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Transition Metal Complexes of Organothiophosphorus Ligands. II.[a] Cobalt(II) Chelates of Some Diphenylthiophosphinyl Thioureas

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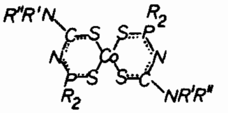
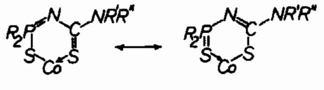
Diphenylthiophosphinyl thioureas, $Ph_2P(S)NH–C(S)NR'R''$, form cobalt(II) chelates, which have been characterised by infrared and electronic spectra. The electronic structure of the chelate ring is discussed on the basis of infrared spectral data.

Introduction

In Part I of this series[1] we have reported the synthesis of some new diphenylthiophosphinyl thioureas and their nickel(II) chelates. This paper reports the use of the same ligands in the synthesis of cobalt(II) chelates and the investigation of their structural features by means of infrared and electronic spectroscopy and magnetic properties.


I

Cobalt(II) chelates of thiophosphinyl thioureas (I) have been previously prepared only in small number, with $R = Ph$, $R' = H$, $R'' = Me$[2]; $R' = R'' = Me$[2,3] and $R' = R'' = Et$[3,4]. The compound with $R' = H$, $R'' = Ph$ was investigated only in solution and has not been isolated in solid state[3]. These chelates were found to have tetrahedral configuration at the cobalt site[3]. It appears from infrared data that the contribution of the canonic form IIb to the electronic structure of the chelate ring is predominant:


IIa IIb

However, the infrared spectra were not investigated in detail.

In this work we have investigated some new cobalt(II) chelates of diphenylthiophosphinyl thioureas, in order to obtain some information concerning the influence of the side groups (NR'R'') upon the electronic structure of the chelate ring.

Experimental

The synthesis of the new ligands used in this work was described in Part I of this series[1]. Other reagents used were of analytical grade purity.

Infrared spectra were recorded in KBr pellets, on a UR-20 Carl Zeiss, Jena, spectrometer, in the range 1600–400 cm^{-1}, where all significant bands were expected. The electronic spectra were recorded in chloroform solution on a Spekord UV–VIS (C. Zeiss, Jena) instrument. Magnetic moments were determined in the solid state by the Faraday method. Elemental analyses (C, H) were made by the Microanalytical Laboratory of the Chemistry Institute, Cluj-Napoca (Romania), and the phosphorus content was determined by the microgravimetric method, as ammonium molybdophosphate.

*Bis-[-3-(diphenylthiophosphinyl)-1-phenylthioureato] cobalt(II), Co(TPTUPh)$_2$**

This compound was prepared from the sodium salt of the ligand (obtained by treating equivalent amounts of sodium ethoxide and ligand in dry ethanol) and cobalt(II) acetate in aqueous solution. The cobalt(II) chelate precipitated almost quantitatively as a light green solid. The crystalline precipitate was filtered, washed with cold ethanol and diethylether and dried. M.p. 104° C. Found: P 7.5%. Calcd. for $C_{38}H_{32}N_4S_4P_2Co$, P 7.85%. The green crystals are insoluble in water, but readily soluble in chloroform, acetone and methylethylketone.

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* See the explanation of abbreviations used in the Discussion.

Bis-[-3-(diphenylthiophosphinyl)-1-α-naphthylthioureato]cobalt(II), Co(TPTUNp-α)₂

The ligand (1 g) was dissolved in chloroform and the solution was treated with an excess of aqueous solution of cobalt(II) acetate, and stirred. The organic layer gradually turned green. The green layer was separated, dried over anhydrous Na_2SO_4 and evaporated to leave green crystals (0.7 g, 65% yield), m.p. 145–8° C. Found: C 63.0, H 3.9, P 6.2%. Calcd. for $C_{46}H_{36}N_4S_4P_2Co$: C 62.6, H 4.0, P 6.9%. The compound was insoluble in water, but readily soluble in chloroform, carbon tetrachloride and acetone.

Bis-[-3-(diphenylthiophosphinyl)-1-β-naphthylthioureato]cobalt(II), Co(TPTUNp-β)₂

A solution of the ligand (1 g) in absolute ethanol was refluxed with stirring for 10 min with 0.36 g cobalt(II) acetate, dissolved in 40 ml ethanol. The mixture was then stirred at room temperature for 2 hr. The green crystals deposited were filtered, washed with ethanol and diethylether, then dried. Yield 0.6 g (56%), m.p. 196–8° C. Found: C 62.0, H 3.6, P 6.6%. Calcd. for $C_{46}H_{36}N_4S_4P_2Co$: C 62.6, H 4.0, P 6.9%. The compound was soluble in chloroform, acetone and carbon tetrachloride.

Bis-[-3-(diphenylthiophosphinyl)-1-m-tolylthioureato]cobalt(II), Co(TPTUTol)₂

The solution of the ligand in acetonitrile, prepared as described in Part I[1], without isolation of the ligand in pure state, was treated with a solution of cobalt(II) acetate in ethanol, and stirred at room temperature for 2 hr. The dark green crystalline precipitate deposited was filtered, washed with ether and dried. M.p. 174–5° C. Found: P 7.3%. Calcd. for $C_{40}H_{36}N_4S_4P_2Co$: P 7.6%. The compound was insoluble in water, but soluble in chloroform, carbon tetrachloride and acetone.

Bis-[-3-(diphenylthiophosphinyl)-1-pentamethylenethioureato]cobalt(II), Co(TPTUPip)₂

This compound was prepared in a manner similar to that used for $Co(TPTUTol)_2$, from a solution of the ligand in acetonitrile, obtained as described in Part I, without isolation. Similar treatment gave blue greenish crystals, m.p. 80° C. Found: P 7.6%. Calcd. for $C_{36}H_{40}N_4S_4P_2Co$: P 7.9%.

Results and Discussion

The ligands used in this work were prepared as described in Part I, by addition of an aromatic amine or piperidine to diphenylthiophosphinyl isothiocyanate. Thus, the following ligands were used:

$Ph_2P(S)NHC(S)Am$
where

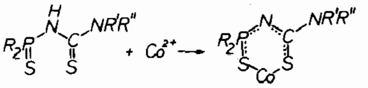
Am =	$NHC_{10}H_7$-α	abbreviated HTPTUNp-α
	$NHC_{10}H_7$-β	abbreviated HTPTUNp-β
	$NHC_6H_4CH_3$-m	abbreviated HTPTUTol
	NC_5H_{10}	abbreviated HTPTUPip
	NHC_6H_5	abbreviated HTPTUPh

For the synthesis of the chelates three alternative procedures were used. i) The ligand was converted into a sodium salt by treatment with sodium ethoxide in ethanol, then treated with an aqueous solution of cobalt(II) acetate, when the chelate precipitated. ii) The ligand, dissolved in ethanol, was treated with an alcoholic solution of cobalt(II) acetate. iii) A solution of the ligand in chloroform or carbon tetrachloride was stirred with an aqueous solution of cobalt(II) acetate and the chelate was extracted in the organic layer. This last procedure was particularly suitable for syntheses of small amounts of chelates or when the second method was not satisfactory.

Infrared Spectra

The significant infrared absorption frequencies of the ligands and cobalt(II) chelates are compared in Table I. Only the frequencies of groups involved in chelate ring formation are discussed.

The infrared spectral data show that the chelate ring formation results in a redistribution of the π-electron density in the ligand. Thus, in the protonated form the free ligand contains a formally single P–N and C–N bond, and formally double P=S and C=S bonds. In the deprotonated anion of the ligand, coordinated to cobalt with ring formation, the additional electron density introduced by the negative charge is distributed along the whole S–P–N–C–S group. This results in a change of the bond orders, which can be detected by infrared spectroscopy:



Thus, the P–N bond is strenghtened, *i.e.* achieves some double bond character, as shown by the shift of ν_{PN} to higher wavenumbers.
However, the PN bond does not become a true "double bond", as indicated by the lack of absorption bands in the region around 1300 cm^{-1}, characteristic for $\nu_{P=N}$. Therefore, the contribution of structure IIb appears as predominant. A shift of ν_{CN} of the ligand, although small, is also detectable. It appears that the exocyclic NHR″ group is involved in a tautomeric relationship with the ring C=N group:

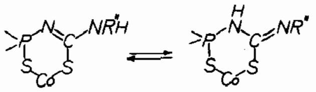


TABLE I. Infrared Spectral Data for the Ligands and Co(II) Chelates.

Compound	Infrared Bands (cm^{-1})		
	ν_{PN}	ν_{PS}	ν_{CN}
HTPTUNp-α	1002s	638m, 615m	1470s
Co(TPTUNp-α)$_2$	1005s	570m	1480s
HTPTUNp-β	995s	632m, 615m	1495s
Co(TPTUNp-β)$_2$	1005s	580m	1500s
HTPTUTol	985s	630m, 615m	1493s
Co(TPTUTol)$_2$	998s	585m	1508s
HTPTUPip	980sh	618m, 595m	1485s
Co(TPTUPip)$_2$	990s	567m	1545m
HTPTUPh	975s	630s, 615m	1500m
Co(TPTUPh)$_2$	996s	587m	1497s

When this is not possible, as in the case of TPTUPip chelate, since there is no NH group present, the shift of ν_{CN} caused by ring formation is more dramatic (from 1485 cm^{-1} in the free ligand to 1545 cm^{-1} in the chelate), showing that the endocyclic C–N bond retains more double bond character, thus indicating again that structure IIb is predominant.

Detectable changes are also observed for ν_{PS} frequencies. The PS bond order is obviously decreased by chelate ring formation, losing much of its double bond character, due both to electron delocalization within the ring and to sulfur–cobalt bond formation.

The infrared spectral data show that chelate ring formation results in a remarkable π electron distribution along the SPNCS group, with the formation of a delocalized system in which structure IIb is the major contributor. Because of the non-identical electronegativity of the ring atoms, a uniform distribution of the π-electron density in the chelate ring cannot be expected, and therefore the ring cannot be described as "aromatic".

Electronic Spectra and Magnetic Moments

Information concerning the coordination of cobalt was obtained from electronic spectra and measurements of magnetic moments. The electronic spectra suggest a tetrahedral configuration for Co(II), supported by the presence of a strong absorption band in the region 14–16 kK. This band is caused by a $^4A_{2g}$–$^4T_1(P)$ transition. Its fine structure, consisting in a splitting of the main band, is due to spin–orbital coupling, which splits the $^4T_1(P)$ state in a singlet and a doublet. The splitting is not resolved in the same way for all compounds investigated. Thus, for all compounds but one, the bands show a maximum at 14–14.5 kK, and a shoulder at higher wavenumbers (Figure 1); in Co(TPTUPip)$_2$ the situation is reversed, the maximum occurring at 16.0 kK, with the shoulder at lower wavenumbers (14.5 kK, Figure 2). This change can be correlated with an inversion in the order of the energy levels A(B) and E, resulting from removal of the degeneration of the $^4T_1(P)$ term. Such behaviour can be caused by the different acceptor ability of the exocyclic amino group and by the existence of the tautomeric equilibrium between the endocyclic nitrogen atom and the exocyclic amino substituent, mentioned above. Such an equilibrium is not possible for TPTUPip, where the exocyclic secondary amino group cannot participate. In this case the electron density within the ring seems to be larger and the coordinated metal atom "feels" it.

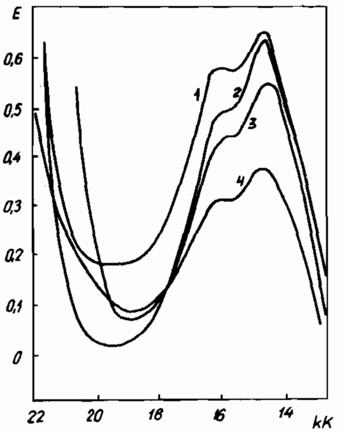


Figure 1. Electronic spectra of Co(TPTUPh)$_2$ (curve 1), Co(TPTUTol)$_2$ (curve 2), Co(TPTUNp-β)$_2$ (curve 3) and Co(TPTUNp-α)$_2$ (curve 4) in chloroform solution.

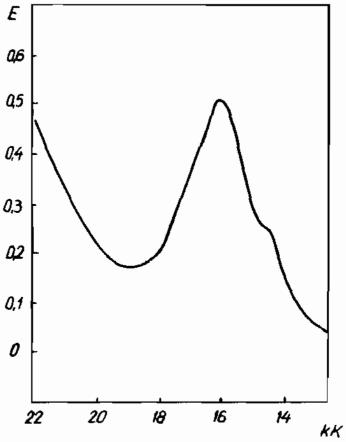


Figure 2. Electronic spectrum of Co(TPTUPip)$_2$ in chloroform solution.

The exact position of the bands, their molar absorption coefficients (ε_{mol}) and the corresponding oscillator strengths (F) are given in Table II. The values of ε_{mol} (*ca.* 10^2) indicate that the absorptions are not Laporte or spin forbidden. This is supported by the order of magnitude (10^{-3}) of the oscillator strenghts.

TABLE II. Electronic Spectral Data for Co(II) Chelates.

Compound	Absorption Maxima (kK)	ε_{mol} (l mol^{-1} cm^{-1})	F × 10^3 (l mol^{-1} cm^{-1})
$Co(TPTUPh)_2$	14.5	392	2.79
	16.0sh	349	2.62
$Co(TPTUNp\text{-}\alpha)_2$	14.42	120	0.87
	15.67sh	103	0.63
$Co(TPTUNp\text{-}\beta)_2$	14.33	550	4.00
	15.67sh	440	2.50
$Co(TPTUTol)_2$	14.50	416	2.87
	15.83sh	323	1.86
$Co(TPTUPip)_2$	14.50sh	147	0.62
	16.0	312	2.28

TABLE III. Magnetic Moments of Some Co(II) Chelates.

Compound	μ_{eff} (B.M.)
$Co(TPTUPh)_2$	5.0
$Co(TPTUNp\text{-}\beta)_2$	4.6
$Co(TPTUTol)_2$	4.5

The conclusion about the tetrahedral coordination in the cobalt(II) chelate investigated in this work is supported by the measurements of magnetic moments. The values found for the three compounds shown in Table III are in accordance with the expected moments for tetrahedral cobalt(II) compounds (in the range 4.4–4.8 B.M.). The magnetic moments found are higher than the spin-only value (3.89 B.M.) due to spin–orbital coupling.

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References

1 A. Ziegler, V.P. Botha and I. Haiduc, *Inorg. Chim. Acta, 15,* 123 (1975).

2 H. Groeger and A. Schmidpeter, *Chem. Ber., 100,* 3216 (1967).

3 I. Ojima, T. Onishi, T. Iwamoto, N. Inamoto and K. Tamaru, *Bull. Soc. Chem. Japan, 44,* 2156 (1971).

4 I. Ojima, T. Iwamoto, T. Onishi, N. Inamoto and K. Tamaru, *Chem. Comm., 1969,* 1501.