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ORGANOTIN AND ORGANOTHALLIUM DITHIOPHOSPHINATES AND DITHIOCARBAMATES*

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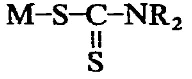
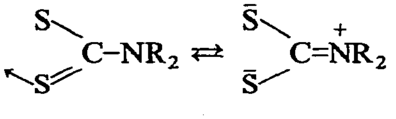
INTRODUCTION

During the study of organotin(IV) N,N-dialkyldithiocarbamates[2] some evidence was found concerning the ability of the dithiocarbamate ring to act as a monodentate (I) or as a bidentate and chelating [(II), (III)] uninegative ligand.



$M{-}S{-}\underset{\underset{S}{\|}}{C}{-}NR_2$

(I)



(II) (III)

We have now extended our investigation to organothallium(III) derivatives for the same purpose and also in order to see whether in these compounds the linear R_2Tl^+ cation, similar to R_2Hg, is present or not. For the latter reason and also because some simple metal P,P-disubstituted dithiophosphinates[3] or N,N-disubstituted dithiocarbamates[4] are associated, in solution or only in the solid state[5], organothallium(III) and organotin(IV) P,P-disubstituted dithiophosphinates were also synthesized. Their degree of association was investigated in order to suggest reasons for this behaviour.

PREPARATION AND PROPERTIES

All the compounds (Tables 1 and 2) were prepared by exchange from the corresponding organotin(IV) or organothallium(III) halide in polar solvents, such as acetone, formamide or water. Only one compound of the type $R_2Sn(SSPR'_2)_2$ was isolated, although two geometric isomers are possible in principle. All compounds are either white or yellow and stable to air and water. The solubility in organic solvents is higher for the organotin(IV) than for organothallium(III) and dihalogenotin(IV) derivatives. All the compounds are insoluble or sparingly soluble in water. They are not conducting in organic solvents (see Tables 1 and 2); the reported[6] conductivity of the related $Me_2TlSSPMe_2$ in aqueous solution might be explained by ionization in this solvent or by hydrolysis. The latter explanation is further supported by the observation made by Menzies[7] on the steam volatility and resistance to hydrolysis

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* A preliminary report was read at the Istituto Lombardo, Milan, on Nov. 25, 1965. The text of the report can be found in ref. 1.

TABLE 1

DERIVATIVES OF P,P-DISUBSTITUTED DITHIOPHOSPHINIC ACID

Compound	*Colour*	*Analyses*[a]			*Cryst.*
	m.p. (°*C*)	*C*	*H*	*M*[b]	*solvent*
$Et_3SnSSPEt_2$	colourless	33.5	7.0		B.p.
	liquid	33.4	7.1		190°/2 mm
$Ph_3SnSSPEt_2$	white	52.5	5.0	23.8	EtOH
	88–89	52.9	5.5	24.2	
$Br_2Sn(SSPEt_2)_2$[c]	yellow	16.5	3.4	20.4	EtOAc
	175	16.3	3.4	20.6	
$Cl_2Sn(SSPEt_2)_2$	yellow[14]	19.4	4.1		EtOAc
	179–80	19.6	4.1		
$Br_2Sn(SSPPh_2)_2$[c,d]	yellow	37.1	2.6		EtOAc
	195	37.0	2.6		
$Cl_2Sn(SSPPh_2)_2$[c,d]	yellow	42.0	2.9	17.2	EtOAc
	206–7	42.3	2.9	17.0	
$Et_2Sn(SSPPh_2)_2$	white	50.0	4.5		EtOAc
	162–3	50.3	4.7		
$Me_2Sn(SSPPh_2)_2$	white	48.2	4.0		Ligroin
	161–2	48.0	3.9		
$Me_2TlSSPEt_2$[c,d]	white	18.6	4.1	52.7	EtOAc
	224–5	18.8	3.9	52.3	
$Me_2TlSSPPh_2$[d,e]	white	34.8	3.3		EtOAc
	153–5	34.4	3.2		
$Ph_2TlSSPEt_2$[f,g]	white	37.5	3.9		Ligroin
	164	37.6	4.1		
$Ph_2TlSSPPh_2$[f,g]	white	47.5	3.3		Ligroin
	197	47.8	3.4		
$TlSSPEt_2$[e,h]	silver[3]	13.4	2.8		EtOAc
	137	13.6	2.8		
$TlSSPPh_2$[d,h]	white	31.8	2.2		EtOAc
	182–3	31.7	2.2		
$(Ph_3P)_2CuSSPPh_2$[i]	white	69.0	4.8	7.6	EtOAc
	176	68.8	4.7	7.5	
$(Ph_3P)_2CuSSPEt_2$[i]	white	65.0	5.4		EtOAc
	186	65.5	5.6		

[a] Calcd./Found. [b] M is the metal. [c] Non-conducting in $PhNO_2$. [d] Sparingly soluble in benzene. [e] Non-conducting in $PhNO_2$, CH_3CN and N,N-dimethylformamide. [f] Insoluble in benzene. [g] The reaction was carried out in formamide and the product was precipitated by addition of water. [h] The reaction was carried out in water, where the compound is insoluble. [i] Non-conducting in $PhNO_2$ and acetone.

of dialkylthallium(III) β-diketonates: the heavier the alkyl group present (indifferently on thallium or on the ring), the better the resistance to hydrolysis.

INFRARED SPECTRA

A characteristic feature of the dialkyldithiocarbamate group is its infrared spectrum. It was found[8,9] that dithiocarbamato complexes exhibit a band of medium intensity in the region 1480–1592 cm^{-1}, that is between the ranges for C–N and C=N. This band was assigned to a C–N stretching mode where the C–N bond order is between 1 and 2. This absorption was found in all the organometallic N,N-disub-

TABLE 2

DERIVATIVES OF N,N-DISUBSTITUTED DITHIOCARBAMIC ACID

Compound	M.p. (°C)	Analyses[a]			Mol. wt[b]	Cryst. solvent	$\nu(C{=}N^+)$[c] (cm^{-1})
		C	H	N			
$Me_2TlSSCNEt_2$[d]	100	22.0	4.2	3.7	382.4	P. ether	1486
		22.2	4.1	3.5	390		
$Me_2TlSSCNPh_2$[d]	225–6	37.6	3.3	2.9	478.4	EtOAc	[l]
		37.6	3.3	2.8	464		
$Ph_2TlSSCNEt_2$[e,f]	118	40.3	3.9	2.8	506.4	P. ether	[l]
		40.4	3.9	2.6	502		
$Ph_2TlSSCNEt_2$[e,g]	232	50.2	3.3	2.3	ins.	PhMe	[l]
		50.2	3.5	2.5			
$Me_2TlSSCNMe_2$[h]	172–3	17.0	3.4	4.0	354.4	Ligroin	1512
		17.3	3.3	3.7	350[k]		
$Tl(SSCNEt_2)_3$[e,i]	200–1[j]	27.7	4.6	6.5	648.4	EtOAc	1503
		27.7	4.8	6.3	625		
$Tl(SSCNMe_2)_3$[e,i]	206–7	19.1	3.2	7.5		MeCN	1530
		19.1	3.2	7.2			

[a] Calculated/found. [b] In chloroform. [c] Nujol mull. [d] Sparingly soluble in benzene. [e] Insoluble in benzene. [f] The reaction was carried out in formamide and the product precipitated by addition of water. [g] The reaction was carried out in pyridine. [h] Non-conducting in $PhNO_2$. [i] The orange compound precipitated from CH_3CN solution. [j] Lit.[17] m.p. 191–2°. [k] Also in C_6H_6. [l] Masked by Ph absorption.

stituted dithiocarbamates reported here unless masked, *e.g.* by the absorption due to the phenyl groups. The values found indicate that the bond order is considerably less than 2. It was found that the $\nu(C{=}N)$ is higher for the $Tl(SSCNR_2)_3$ compounds than for the corresponding $Me_2TlSSCNR_2$, indicating a higher C–N bond order and a higher effective electronegativity of the thallium atom for the former than for the latter compounds.

From a comparison of the dimethylthallium(III) dimethyl- and diethyldithiocarbamates, it can be seen that the former has higher $\nu(C{=}N)$ than the latter. The difference (26 cm^{-1}) can be assigned to the stronger inductive effect of the ethyl group, compared with that of a methyl group. Strong inductive groups bound to the nitrogen reduce the contribute of the canonic form (III); therefore, the C–N bond order is lowered as seen by the frequency shift. Similarly the difference between the $\nu(C{=}N)$ in $Tl(SSCNMe_2)_3$ and $Tl(SSCNEt_2)_3$ was found to be the same. A similar, but lower difference was observed for the 980 cm^{-1} band.

No use was made here of the proposed correlation between the position of $\nu(C{=}N)$ and the coordination number of the metal: even a change of the alkyl group, *e.g.* from methyl to ethyl, was found to cause a frequency shift bigger than the average value found for planar (1510 ± 5 cm^{-1}) and octahedral (1496 ± 2 cm^{-1}) coordination[8]. This frequency seems to be influenced not only by the stereochemistry of the complex, but also by the oxidation number of the central ion and by the nature of the substituent groups when the oxidation number of the metal is left unchanged.

When the infrared spectra of $Zn(SSCNEt_2)_2$ or those of other metal dithiocarbamates[8] and that of $EtSSCNEt_2$ were compared, they were found to be practically identical in the NaCl region, except for the 980 ± 70 cm^{-1} region, where only one intense vibration was found in the zinc derivative and two in the ethyl ester. One of the two bands was therefore assigned to uncomplexed $\nu(C{=}S)$[2]. The assignment was supported by the recent infrared study of the stretching frequency in many organic compounds[10]. Further, quite recently[11] $Ru(NO)(SSCNEt_2)_3$ was shown to contain one unchelated dithiocarbamato ring, according to an X-ray structural determination; correspondingly, more infrared bands were found here[11], including one more at 970–980 cm^{-1} (intensity and matrix not specified), than in the common, chelated derivatives of N,N-disubstituted dithiocarbamic acid.

The presence of only one intense band at 980 cm^{-1} in $Me_2TlSSCNEt_2$, at 965 cm^{-1} in $Me_2TlSSCNMe_2$ and at 978 cm^{-1} in $TlSSCNEt_2$ is evidence in favour of the presence of a bidentate dithiocarbamato moiety. However, a strong doublet (987 and 977 cm^{-1}) was found in the spectrum of $Tl(SSCNEt_2)_3$; this fact may be taken either as evidence of at least one monodentate dithiocarbamato group or, more simply, as solid state splitting. Indeed the rather low dipole moment (2.0 Debye) in benzene solution is comparable to that of other completely chelated $M(SSCNEt_2)_3$ compounds (1.6–1.9 Debye)[12]. Further, the solution spectrum (CS_2 or $CHCl_3$) shows only one strong band at nearly 980 cm^{-1}, plus only a weak shoulder. It seems then that thallium(III) is six-coordinated in solution in $Tl(SSCNEt_2)_3$.

Owing to the difficulty in assigning the P=S stretching in the dithiophosphinato derivatives, it was not possible to find spectroscopic evidence for chelation for such ligands.

MOLECULAR WEIGHTS

The molecular weights of the P,P-dithiophosphinates were determined both in benzene and chloroform, when possible, and at different concentrations: the results are given in Table 3. When a compound was found to be associated or not associated in benzene solution, the same result was found also in chloroform solution. The degree of association at the same concentration cannot be the same in these two solvent, owing to the different value of their dielectric constant, to hydrogen bond formation, etc.

The degree of association $\bar{n}$ (molecular weight found/formula weight) is significantly lower than unity only in the case of the two copper(I) complexes, pointing out the existence of an equilibrium such as

$$(Ph_3P)_2CuSSPR_2 \rightleftarrows (Ph_3P)CuSSPR_2 + Ph_3P$$

The equilibrium is shifted more to the left when R = phenyl, than when R = ethyl; the more electronegative phenyl groups are better electron drains than the ethyl groups, thus making the metal atom a better acceptor in the former than in the latter case. Since the copper complexes are nonelectrolytes in nitrobenzene and in acetone, ionic dissociation to yield $(Ph_3P)_2Cu^+$ and $^-SSPR_2$ cannot explain the low molecular weight found.

All the organotin(IV) dithiophosphinates were found to be monomeric, like the diphenylthallium(III) derivatives. In contrast, compounds having electronegative or small groups bonded to the metal, like $Cl_2Sn(SSPR_2)_2$ or $Me_2TlSSPR_2$, were found to be associated in chloroform and also in benzene solution. Since the degree of association is not an integer, an equilibrium between an associated form (*e.g.* a dimer) and the monomer is required. The association may be the result of the

TABLE 3

MOLECULAR WEIGHTS OF P,P-DITHIOPHOSPHINATES

Compound	*Chloroform solution*			*Benzene solution*		
	Conc.[a]	*Mol. wt. found*	$\bar{n}$[b]	*Conc.*[a]	*Mol. wt. found*	$\bar{n}$[b]
$TlSSPEt_2$	1.10	700	1.96	[d]		
$TlSSPPh_2$	0.52	1000	2.20	0.48	744	1.64
$Me_2TlSSPEt_2$	0.83	542	1.40	[d]		
$Me_2TlSSPPh_2$	0.61	790	1.64	[d]		
$Ph_2TlSSPEt_2$	1.19	485	0.95	[d]		
$Ph_2TlSSPPh_2$	0.63	660	1.09	[d]		
$Et_3SnSSPEt_2$	1.17	376	1.05	2.26	353	0.99
	0.29	392	1.09			
$Ph_3SnSSPPh_2$	0.98	467	0.95	6.48	470	0.94
				1.62	470	0.94
				0.65	465	0.93
$Cl_2Sn(SSPEt_2)_2$[c]	0.86	584	1.18	0.44	745	1.50
	2.62	593	1.20	0.84	806	1.63
				1.11	809	1.63
				1.51	750	1.51
$Cl_2Sn(SSPPh_2)_2$	0.38	843	1.23	[d]		
	1.23	770	1.12			
$Br_2Sn(SSPEt_2)_2$	1.27	617	1.05	[d]		
$Br_2Sn(SSPPh_2)_2$	0.66	980	1.26	[d]		
$Me_2Sn(SSPEt_2)_2$	3.18	630	0.98	8.71	650	0.99
$Et_2Sn(SSPPh_2)_2$	2.11	680	1.01	3.16	658	0.99
$(Ph_3P)_2CuSSPEt_2$	0.77	560	0.75			
$(Ph_3P)_2CuSSPPh_2$	0.68	772	0.92			
$Zn(SSPEt_2)_2$	2.04	488	1.31			
	1.31	469	1.26			

[a] Mg solute/g solvent. [b] Molecular weight found/formula weight. [c] Monomer according to ref. 14; see text. [d] Insufficiently soluble.

dithiophosphinate ion acting as a bridging bidentate ligand or the result of a three-coordinate sulphur atom. The latter explanation is rather improbable for the dihalotin derivatives, since it would require seven-coordinate tin(IV); though never considered, it cannot be ruled out for the dimethylthallium(III) or for the more strongly associated thallium(I) derivatives reported here. If only electronic effects alone were operative in determining the degree of association, diphenylthallium(III) derivatives should be more associated than dimethylthallium(III) derivatives, in contrast with the experimental results. This leads to the conclusion that steric requirements of the group on the thallium atom are more important than the electronic effects; this is in better agreement with a bidentate $^-SSPR_2$ group with one three-coordinate sulphur and with a thallium(III) atom with a coordination number higher than four rather than with a bridging bidentate ligand and a four coordinate thallium(III).

The molecular weight of the compound $Cl_2Sn(SSPEt_2)_2$ was measured both in benzene and in chloroform ($\bar{n} = 1.56$ and 1.19 resp.). The reported[14] molecular weight determination in benzene by the cryoscopic method ($\bar{n} = 1.00$) is unreliable, since the compound is only slightly soluble in benzene. Its dipole moment[14] (7.3

Debye) is characteristic of a polar molecule, but the presence of association makes the choice between a simple *cis* or *trans* structure meaningless. Similarly, the dipole moments reported for $Ph_2Sn(SSPEt_2)_2$ and for $(n\text{-}C_4H_9)_2Sn(SSPEt_2)_2$ (3.3 and 3.2 Debye resp.) do not allow a sure assignment to a *cis* structure: a high contribution of the atomic polarization, a small percentage of associated form, and some amount of distortion from octahedral symmetry or some deformation of the assumed planar $SSPR_2$ ring might add up to the value found for the dipole moment also in the case of a trans form.

All the organothallium(III) N,N-disubstituted dithiocarbamates, like the corresponding organotin(IV) derivatives[2], were found to be monomeric in chloroform and benzene solution (Table 2). Because the infrared spectrum (nujol mull and solution) shows evidence for a bidentate dithiocarbamate ring, a four-coordinate thallium(III) seems to be present here. There is no available evidence in favour of a three-coordinate sulphur atom, like that found in crystalline $Zn(SSCNEt_2)_2$[13] or $Cu(SSCNEt_2)_2$[5] by X-ray structural determination.

^{1}H NMR SPECTRA

The proton magnetic resonance spectrum of $Me_2Sn(SSPPh_2)_2$ showed two groups of signals: a complex one due to the phenyl groups ($\tau = 1.5$–2.8) and a singlet due to the tin-bonded methyl groups [$\tau = 8.50$; $J(^{119}Sn\text{–}H) = 80$ cps; $J(^{117}Sn\text{–}H) = 76$ cps]. The NMR spectrum in $CHCl_3$ of $Zn(SSPEt_2)_2$, for which $\bar{n}(CHCl_3) = 1.3$, shows only one type of ethyl protons, thus proving that the equilibrium between the monomer and the associated species is too fast at 33° to allow the two types of signals to be detected by NMR. The same consideration applies to $Cl_2Sn(SSPEt_2)_2$, for which $\bar{n}(CHCl_3) = 1.2$: the same spectrum was found as for the zinc derivative. In any case, the presence of an equilibrium with at least trace amounts of an associated species in those compounds where $\bar{n} = 1.0$ makes the assignment of a configuration to the $R_2Sn(SSPR'_2)_2$ compounds dubious, at best, unless variable temperature NMR spectra are available.

CONCLUSIONS

It appears that dithiophosphinate derivatives of dihalogenotin(IV), dimethylthallium(III) and of thallium(I) show a remarkable association in solution, like the zinc(II) derivatives, possibly also through a bridging and three-coordinate sulphur atom. A coordination number higher than four for thallium(III) derivatives, as well as for zinc(II), is reasonable.

In the case of dihalogenotin(IV) derivatives, this explanation would require a seven-coordinate tin(IV) atom; there is no reason to rule out a six-coordinate tin(IV) bridged by two dithiophosphinato groups with another identical six-coordinate tin(IV). In the case of the diorganothallium(III) N,N-disubstituted dithiocarbamates, no ionic dissociation to yield linear R_2Tl^+ is evident. Owing to the lack of association in solution and to the chelating property of the dithiocarbamato group a four-coordinate thallium(III) is present here, in spite of the fact that association via three-coordinate sulphur is possible[5,13] and that six-coordinated thallium(III) is well documented in the related $Tl(SSCNEt_2)_3$. It appears, therefore, that the choice between a four-coordinate and a six-coordinate thallium(III) depends from its effective electronegativity, which here can be correlated with the C=N stretching frequency.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin Elmer Infracord or 621 (grating) instrument. Nuclear magnetic spectra were recorded on a Perkin Elmer R-10 instrument, in $CDCl_3$ solution using tetramethylsilane as internal standard. Molecular weight determinations were carried out on a Mechrolab Osmometer at 37°; in order to obtain reasonably concentrated solutions, these were prepared at a temperature near 37°.

The compounds prepared, the analytical and some physical data are collected in Table 1 and 2. They were prepared according to the following example.

Triphenyltin(IV) diethyldithiophosphinate

A saturated acetone solution of $NaSSPEt_2 \cdot 2\,H_2O$ (0.70 g) was added to an acetone solution of triphenyltin(IV) chloride (1.24 g). The precipitate was filtered off and the solution was evaporated to dryness. The residue was extracted with hot benzene, the solvent evaporated under reduced pressure and the residue was crystallized from ethanol to yield the pure compound in 55% yield.

Infrared data of some compounds (nujol mull)

$Me_2TlSSCNMe_2$: 1512m, 1488m, 1390m, 1362m, 1242m, 1156m, 1140m, 1127m, 1044w, 1018w, 965s, 910s, 783m.

$Tl(SSCNEt_2)_3$: 1503s, 1493s, 1460s, 1448s, 1428s, 1388s, 1353s, 1298m, 1266s, 1261s, 1210s, 1150s, 1097w, 1080s, 987m, 977m, 920m, 912m, 848s, 778w.

$Cl_2Sn(SSPEt_2)_2$: 1455s, 1403m, 1380s, 1263w(broad), 1053m, 1028w, 1008w, 767s, 744s, 710s, 680s, 581s, 575sh, 505w, 485s, 397w, 340m, 319sh, 297s.

$Br_2Sn(SSPEt_2)_2$: 1455s, 1400m, 1377s, 1263w(broad), 1053w, 1044s, 1034w, 1008w, 764s, 750w, 748w, 713m, 682m, 672m, 581m, 570m, 503w, 483w,

$Zn(SSPEt_2)_2$: 1452s, 1400m, 1377s, 1260w(broad), 1240w, 1048m, 1035m, 1005w, 995w, 762s, 746s, 718s, 708s, 673s, 598s, 585sh, 485s, 400w, 338w, 293m.

$Me_2TlSSPEt_2$: 1452s, 1400m, 1370m, 1260m, 1235m, 1160w, 1018m, 1010s, 800m(broad), 770vs, 715vs, 690w(broad).

$Tl(SSCNMe_2)_3$: 1530s, 1389s, 1250s, 1158m, 1132sh, 1048m, 967s.

$Me_2TlSSCNEt_2$: 1485s, 1358m, 1345w, 1299m, 1263s, 1215m, 1158w, 1138m, 1095w, 1078w, 1070w, 985m, 908m, 847w, 778w(broad).

Electric dipole moments

The dipole moment in benzene of $Tl(SSCNEt_2)_3$ was calculated by the Halverstadt and Kumler's formula[15]:

$$ {}_{\infty}P_2 = \frac{3 \cdot V_1 \alpha_0}{(\varepsilon_1+2)^2} + (V_1+\beta)\frac{\varepsilon_1-1}{\varepsilon_1-2} $$

$w_2 \times 10^3$	α_0	β_0	P_2	P_E*	P_0	μ	$\mu_{20\%}$
9.188	0.96	—	—	—	—	—	—
15.55	—	0.42	254.2	130.7	124.5	2.4	2.0

* Calculated according to the literature[16].

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SUMMARY

Compounds with general formula $R_2Tl(SSPR'_2)$, $R_2Sn(SSPR'_2)_2$, $R_3Sn(SSPR'_2)$, $X_2Sn(SSPR'_2)_2$, $R_2Tl(SSCNR''_2)$ were prepared (R = methyl, ethyl, phenyl; X = chlorine, bromine; R' = ethyl, phenyl; R'' = methyl, ethyl, phenyl). The dithiocarbamato derivatives appear to be chelated and monomeric in solution with a four-coordinate thallium(III). $Tl(SSCNEt_2)_3$ was found to be six-coordinate in solution. The dithiophosphinates were found to be associated in solution and possible explanation for this are discussed. Owing to the presence of association, the assignment of *cis* or *trans* structure to $X_2Sn(SSPR'_2)_2$ or $R_2Sn(SSPR'_2)_2$ compounds is difficult.

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