17.9	204	3.58×10^{-6}
Ni(TPTUNp-β)$_2$, II	15.7	206	3.02×10^{-6}
	17.9	174	2.80×10^{-6}
Ni(TPTUTol)$_2$	15.8	43.7	4.62×10^{-7}
	18.5	33.4	4.15×10^{-7}

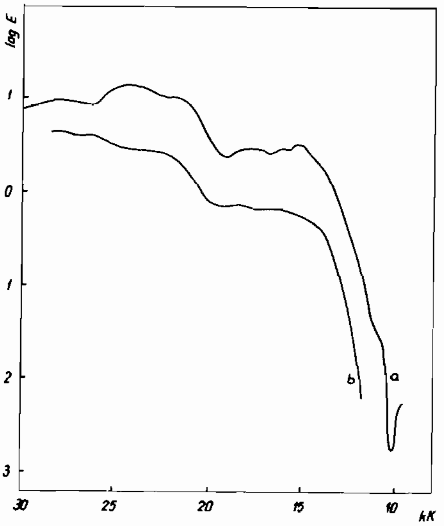


Figure 1 Diffuse reflectance spectra of Ni(TPTUNp-β)$_2$ I (curve a) and II (curve b)

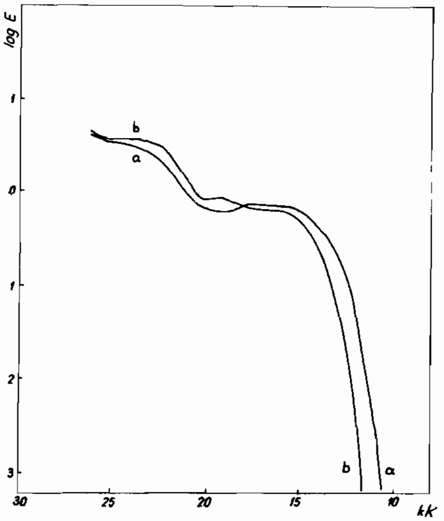


Figure 2 Diffuse reflectance spectra of Ni(TPTUTol)$_2$ (curve a) and Ni(TPTUNp-α)$_2$ (curve b)

and square-planar (diamagnetic) forms in a 1 2 ratio, whereas the value of 2 4 B M would indicate a reversed (2 1) ratio between the tetrahedral and square planar forms The occurrence of both forms in the solid state is not completely unexpected since the NiS$_4$ chromophore is usually square-planar but in the structurally related chelate ring (**X**) the nickel(II) atom is tetrahedrally coordinated as found by an X-ray structure determination[13] In fact compound **X** is so far the only reported tetrahedral Ni(II) complex containing the NiS$_4$ chromophore

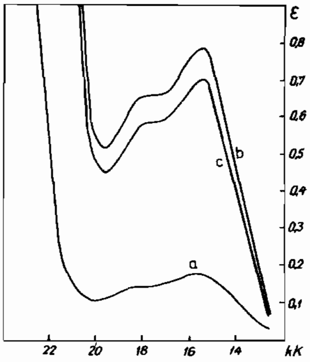
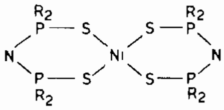


Figure 3 Solution electronic spectra of Ni(TPTUTol)$_2$ (curve a) Ni(TPTUNp-β)$_2$ I (curve b) and Ni(TPTUNp β)$_2$ II (curve c)



X

It seems from the data presented that the above chelates have different geometry in solution and in solid state Thus in solution square-planar coordination around nickel(II) occurs whereas in the solid state both tetrahedral and square-planar species seem to be present simultaneously This would explain the poor resolution of the diffuse reflectance spectra (resulting from the superposition of two types of spectra with close broad bands) The isomerism of Ni(TPTUNp-β)$_2$ I and II may be therefore a solid state effect The bulky β-naphthyl groups may also contribute to the occurrence of such an isomerism by adopting different orientations towards the rest of the molecule and forcing – *via* packing forces – a change in the coordination geometry favoured by the small energy difference between the tetrahedral and square-planar configurations However, our data do not permit a definite proof of this hypothesis

Acknowledgements

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