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Transition Metal Complexes of Organothiophosphorus Ligands. V. Some Aryl Esters and Amides of Dithiophosphoric Acid and their Nickel(II) and Cobalt(II and III) Complexes*

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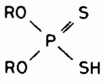
Tetraphosphorus decasulfide reacted with phenoxyethanol, α- and β-naphthol, ortho-*toluidine,* ortho-*aminophenol and* ortho-*phenylenediamine to give aryl esters or amides of dithiophosphoric acids. These were used as ligands in the synthesis of some nickel(II) and cobalt(II and III) complexes. With* para-*toluidine only the amide (*p-$CH_3C_6H_4NH)_3PS$ *was isolated.*

Introduction

The transition metal complexes of O,O′-dialkyl esters of dithiophosphoric acid (*I*) were the subject of much interest [1]. The ligands *I* are readily prepared by reaction of alcohols with tetraphosphorus decasulfide [2]. Similar reactions of P_4S_{10} with primary and secondary amines yield various products [2–5], among which the dithiophosphoric acid diamides (*II*) may serve as useful ligands. Diols, diamines or aminoalcohols are expected to give cyclic derivatives (*III*), (X, Y = O or NH), but only few such examples are known, *e.g.* from 1,3-propanediol [1] and cyclohexane-1,2-diol [6].



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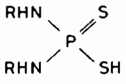

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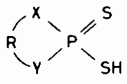

III

In order to explore further possibilities of preparing ligands *I–III* and their transition metal complexes, we have investigated the reactions of tetraphosphorus decasulfide with phenoxyethanol, α- and β-naphthol, *ortho*- and *para*-toluidine, *ortho*-aminophenol, *ortho*-phenylenediamine, pyrocatechol and hydroquinone. Aromatic functional derivatives were selected for comparison with the more frequently investigated aliphatic thiophosphorus acid derivatives.

Experimental

Materials and Methods

The reagents used were of analytical grade purity and were used as received from commercial sources. Infrared spectra were recorded in KBr pellets on a U.R.-20 Carl Zeiss instrument, and electronic spectra (absorption or diffuse reflectance) on a VSU-2G Carl Zeiss instrument.

The metal content was determined as Ni(II) bis-(dimethylglyoximate) and phosphorus as ammonium 12-molybdophosphate (gravimetrically). Nitrogen was determined by combustion.

Preparation of Ligands

The reaction of tetraphosphorus decasulfide with alcohols, phenols or amines was carried out in the absence of a solvent or in a suspension.

The reactions carried out in the absence of a solvent were performed at temperatures near the melting point of the functional derivative, on an oil bath under stirring, until all P_4S_{10} dissappeared in a homogeneous reaction mixture, and evolution of hydrogen sulfide ceased. The products were purified by recrystallization from benzene, to remove the impurities or the decomposition products.

In the reactions performed in a suspension, the nature of solvent used influenced the reaction duration and purity of the product. The latter was isolated by precipitation promoted by addition of petroleum ether to the reaction mixture, after all P_4S_{10} was dissolved and H_2S evolution ceased.

The reaction conditions used, yields, melting points and analytical data are summarised in Table I and Table II.

The least successful reactions were those with pyrocatechol and hydroquinone which gave viscous oils, which could not be purified. However, the presence of some dithiophosphoric acid derivative in

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*Part IV; R. Constantinescu, F. Martinas and I. Haiduc, *Inorg. Chim. Acta, 19,* 105 (1976). Part III; L. Dumitrescu-Silaghi, R. Micu-Semeniuc and I. Haiduc, *Inorg. Chim. Acta, 17,* 5 (1976).

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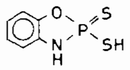
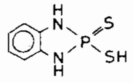
TABLE I. Compounds Prepared by Reactions of P_4S_{10} with Some Functional Derivatives.

Reagent	Solvent	Temp., °C	Duration hr	Product	Yield %	M.P., °C
2-Phenoxyethanol	none	*ca.* 120	2	$(PhOCH_2CH_2O)_2P(S)SH$	49	43
α-Naphthol	none	*ca.* 90	1	$(\alpha\text{-}C_{10}H_7O)_2P(S)SH$	55	88–89
	toluene	reflux	3	same	75	
	benzene	reflux	3	same	35	
β-Naphthol	none	*ca.* 100	2	$(\beta\text{-}C_{10}H_7O)_2P(S)SH$	75	119[a]
	toluene	reflux	5	same	48	
Pyrocatechol	ether:toluene 1:3	reflux	6	impure oil	15	
Hydroquinone	"	reflux	6–7	impure oil	18	
ortho-Toluidine	"	40	3–4	$(o\text{-}CH_3C_6H_4NH)_2P(S)SH$	27	149–150
para-Toluidine	"	50	2	$(p\text{-}CH_3C_6H_4NH)_3PS$	45	164
ortho-Aminophenol	"	50	3		8	127 dec.
ortho-Phenylenediamine	"	40	5		12	164 dec.
Aniline	ether	reflux	5	$(Ph\text{-}NH)_2P(S)SH$	60	163[b]

[a]Literature value 110–112 [7]. [b]Literature value 161–163 [3, 5].

these oils is suggested by presence of ν_{SH} bands in the solution infrared spectra of the pyrocatechol and hydroquinone derivatives, at 2580 cm^{-1} (Table II).

The reaction of P_4S_{10} with $C_6H_5NH_2$ and o-Cl-$C_6H_4NH_2$ have been investigated and the Ag, Hg and Pb salts of dianilide were prepared [3, 5]. We synthesized the dianilide of dithiophosphoric acid by a modified route (see Table I).

Ni(II) and Co(II) complexes were prepared by reacting the ligand with the metal acetate in chloroform or carbon tetrachloride; the reaction mixture was filtered and evaporated to isolate the complex.

The characterization of the compounds isolated in solid state is given in Table II. Other complexes were left as oily liquids after evaporation and were investigated only in solution.

Results and Discussion

The reaction of P_4S_{10} with 2-phenoxyethanol and aromatic phenols or amines was used to prepare several new dithiophosphoric acids, of potential interest as ligands. The compounds are listed in Table I.

The dithiophosphorus ligands prepared in this work were used in the synthesis of Ni(II) and Co(II) complexes. Some derivatives were isolated in solid state as crystalline solids and were investigated in this state (see Table II). Others were studied only in solution.

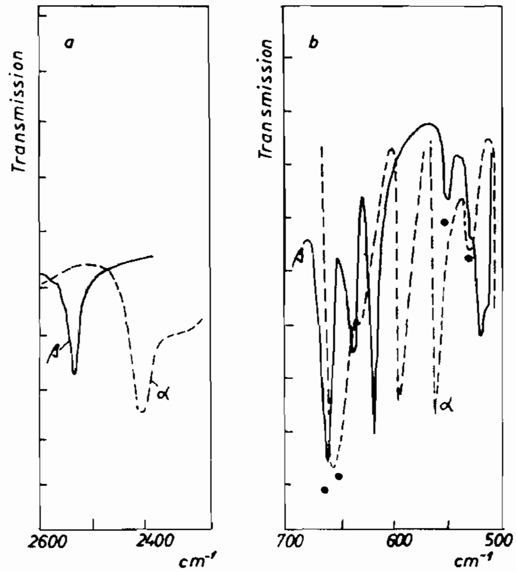


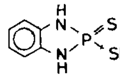
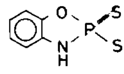
Figure 1. Infrared spectra of α- and β-dinaphthyldithiophosphoric acids: a) ν_{SH} range, b) ν_{PS} range.

Infrared Spectra

Infrared spectra were recorded for all ligands and their complexes, including those investigated only in solution.

The free dithiophosphoric acids exhibit the ν_{SH} band in the range 2600–2400 cm^{-1} and the ν_{PS} bands in the range 700–500 cm^{-1}. The position of these bands is strongly influenced by the nature of

TABLE II. Elemental Analysis and Infrared Spectra of Synthesised Compounds.

	Compound	Elemental Analysis			Infrared Spectra		
		%P found calcd.	%N found calcd.	%M found calcd.	$\nu_{a(PS_2)}$	$\nu_{s(PS_2)}$	ν_{SH}
1	$(PhOCH_2CH_2O)_2P(S)SH$	8.03	–	–	654	545	2550
		8.37					
2	$(\alpha\text{-}C_{10}H_7O)_2P(S)SH$	8.41	–	–	657	535	2405
		8.11					
3	$(\beta\text{-}C_{10}H_7O)_2P(S)SH$	7.93	–	–	665	550	2630
		8.11					
4	$(o\text{-}CH_3C_6H_4NH)_2P(S)SH$	10.13	9.11	–	670	520	2600
		10.06	9.09				
5		15.88	14.33	–	665	525	2580
		15.38	13.86				
6		14.83	6.56	–	640	530	2580
		15.27	6.89				
7	$o\text{-}C_6H_4O_2P(S)SH$[a]	–	–	–	670	520	2580
8	$(C_6H_5NH)_2P(S)SH$[b]	–	–	–	665	525	2580
9	$(p\text{-}CH_3C_6H_4NH)_3PS$	8.01	7.18	–	–	–	–
		8.14	7.37				
10	$Ni[(PhOCH_2CH_2O)_2PS_2]_2$	7.56	–	7.68	642	544	–
		7.35	–	7.88			–
11	$Ni[(\alpha\text{-}C_{10}H_7O)_2PS_2]_2$	7.48	–	7.41	660	525	–
		7.13		7.54			
12	$Ni[(\beta\text{-}C_{10}H_7O)_2PS_2]_2$	7.53	–	7.36	655	545	–
		7.13		7.54			
13	$Ni[(C_6H_5NH)_2PS_2]_2$	10.43	–	9.34	640	515	–
		10.05		9.51			
14	$Co[((PhOCH_2CH_2O)_2PS_2]_3$	7.53	–	5.02	623	550	–
		7.75		5.05			

[a] Impure oil. [b] Synthesised by other authors [3, 5].

organic groups, e.g. α- and β-naphthyldithiophosphoric acids (Fig. 1 and Table II).

The normal coordinate analysis carried out for $(CH_3)_2P(S)SNa$ [8] and $[(CH_3O)_2P(S)S]_2Ni$ [9] pointed out that the $\nu_{s(PS)}$ band has a great amount of PC stretching vibration (PO, respectively). Therefore, the $\nu_{s(PS)}$ band is more sensitive to the nature of organic groups than $\nu_{a(PS)}$, which does not contain other important contributions.

The ν_{PS} bands of diphenoxyethylphosphorodithioic acid are in the proximity of those of diethylphosphorodithioic acid (654 and 540 cm^{-1}). The value of $\nu_{s(PS)}$ in diphenoxyethyldithiophosphoric acid is slightly lower than that of diethyldithiophosphoric acid (Table II) in accordance with the contributions of organic groups to the $\nu_{s(PS)}$ vibrations.

The pyrocatecholphosphorodithioic acid exhibits a low value for the $\nu_{s(PS)}$ frequency (Table II). This may be correlated with the formation of the five-membered PO_2C_2 ring, and with its influence upon this type of vibration.

The infrared spectra of aminophosphorodithioic acids, compared to those of the O-arylesters, exhibit lower values for the $\nu_{s(PS)}$ and slightly higher values for $\nu_{a(PS)}$ (Table II) in agreement with the lower electronegativity of nitrogen *versus* oxygen.

In the infrared spectra of the complexes (Table II) compared to those of free ligands, the ν_{PS} bands are shifted, in accordance with the redistribution of electronic density in P–S bonds, as a result of coordination. No important differences between the IR spectra of Ni(II) and Co(II) complexes with the same dithiophosphoric acid occur.

Nickel(II) Complexes

With the new ligands, nickel(II) formed readily square planar complexes only with the phenoxyethoxy and naphthyloxy derivatives. Their electronic spectra were similar to those of other Ni(II) dithio-

TABLE III. Electronic Spectra of Nickel and Cobalt Complexes (cm^{-1}).

Compound		Transitions	
Nickel Complexes		$^1B_{1g} \leftarrow {}^1A_{1g}$	$^1B_{2g} \leftarrow {}^1A_{1g}$
1	$Ni[(PhOCH_2CH_2O)_2PS_2]_2$	14,400	19,500
2	$Ni[(\alpha\text{-}C_{10}H_7O)_2PS_2]_2$	14,200	19,000
3	$Ni[(\beta\text{-}C_{10}H_7O)_2PS_2]_2$	15,100	19,500
4	$Ni[(o\text{-}C_6H_4O_2)PS_2]_2$	14,700	18,780
5	$Ni[(p\text{-}C_6H_4O_2)PS_2]_2$	14,700	19,200
6	$Ni[(C_6H_5NH)_2PS_2]_2$	14,700	19,100
7	$Ni[(o\text{-}CH_3C_6H_4NH)_2PS_2]_2$	14,800	19,200
Cobalt Complexes		Fresh Solutions (blue)	Old Solutions (brown–oxidized to Co(III)
1	$Co[(PhOCH_2CH_2O)_2PS_2]_2$	15,000 16,000	13,750 24,500 29,500
2	$Co[(o\text{-}C_6H_4O_2)PS_2]_2$	11,100 13,900	12,000 16,000
3	$Co[(p\text{-}C_6H_4O_2)PS_2]_2$	13,500 15,100	

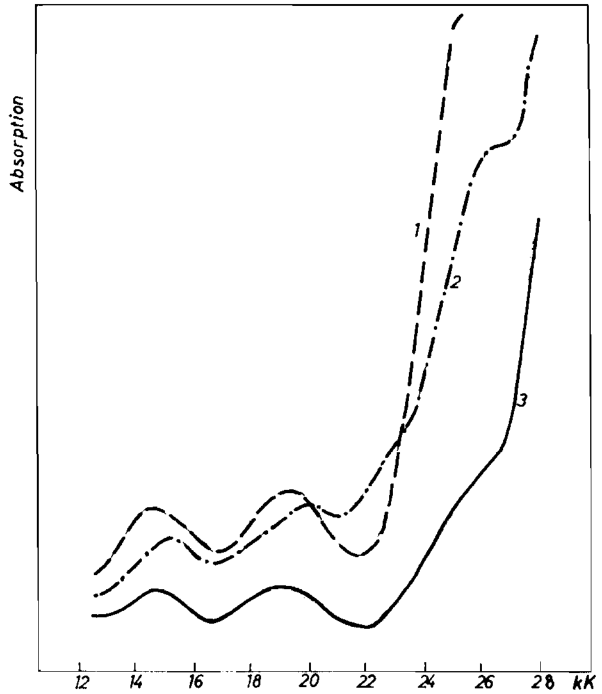


Figure 2. Electronic spectra of some Ni(II) dithiophosphates: 1, $Ni[(\alpha\text{-}C_{10}H_7O)_2PS_2]_2$; 2, $Ni[(\beta\text{-}C_{10}H_7O)_2PS_2]_2$; 3, $Ni[(C_6H_5NH)_2PS_2]_2$.

phosphate chelates, and the assignment of bands was readily made in accordance with literature data, *e.g.* for $Ni[(C_2H_5O)_2PS_2]_2$ (14.5 and 19.1 kK [10, 11]) (see Table III and Fig. 2). Similar bands were observed in the purple solutions obtained from Ni(II) salts and the oily derivatives of pyrocatechol and hydroquinone (Table III). This suggests that these oils contain a dithiophosphoric acid derivative, which cannot be isolated in a pure state.

Of the dithiophosphoric acid amides only the dianilide gave an isolatable complex $Ni[(C_6H_5NH)_2PS_2]_2$. All the aromatic derivatives of dithiophosphoric acids reported in this paper appear less stable than dialkyldithiophosphoric acid Ni(II) complexes, handled in our laboratory.

Cobalt(II) Complexes

Only one of the ligands prepared here formed an isolatable cobalt complex, namely $Co[(C_6H_5OCH_2CH_2O)_2PS_2]_3$.

In CCl_4, cobalt(II) acetate forms with the dithiophosphoric acids derivatives green-blue solutions, which on standing for several hours turn brown due to oxidation to Co(III) dithiophosphate. The behaviour of cobalt dithiophosphates is similar to that previously described for diethyldithiophosphate [12]. The electronic spectra of freshly-prepared blue-green Co(II) solutions can be interpreted in terms of a T_d local symmetry of Co(II) ions [13], with the ν_3 band ($^4T_1(P) \leftarrow {}^4A_2(F)$) split into several components. Thus, the isolated green-olive complex $Co[(C_6H_5OCH_2CH_2O)_2PS_2]_3$ (Table III) exhibits a spectrum with bands differing significantly from that of the freshly-prepared blue-green solutions. If the blue-green solution is treated with pyridine, the colour turns pink-purple, and the spectrum exhibits a band

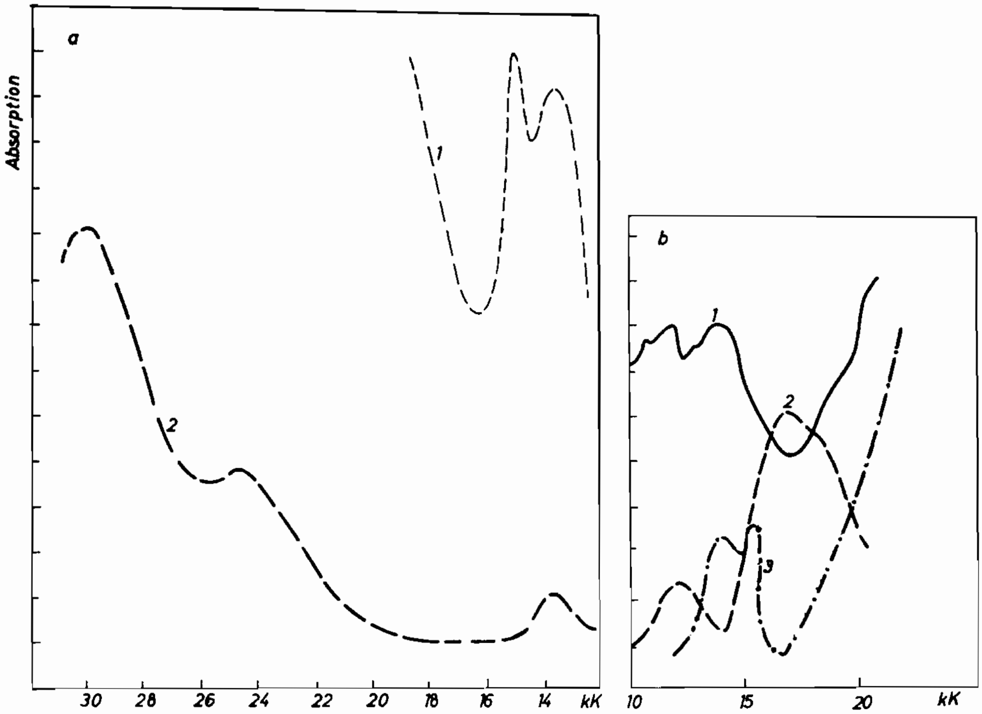


Figure 3. Electronic spectra of Co(II) dithiophosphates: a) Cobalt bis(diphenoxyethyl)dithiophosphate: 1) fresh solution; 2) solution obtained from the solid (see the text). b) Other Cobalt dithiophosphates: 1) Co[(o-$C_6H_4O_2$)PS_2]$_2$, fresh solution; 2) idem, aged solution; 3) Co[(p-$C_6H_4O_2$)PS_2]$_2$.

at 17.5 kK due to the adduct Co[($C_6H_5OCH_2CH_2O$)$_2PS_2$]$_2$·2py, in which the cobalt(II) ions became six-coordinate. If pyridine is added to the solution obtained from the olive-green precipitate no change occurs, since pyridine cannot replace the dithiophosphato-ligand in the very stable six-coordinate complex Co[($C_6H_5OCH_2CH_2O$)$_2PS_2$]$_3$. In addition, the olive-green complex was found to be diamagnetic, in agreement with the oxidation degree 3+. It should be mentioned that the related tris(diethylphosphorodithioato)Co(III), Co[(EtO)$_2PS_2$]$_3$, exhibits absorption maxima at 13.5 kK ($^1T_{1g} \leftarrow {}^1A_{1g}$), 19.0 kK ($^1T_{2g} \leftarrow {}^1A_{1g}$) and 24.6 kK (charge transfer [12]), which agree with those observed for our compound (Table III and Fig. 3).

The dithiophosphoric acid derivatives obtained from hydroquinone and pyrocatechol also form blue solutions with Co(II) ions; these solutions exhibit absorption maxima at 13.5, 15.1, 11.1 and 13.9 kK, respectively (Table III and Fig. 3). No complex could be isolated, however, in crystalline state.

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