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Thallium Dithiophosphates

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Preparation and properties of thallium(I) and dialkylthallium(III) derivatives of O,O-disubstituted dithiophosphoric acid have been investigated. The $R_2TlS_2P(OR')_2$ compounds are not ionic in the solid state; they contain four coordinate thallium(III) in chloroform solution, with the exception of $Me_2TlS_2P(OMe)_2$ where species with a coordination number higher than four are possible. Ionic species, e.g. solvated Me_2Tl^+, are present only to a small extent in acetonitrile solution and to a larger extent in dimethylformamide solution.

Introduction

During our investigations of thallium derivatives[1,2] it was found that R_2Tl^{III} or Tl^{III} derivatives of dithiocarbamates did not exhibit any tendency towards association in benzene or chloroform solution. On the other hand, related compounds with the dithiophosphinate group, $R_2PS_2^-$, in place of dithiocarbamate group, were found to be associated in chloroform solution, and possible reasons were suggested. It was therefore decided to investigate the associative behaviour of the compounds formed from thallium(III) and diorganothallium(III) with disubstituted dithiophosphate ligands. Besides, it was our purpose to see whether any simple explanation could be found to rationalize an eventual association.

The compounds were of interest also in view of a possible ionic structure, *e.g.* $[R_2Tl]^+[S_2P(OR)_2]^-$. The linear $[R_2Tl]^+$ ion is isoelectronic with dimethyltin(IV) cation[3] and with diorganomercury compounds; besides, it had been found in dimethylthallium(III) perchlorate, nitrate, and hydroxide.[4] An ionic structure had been suggested for dialkylthallium(III) derivatives with ligands which are generally bidentate, such as acetylacetonate or dimethyldithiophosphinate in aqueous solution.[5] An ionic structure was not in agreement with data relating to solutions of similar diorganothallium(III) derivatives in certain organic solvents.[2]

Experimental Section

The ligands were prepared according to published methods.

Zinc(II) bis(dimethyldithiophosphate). Dimethyldithiophosphoric acid (2.0 ml) and 85% zinc dust (0.608 g) were heated at 50-60° in benzene till gas was evolved; excess zinc dust was then added. After a few hours the solution was filtered, and the filtrate was evaporated to dryness under vacuum. The oily residue was dissolved in diethyl ether; on slow evaporation white crystals formed. The desired compound was not obtained from basic zinc carbonate and the acid in refluxing toluene.

Thallium(I) dialkyldithiophosphate. 1) (General preparation) Mixing aqueous solutions of thallium(I) sulphate and of the potassium salt of the required ligand gave the required compound as a white, crystalline precipitate. The methyl derivative was used as obtained, the ethyl and the *p*-chlorophenyl derivative were crystallized from toluene, taking care to avoid prolonged heating.

2) A solution of potassium dimethyldithiophosphate was added to a solution of anhydrous thallium(III) chloride; the solvent (acetonitrile) was evaporated under vacuum, and the residue extracted with hot benzene several times. Thallium(I) dimethyldithiophosphate crystallized out of the solution, and was identified by m.p., mixed m.p. with an authentic sample obtained according to 1) and infrared spectrum.

Dialkylthallium(III) dialkyldithiophosphate. All the compounds were prepared from an acetone suspension of dialkylthallium(III) chloride to which an acetone solution of the potassium salt of the required ligand was added. After overnight stirring, and filtering, the soluton was evaporated to dryness in vacuo. The residue was then either extracted with hot toluene and the extracts concentrated to small volume or crystallized, as stated in Table I.

Infrared data (nujol mull; recorded on Perkin Elmer 621 or 457 instrument):

Potassium *O,O*-dimethyldithiophosphate: 1452 s, 1435 sh, m, 1375 m, 1364 sh, 1181 m, 1010 br, s, 760 br, s, 720 br, s, 690 sh, 551 m, 418 m, 321 m, 306 m, 227 w.

$Zn[S_2P(OMe)_2]_2$: 1449 s, 1372 m, 1362 sh, 1172 m, 1041 s, 1017 s, 801 s, 774 s, 660 s, 501 s, 384 m, 343 m.

$TlS_2P(OMe)_2$: 1450 m, 1371 m, 1173 w, 1040 sh, s, 1010 vs, 768 s, 652 s, 520 m, 378 w, 339 w.

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[2] F. Bonati, S. Cenini, and R. Ugo, *J. Organomet. Chem.*, *9*, 345 (1967).
[3] M. M. McGrady, and R. S. Tobias, *J. Am. Chem. Soc.*, *81*, 1909 (1965).
[4] P. L. Goggin, and L. A. Woodward, *Trans. Faraday Soc.*, *56*, 1591 (1960).
[5] G. E. Coates, and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964).

$Me_2TlS_2P(OMe)_2$: 1462 s, 1373 m, 1172 m, 1040 vs, 1020 vs, 777 vs, 762 vs, 649 s, 540 w, 523 m, 483 w, 432 w, 379 m, 347 m, 287 w, 251 m.

$Et_2TlS_2P(OMe)_2$: 1460 s, 1373 s, 1163 m, 1080 w, 1019 s, 960 w, 778 s, 742 sh, m, 695 m, 680 m, 633 s, 550 w, 505 m, 389 w, 350 w, 271 w.

$Me_2TlS_2P(OEt)_2$: 1460 s, 1405 w, 1388 m, 1378 m, 1365 sh, 1170 sh, w, 1158 w, 1100 w, 1059 sh, m, 1023 s, 948 s, 800 s, 636 s, 537 m, 526 m, 361 m, 253 m.

$TlS_2P(OC_6H_4Cl)_2$: 1582 w, 1479 s, 1460 s, 1396 m, 1373 m, 1202 s, 1181 s, 1160 s, 1083 s, 1014 s, 939 w, 935 w, 880 s, br, 827 s, 760 s, 758 s, 749 s, 702 m, 673 m, 638 s, 539 s, 519 m, 490 m, 457 w, 410 w, 363 w, 333 w, 304 w, 286 w, 250 w.

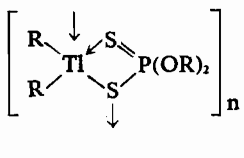
$Me_2TlS_2P(OC_6H_4Cl)_2$: 1583 w, 1483 s, 1460 s, 1398 w, 1373 s, 1365 sh, 1216 w, 1195 s, 1160 s, 1090 s, 1028 m, 935 m, 912 s, 888 br, s, 837 s, 818 m, 808 m, 767 m, 757 m, 724 w, 703 w, 692 w, 655 s, 644 s, 533 s, 489 m, 447 m, 455 w, 427 w, 354 w, 316 w, 266 w.

Results

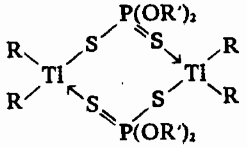
The thallium(I) and dialkylthallium(III) derivatives of *O,O*-dimethyl-, *O,O*-diethyl-, and *O,O*-di(*p*-chlorophenyl)-dithiophosphoric acid were obtained by double exchange. They are white crystalline compounds, moderately soluble in organic solvents (Table I). Attempts to prepare the corresponding thallium(III) derivatives were unsuccessful, the corresponding thallium(I) derivative being the main reaction product. This failure may be ascribed to the oxidizing nature of trivalent thallium toward dithiophosphate; however thallium(III)[2] or tin(IV)[6] are not effective in oxidizing the dithiocarbamate group to *N,N,N',N'*-tetralkyldithiourame disulphide.

Structure of the compounds in solution.

Molecular weights. Our results (Table II) indicate that nearly all compounds are monomeric. There are two exception, $Me_2TlS_2(OMe)_2$ and $Zn[S_2P(OMe)_2]_2$. The small amount of association found for the thallium compounds is probably allowed by the minor steric requirement of the four methyl groups in comparison with those of bulkier groups (*e.g.* ethyl group). This point might be taken as a hint that, in chloroform solution, association takes place through three-coordinate sulphur atom(s), as in *A*, where steric requirements are important, rather than by bridging dithiophosphate groups, as in *B*, where electronic rather than steric effects can be operative.



A



B (R = alkyl)
C (R missing)

Unfortunately the derivatives with aryl groups on the oxygen atoms were insufficiently soluble for molecular weight determination.

The thallium(I) derivatives were found to be dimeric in chloroform solution; similar results were found for dithiophosphinates[2] and for dithiocarbamates.[7] Association is probably due to the need of the thallium atom of reaching a coordination number of at least two with a structure having bridging dithiophosphate groups, like *C*.

Table I.

Compound	m.p. °C	C% Calcd.	C% Found	H% Calcd.	H% Found	Solvent of crystallization
$TlS_2P(OMe)_2$	122	6.65	6.59	1.66	1.66	—
$TlS_2P(OEt)_2$	86	12.35	12.37	2.58	2.62	toluene
$TlS_2P(OC_6H_4—pCl)_2$	180	26.0	25.93	1.45	1.42	toluene
$Me_2TlS_2P(OMe)_2$	181	12.3	12.74	3.07	3.06	toluene [a]
$Me_2TlS_2P(OEt)_2$	135-6	17.20	17.38	3.89	3.65	toluene [a]/ether
$Me_2TlS_2(OC_6H_4—p\text{-}Cl)_2$	*ca.* 234	28.8	28.40	2.40	2.43	ethyl acetate
$Et_2TlS_2P(OMe)_2$	153	17.20	17.46	3.83	3.82	toluene [a]
$Et_2TlS_2P(OEt)_2$	132	21.42	21.49	4.48	4.52	toluene [a]
$Zn[S_2P(OMe)_2]_2$	79	12.66	12.80	3.17	3.21	ether

[a] This solvent was used in the extraction of the compound from the reaction mixture.

Table II. Molecular weight determinations [a]

Compound	Concentration (% w/w)	M.W.	n [b]
$Tl_2P(OMe)_2$	0.64	756	2.09
$Tl_2P(OEt)_2$	2.26	765	1.96
$Me_2TlS_2P(OMe)_2$	1.98	501	1.28
$Me_2TlS_2P(OMe)_2$	2.00	485	1.24
$Me_2TlS_2P(OEt)_2$	0.86	430	1.02
$Et_2TlS_2P(OMe)_2$	1.45	405	0.98
$Et_2TlS_2P(OEt)_2$	0.99	445	0.99
$Zn[S_2P(OMe)_2]_2$	1.31	426	1.14
$Zn[S_2P(OMe)_2]_2$	2.79	432	1.15
$Zn[S_2P(OMe)_2]_2$	3.95	454	1.21

[a] Chloroform solution, 37°C, Mechrolab Osmometer.
[b] n = M.W. found/formula weight.

^1H n.m.r. data. As already observed,[2] small amounts of association, as detected by molecular weight measurements, have no remarkable effects on n.m.r. spectra (at 33°C) of this type of compounds.

The position of the signals due to the thallium bonded methyl groups[8] is markedly lower in our compounds than in Me_3Tl (τ = 9.48 in CH_2Cl_2) in agreement with the electronegative character of the dithiophosphate anion. Similar considerations are valid

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(7) S. Akerstroem, *Arkiv for Kemi*, *24*, 495 (1965).
(8) J. W. Elmsley, J. Feeney, and L. H. Sutcliffe, High Resolution N.M.R. Spectroscopy, Pergamon Press, Oxford, 1966, p. 1088 and references listed.

Table III. ^1H n.m.r data [a]

	O bonded groups [b]			Tl bonded groups [b]				
	$\tau(CH_3)$	J	$\tau(CH_2)$	$\tau(CH_3)$	$J(Tl{-}CH_3)$	$\tau(CH_2)$	$J(TlCH_2)$	$J(CH_2CH_3)$
$TlS_2P(OMe)_2$	6.33 d	14	—	—	—	—	—	—
$TlS_2P(OEt)_2$	8.70 t	7	5.90 c	—	—	—	—	—
$Me_2TlS_2P(OMe)_2$	6.30 d	15	—	8.48 d	347	—	—	—
$Me_2TlS_2P(OEt)_2$	8.65 t	7	5.88 c	8.50 d	364	—	—	—
$Et_2TlS_2P(OMe)_2$	6.29 d	14	—	8.22 t, c	632	7.89 q	275	7
$Et_2TlS_2P(OEt)_2$	8.66 t	7	5.90 c	8.25 t	635	7.88 q	274	8
$Zn[S_2P(OMe)_2]_2$	6.19 d	16	—	—	—	—	—	—

[a] Data recorded on Perkin Elmer R—10 instrument at 60 Mc in chloroform solution with tetramethylsilane as internal standard, at 33°C. [b] d = doublet, t = triplet, q = quartet, c = complex; when J relating to ^{203}Tl and ^{205}Tl were different only the former is given; the latter is *ca.* 5 cps lower.

Table IV. Conductivity data [a]

Compound	Solvent	Concentration ($M \times 0.001$)	Λ [b]	Remarks
$TlS_2P(OMe)_2$	DMF [e]	0.776	19.2	[c]
$TlS_2P(OEt)_2$	DMF	0.97	21.4	[c]
$TlS_2P(OC_6H_4Cl)_2$	DMF	0.82	52	[c]
$Me_2TlS_2P(OMe)_2$	CH_3CN	0.92	9.5	
	DMF	0.97	39.9	
$Me_2TlS_2P(OEt)_2$	CH_3CN	1.05	7.1	[d]
$Me_2TlS_2P(OC_6H_4Cl)_2$	CH_3CN	0.49	27	
	DMF	0.70	54.2	
$Et_2TlS_2P(OMe)_2$	CH_3CN	0.95	9.6	
	DMF	1.15	30.5	
$Et_2TlS_2P(OEt)_2$	CH_3CN	1.0	7.5	
	DMF	1.35	21.7	
$Zn[S_2P(OMe)_2]_2$	CH_3CN	0.97	2.7	

[a] At 22°C. [b] $Ohm^{-1}\ cm^2\ mole^{-1}$. [c] Insufficiently soluble in acetonitrile and nitrobenzene. [d] Resistence too high to allow measurement in nitrobenzene. [e] N,N-dimethylformamide.

for the signals due to the thallium bonded methylene groups in the complexes and in triethylthallium ($\tau = 8.71$ in CH_2Cl_2). The signals due to the methyl protons of the Et_2Tl moiety are far enough not to be affected by changes on the thallium atom; they are roughly in the same position as those of Et_3Tl ($\tau = 8.21$ in methylene chloride). Similarly, the positions of signals due to MeO— or $-CH_2O-$ groups and $J(CH_3OP)$ or $J(CH_3CH_2P)$ are unaffected by substitution at the thallium atom and are not very different from those of the zinc(II) derivative.

Coupling constants involving thallium, $J(TlCH_2CH_3)$, $J(TlCH_2CH_3)$ and $J(TlCH_3)$, are remarkably high. The higher value found for the second than for the first results from the former being the sum and the latter the difference of two large Fermi contact terms. As a consequence of the magnitude of the $J(TlCH_2CH_3)$ coupling constants it is possible to observe separate bands ($\Delta = ca.$ 5 cps) for methyl protons coupled to ^{205}Tl and to ^{203}Tl. Generally these two satellites cannot be separated, as it happens here in the case of $-CH_2Tl$ protons, which have less than half $J(TlCH_2CH_3)$ than $J(TlCH_2CH_3)$.

Consideration of the coupling constants found here for $TlCH_3$ and $TlCH_2$-protons with the corresponding ones determined for salts of dimethylthallium (>400 cps) and for salts of diethylthallium(III) (>338 cps)[9] would not be in agreement with an ionic structure. The signals due to the methyls of the thallium bonded ethyl groups are scarcely affected by changes at the thallium atom; similar values were found for Et_2Tl^+ derivatives, as well as similar coupling constants. Contrarily, $J(TlCH_3)$, being large (*ca.* 350 cps), is sensitive to changes at the alkyl group bonded at the oxygen: substitution of two methyl with two ethyl groups brings about an increase of 17 cps. Unfortunately the *O,O*-diaryldithiophosphate prepared was too insoluble for carrying out any measurement.

N.m.r. spectra of those soluble thallium(I) derivatives support the formulae proposed, but do not show any additional feature worth considering.

Conductivity. The values of the conductivities of thallium(III) derivatives in acetonitrile solution are reported in Table IV, together with that of a reference zinc(II) compound. Thallium(I) derivatives were insufficiently soluble both in this solvent and in nitrobenzene. It is evident that the compounds are not electrolyte, though the value found for $Me_2TlS_2P(OC_6H_4Cl)_2$ requires a not negligible amount of dissociation.

The values of the conductivities of thallium(III) and thallium(I) derivatives in dimethylformamide are reported in Table IV. The amount of dissociation is not negligible in all case, and, although the value required by a 1:1 electrolyte is not reached, a certain amount of ionization to $[Me_2Tl(solvent)_n]^+[S_2P(OR)_2]^-$ is evident. It should be noted that electron withdrawing substituents on the oxygen atom, such as *p*-chlorophenyl group, lower the donating ability of the chelating ligand. This fact is reflected in turn by the higher conductivity value of $S_2P(OC_6H_4Cl)_2^-$

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(9) G. D. Shier, and R. S. Drago, *J. Organomet. Chem.*, 5, 330 (1966).

derivative in comparison with those of $S_2P(Oalkyl)_2^-$, both in dimethylformamide and in acetonitrile solution.

Structure in the solid state

The infrared spectra (nujol mull) of the thallium compounds do not show many remarkable differences in the bands due to the ligand, when derivatives of the same ligand are compared. P–S stretching frequencies are observed at *ca.* 650 and 520 cm^{-1}, and a very strong P–O–C vibration at slightly above 1000 cm^{-1}.

A difference is found when dialkylthallium(III) compounds, and zinc or potassium derivatives are compared. The latter derivatives do not show any absorption between 250 and 300 cm^{-1}, while the former do. It is reasonable to assume that the difference migth be due to vibration likely to contain a major contribution from a Tl–S stretching vibration. This fact is therefore in agreement with the presence of a Tl–S bond in the solid state. This conclusion should be supported independently by consideration of the number of Tl–C stretching frequencies in the infrared spectrum. A linear C–Tl–C arrangement like that required by a dialkylthallium(III) cation requires only one infrared active Tl–C stretching frequency in the infrared spectrum, while a four-coordinate thallium atom requires two bands. The former case is that of Me_2TlCl: only one vibration is observed (550 cm^{-1}), in agreement with a partial structure determination.[10] The latter case is that of $Me_2TlS_2P(OMe)_2$: a stronger and a weaker band are observed in the infrared spectrum 540 and 483 cm^{-1}). Unfortunately this criterion cannot be applied generally, as another intense band, due to the ligand, is present in the region, as happens also with organotin dithiocarbamate.[11]

Conclusion

Although thallium(I) and diorganothallium(III) derivatives of strong acids behave as « salt like » compounds, their dithiophosphates do not have the same behaviour. To obtain a substantial presence of the ionic structure a strong solvating and ionizing solvent, like dimethylformamide, is required. The thallium(III) compounds are generally not associated in chloroform solution, except when steric hindrance is so small that association is allowed, probably via a three-coordinated sulphur atom. Thallium(I) derivatives are dimeric in chloroform solution, as many other thallium(I) derivatives of chelating anions; a bridging dithiophosphate anion is likely here.

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