Reactions of pentachlorothiophenol. I. Preparation of some simple metallic and non-metallic derivatives

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The preparation and properties of simple metal derivatives of pentachlorothiophenol are described: MSC_6Cl_5 (M = Na, K, Rb, Cs, Tl, Cu, Ag, Au, Ph₃Sn, *n*-Bu₃Sn, Ph₃Pb, Ph₄As), M(SC₆Cl₅)₂ (M = Zn, Cd, Hg, Ni, Pd, Pb, *n*-Bu₂Sn, Sn), Ge(SC₆Cl₅)₄, and Pt(SC₆Cl₅)₃Cl. Non-metallic derivatives of group V, $M(SC_6Cl_5)_3$ (M = P, As, Sb) and PhP(SC₆Cl₅)₂ have also been prepared from Pb(SC₆Cl₅)₂ and the corresponding non-metallic chloride. The infrared spectra of these compounds and the mass spectra of C_6Cl_5SH and (C₆Cl₅S)₂ have been examined.

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This paper is an extension and amplification of work described previously in a short communication (1). The preparation and properties of various derivatives of the main group elements and transition metals are described.

While the chemistry of pentafluorothiophenol and its derivatives has been studied in some detail (2, 3) little is known about the chemistry of pentachlorothiophenol (4). Commercially available pentachlorothiophenol contains about 40% of bis(pentachloro-phenyl)disulfide, from which it may be separated by dissolution in basic solution. Pure pentachlorothiophenol has a m.p. 241.5-242°. In basic solution thiols are readily oxidized to disulfides. Polymerization is observed to occur in basic solutions of pentafluorothiophenol in air, but not in a nitrogen atmosphere (3, 5); pentachlorothiophenol in air will not polymerize in basic solution. The polymerization of pentafluorothiophenol probably involves initial oxidation, giving bis(pentafluoro-phenyl)disulfide, which is subsequently attacked nucleophilically by the $C_6F_5S^-$ ion. That a similar reaction does not occur with pentachlorothiophenol must be due either to the poor properties of the $C_6Cl_5S^-$ ion as a nucleophile, or to the low susceptibility to nucleophilic attack of the C₆Cl₅ nucleus. Pentachlorothiophenol is readily oxidized to the disulfide.

Simple Derivatives

The thiols, in general, show properties of the type classified as hydrogen pseudohalide, and are somewhat acidic. The pK_a of pentachlorothiophenol is 5.21 ± 0.04 in 50% dioxane-water. The acidity can be utilized in various synthetic reactions. Pentachlorothiophenol reacted in

ethanol with some oxides, such as ZnO, PbO, PbO₂, and Cu₂O, but did not react with MnO_2 and GeO₂; similar reactions have been observed with pentafluorothiophenol (3). The thiol dissolves in aqueous sodium or potassium hydroxides, from which the sodium or potassium salt can be isolated on removal of the solvent. The thiol also forms salts with rubidium and cesium carbonates. The acidic properties of the thiol were shown in its reaction with *n*-butyllithium forming *n*-butane and the lithium salt. All the alkali metal salts are soluble in water forming basic solutions, as would be expected from the salt of a weak acid and a strong base.

Several metal mercaptides are insoluble in water or ethanol (6). Using pentachlorothiophenol, ethanol is a more convenient solvent as both the thiol and some metal salts are soluble. Precipitation is effected by mixing the two solutions; in this way derivatives were prepared of Tl(I), Ph₃Sn, Ph₃Pb, Pb(II), Ag(I), Cu(I), Cd(II), Hg(II), and Pt(IV). In a similar reaction (7) palladium(II) mercaptide, Pd(SC₆Cl₅)₂, was prepared by shaking a benzene solution of the thiol with an aqueous solution of the metal ion causing precipitation of the metal mercaptide in the aqueous phase.

Thiol derivatives of the non-metals may be prepared by two general techniques (8). In one, the thiol is allowed to react with a non-metallic halide in a suitable solvent; when the product is susceptible to attack by the hydrogen halide generated, a hydrogen halide acceptor, such as triethylamine is added. In the other technique the reaction of a lead mercaptide with a non-metallic halide totally eliminates the need for a hydrogen halide acceptor as lead(II) halide is formed (eqs. [1] and [2]). Using these methods it was

stibine. $GeCl_4 + 4 Et_3N + 4 C_6Cl_5SH \rightarrow Ge(SC_6Cl_5)_4$

Redox Reactions

$$[2] \quad 2 \operatorname{PCl}_3 + 3 \operatorname{Pb}(\operatorname{SC}_6\operatorname{Cl}_5)_2 \to 2 \operatorname{P}(\operatorname{SC}_6\operatorname{Cl}_5)_3$$

+ 3 PbCl₂

+ 4 Et₃NHCl

possible to prepare derivatives of Ge(IV), Sn(II) (from SnCl₄), P(III), PhP(III), As(III), Sb(III), and Bi(III). The triethylamine method can be applied to some of the earlier transition metal halides, such as titanium tetrachloride where a very unstable product was isolated. No reactions were observed with trimethylchlorosilane, phosphoryl chloride, and vanadium and tungsten trichlorides, but partial reaction occurred with silicon tetrachloride and boron trichloride.

The Sn—S bond in organotin compounds such as $R_2 Sn(SR')_2$, is susceptible to fracture by metal halides in methanol (9) and has been found to be fractured by germanium tetrachloride, but not silicon tetrachloride (eq. [3]). This type of reaction is of more synthetic utility than a similar one

[3] 2 n-Bu₂Sn(SC₆Cl₅)₂ + GeCl₄ $\rightarrow 2 n$ -Bu₂SnCl₂

 $+ \text{Ge}(\text{SC}_6\text{Cl}_5)_2$

involving the fracture of the Si-S bond in the alkyl(alkylthio)silanes (10) as the corresponding organotin thiol derivatives are not hydrolytically sensitive and are easily prepared from the organotin oxide and the thiol (11). Trimethyl-(pentafluoro-phenylthio)silane can be prepared by refluxing hexamethyldisilazane and pentafluorothiophenol in benzene (5) (eq. [4]). A

 $Me_3SiNHSiMe_3 + 2 C_6F_5SH \rightarrow 2 Me_3SiSC_6F_5$ [4]

 $+ NH_3^{\uparrow}$

similar reaction did not occur with pentachlorothiophenol and hexamethyldisilazane. The inability to prepare fully substituted derivatives of silicon parallels observations noted in the chemistry of pentafluorothiophenol (5), and may be due to the inherent thermal instability of the higher molecular weight orthothiosilicates (12), or due to their extreme hydrolytic sensitivity. This latter is undoubtedly the reason for the inability to prepare $B(SC_6Cl_5)_3$ since several orthothioborates are known (13).

Triphenylbismuthine reacts with thiophenol in refluxing xylene to form Bi(SPh)₃ (14). Little reaction was observed to occur in refluxing benzene between pentachlorothiophenol and

If pentachlorothiophenol acts as a hydrogen pseudohalide it ought to be fairly readily oxidized to the disulfide. Conversely the disulfide should act as an oxidizing agent. No oxidizing properties of bis(pentachloro-phenyl) disulfide have been observed, and only very few reactions are known in which an organic disulfide acts as an oxidizing agent (15).

triphenylbismuthine and none with triphenyl-

Pentachlorothiophenol is similar to other thiols in being readily oxidized by iron(III), copper(II), and gold(III) ions and lead dioxide; except with iron(III) ions an insoluble mercaptide is formed with the metal ion in its lower valence state (3). Phosphorus pentachloride oxidizes the thiol forming the disulfide and $P(SC_6Cl_5)_3$. Two features are different from those observed with other thiols; no tin(IV) mercaptide was formed, and a platinum(IV) mercaptide was prepared. Tin(IV) mercaptides are generally stable (16), but all successful attempted preparations of tin(IV) mercaptide yielded tin(II) mercaptide and the disulfide, the reaction probably proceeding via an unstable tin(IV) mercaptide, (eq. [5]). The

 $Sn(SC_6Cl_5)_4 \rightarrow Sn(SC_6Cl_5)_2 + (C_6Cl_5S)_2$ [5]

reaction of a solution of platinum(IV) chloride with a thiol usually produces platinum(II) mercaptide and the corresponding disulfide, the reaction presumably proceeding via an unstable platinum(IV) mercaptide. In the reaction of platinum(IV) chloride with pentachlorothiophenol $Pt(SC_6Cl_5)_3Cl$ was isolated and showed no signs of thermal instability.

Chlorine and bromine react with the thiol in an inert solvent to give pentachlorobenzenesulfenyl chloride and bromide respectively (4).

Structures

Various nickel mercaptides have a polymeric R Ni bridges (17). This structure involving Ni

type of structure is fairly general in the insoluble transition metal mercaptides, where bridges of R the type --- M--- may also be formed. It

R

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1870

[1]]

LUCAS AND PEACH: PENTACHLOROTHIOPHENOL. I

TABLE 1

Assignment of some i.r. frequencies (cm⁻¹)

Compound	C—C ring	C—C ring	C—S stretching	CCl stretching
C₅Cl₅SH	1338 s	1288 m	872 w	668 s; 679 s
$(C_6Cl_5S)_2$	1330 s	1308 s	870 m	672 m; 688 s
$Ge(SC_6Cl_5)_4$	1335 s	1306 s	masked	681 s; 692 s
$P(SC_6Cl_5)_3$	1332 s	1305 s	872 m	680 s; 691 s
NaSC ₆ Cl ₅	1325 s	1280 s	870 vw	678 s
KSC ₆ Cl ₅	1320 s	1288 s	872 vw	688 s
CuSC ₆ Cl ₅	1328 s	1290 s	870 vw	678 m; 688 m
NiSC ₆ Cl ₅	1330 s	1300 s	870 m	678 m: 692 m
[PhaAs], [Co(SCcCla)]	1322 s	1308 s	865 w	681 s
$K_2[Pt(SC_6Cl_5)_4]^*$	1325 s	1291 s	870 w	682 s
*See ref. 1.				



FIG. 1. Mass spectrum of pentachlorothiophenol: direct introduction, block temperature 143°.

would be expected with the class B metals (18) where the partially filled d orbitals on the metal atom can form back π bonds by overlapping with the empty d orbitals on the sulfur.

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The effect of the d orbitals of the metal ion may account for the non-preparation of the mercaptides, by the methods described, of titanium(III and IV), vanadium(III), chromium(III), manganese(II), and iron(II and III), where the d orbitals are only partially occupied. The actual stable transition metal mercaptides and complex ions prepared (1, 2) are restricted to the latter transition elements, which have d^7 , d^8 , and d^{10} configurations and the d orbitals involved in metal to ligand π bonding are filled. Chromium and molybdenum mercaptides, $M(SR)_3$, have recently been prepared from the carbonyls and the disulfides (19, 20), both presumably having d^3 configurations. The two slightly different nickel mercaptides formed may be different types of polymer.

It can be assumed that the alkali metal mercaptides, and the tetraphenylarsonium salt, are all ionic in the solid state; they are partially hydrolyzed in aqueous solution. The non-metallic derivatives have properties that are typical of covalent compounds, i.e. solubility in organic solvents and ease of hydrolysis.

Spectra

The infrared (i.r.) spectra of all the products have been recorded; various frequencies characteristic of the C_6Cl_5S group are shown in Table 1. The ionic species show a relatively strong adsorption between 1215 and 1200 cm⁻¹, that is either weaker or totally absent in compounds with other types of bonding. The detailed spectra of a selection of compounds are tabulated in the Experimental section.

The mass spectra of the thiol and the disulfide are shown diagrammatically in Figs. 1 and 2. No metastable peaks were observed, so it is not possible to predict a specific decomposition mechanism. The mass spectra of $(C_6F_5S)_2$ (indirect introduction, sample sublimation $\leq 84^\circ$, inlet reservoir 100°, ionization chamber 205°) (5)

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TABLE 2
Products and analyses

Melting			Found (%)				Calculated (%)				37' 1 1	
Product (°C)	Color	С	н	M	S	С	Н	М	S	(%)*	Solubility†	
LiSC ₆ Cl ₅ ·2H ₂ O	> 300	none	22.4	2.0			22.2	1.3			94	5, 6
NaSC ₆ Cl ₅	> 300	none	24.3	0.0			23.7	0.0			75	1, 2, 6
KSC ₆ Cl ₅	> 300	none	22.1	0.0			22.5	0.0			60	1, 2, 6
RbSC ₆ Cl ₅	> 300	none	19.2	0.0			19.6	0.0			63	1, 2, 6
CsSC ₆ Cl ₅	> 300	none	17.8	0.0			17.4	0.0			25	1, 2, 6
TISC ₆ Cl ₅	> 300	pale yellow	15.1	0.0		6.2	14.8	0.0		6.6	60	nil
$Ge(SC_6Cl_5)_4$	> 300	none	23.8	0.0		10.4	24.1	0.0		10.7	58(a), 67(b)	nil
Ph ₃ SnSC ₆ Cl ₅	218-219	none	45.9	2.3			45.7	2.4			24	4, 5, 6
n-Bu ₃ SnSC ₆ Cl ₅	b.p. 195/0.4 mm	none	38.1	4.8			37.8	4.8			95	3, 4, 5, 6
$n-Bu_2Sn(SC_5Cl_5)_2$	104-105	none	30.4	2.5			30.2	2.3			80	3, 4, 5, 6
$Sn(SC_6Cl_5)_2$	> 300	light yellow	21.3	0.0	16.8		21.2	0.0	17.4		74	nil
Ph ₃ PbSC ₆ Cl ₅	214 (decomp.)	none	40.7	2.1			40.0	2.1			62	3, 5, 6
$Pb(SC_6Cl_5)_2$	> 300	yellow	18.7	0.0			18.7	0.0			75(c), 93(d)	nil
$P(SC_6Cl_5)_3$	223-224	none	24.6	0.0		10.6	24.7	0.0		11.0	96	3, CCl₄
$PhP(SC_6Cl_5)_2$	249-250	none	31.4	0.7		9.6	32.2	0.7		9.6	49	3, 5, CCl₄
$As(SC_6Cl_5)_3$	260 (decomp.)	pale yellow	22.5	0.0		10.5	23.5	0.0		10.5	82(e), 94(f)	3, CCl₄
Ph₄AsSC ₆ Cl₅	> 300	orange	53.4	2.9			54.2	3.0			99	2, 3, 6
$Sb(SC_6Cl_5)_3$	245 (decomp.)	yellow	22.3	0.0		10.1	22.4	0.0		10.0	47(b), 73(f)	3
$Zn(SC_6Cl_5)_2$	> 300	none	22.8	0.0			22.9	0.0			88	2
$Cd(SC_6Cl_5)_2$	> 300	none	21.7	0.0			21.4	0.0			89	nil
$Hg(SC_6Cl_5)_2$	> 300	none	19.6	0.0			18.9	0.0			88(e), 97(d)	nil
CuSC₀Cl₅	> 300	grey-green	20.4	0.0			20.9	0.0			35(e), 86(d)	nil
AgSC ₆ Cl ₅	> 300	yellow	18.6	0.0			18.5	0.0			48	nil
AuSC ₆ Cl	265 (decomp.)	brown	15.8	0.0			15.1	0.0			74	nil
Ni(SC6Cl5)2	282(d), > 300(g)	black	23.3	0.0			23.2	0.0			39(d), 43(g)	6
$Pd(SC_6Cl_5)_2$	> 300	brown	21.1	0.0			21.5	0.0			22	nil
Pt(SC ₆ Cl ₅) ₃ Cl	> 300	flesh	20.1	0.0	18.1	9.3	20.1	0.0	18.1	9.0	65	nil

•(a) = from n-Bu₂Sn(SC₆Cl₅)₂; (b) = from C₆Cl₅SH + Et₃N; (c) = from PbO₂; (d) = from Mⁿ⁺; (e) = from MO_x; (f) = from Pb(SC₆Cl₅)₂; (g) = anhydrous media. †Solubilities: 1 = water; 2 = ethanol (95%); 3 = benzene; 4 = petroleum ether; 5 = ether; 6 = acetone.

LUCAS AND PEACH: PENTACHLOROTHIOPHENOL. I





and $(C_6Cl_5S)_2$ (direct introduction, block temperature 152°) are quite different. In the chlorocompound the C-6 nucleus is retained and Cl, or multiples thereof, are split off, whereas in the fluoro-compound the C-6 nucleus is only found in the $C_6F_4S^+$ ion with molecular weight less than $C_6F_5S^+$ and is decomposed by loss of CF, CSF, etc.; metastable peaks indicate the decompositions $C_6F_5S^+ \rightarrow C_5F_5^+ + CS$ and $C_6F_5S^+ \rightarrow C_5F_3S^+ + CF_2$. The chloro-compound rearranges with loss of sulfur, i.e. ions such as $C_{12}Cl_8S^+$ and $C_6Cl_6S^+$ are found; there are no corresponding ions formed in the decomposition of the fluoro-compound. In the fluorocompound the S-S bond is retained in various ions, $C_{12}F_9S_2^+$, $C_6F_5S_2^+$, $C_5F_4S_2^+$, $C_5F_3S_3^+$, but there is only one ion, other than the parent ion, containing two S in the chlorocompound, $C_6Cl_3S_2^+$. Similarly a comparison of the spectra of the thiols C_6F_5SH (indirect introduction, sample sublimation $\leq 105^{\circ}$) and C₆Cl₅SH (direct introduction, block temperature 143°) shows that the C-6 nucleus is retained and sulfur lost in many more ions from the chloro-thiol than from the fluoro-thiol.

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Experimental

All reagents were available commercially. Microanalyses were performed by Mikroanalytisches Laboratorium Beller, Göttingen, Western Germany. Analytical data for the new compounds prepared are shown in Table 2. All experiments were performed using approximately 1 to 2 mmoles of reagents; products were purified, where possible, by recrystallization or distillation. The i.r. spectra were recorded as mulls with Nujol or hexachlorobutadiene, or as thin films, on a Perkin-Elmer 457. Mass spectra were recorded on a Consolidated Electrodynamics Corporation 21-110B high resolution mass spectrograph.

Pentachlorothiophenol and Bis(pentachloro-phenyl)disulfide

Technical grade pentachlorothiophenol was extracted three times with aqueous caustic soda; the insoluble residue was mainly bis(pentachloro-phenyl)disulfide, together with traces of hexachlorobenzene. Acidification of the filtrate precipitated the thiol, which was filtered off, washed with water, and dried. The thiol was further purified by decolorizing with charcoal in benzene and recrystallizing. Any disulfide formed in this step was removed by dissolving the product in ammoniacal 50% aqueous ethanol and filtering; the thiol reprecipitated on acidification. The white thiol has a m.p. 241.5-242° and sublimes readily at 100°/0.4 mm. Its molecular weight was confirmed from its mass spectrum. It was soluble in organic solvents such as carbon tetrachloride, chloroform, petroleum ether, ethanol, methanol, and aromatic hydrocarbons. In hot or basic solutions it is susceptible to air oxidation to the disulfide.

Bis(pentachloro-phenyl)disulfide was obtained from the insoluble residue left after dissolution of the impure thiol in aqueous base; it was further purified by recrystallization from benzene or chlorobenzene. It is an orange solid, m.p. 234–235°, soluble in petroleum ether and sublimes at $170^{\circ}/0.4$ mm; its molecular weight was confirmed from its mass spectrum.

1873



The pK_a of pentachlorothiophenol in 50% dioxanewater was found, by conventional spectroscopic techniques (21), to be 5.21 ± 0.04 at ionic strength 0.5 and 22.5°.

Attempts to polymerize the thiol by fusing with solid sodium hydroxide in a platinum crucible produced a violent reaction at about 300° giving off a pungent gas and leaving a black solid. The water extract of this solid contained Cl⁻ ions, and on acidification H₂S was evolved; the black solid remaining was carbon.

Reactions Due to the Acidity of the Thiol

A 95% ethanol solution of the thiol was stirred with suspensions of various oxides (Cu(I), Zn, Hg(II), n-Bu₃Sn(IV) (in C₆H₆), *n*-Bu₂Sn(IV), Pb (II and IV) and As(III) (NH₃ added)). The precipitated mercaptide was isolated. The Zn, As(III), and n-Bu₃Sn(IV) products were isolated after removal of the solvent. In the Pb(IV) oxide reaction Pb(SC₆Cl₅)₂ precipitated leaving the disulfide in solution. Under similar conditions GeO2 and MnO2 did not react. LiSC₆Cl₅·2H₂O precipitated on mixing stoichiometric amounts of n-butyllithium (hexane) and the thiol (benzene); the water was not removed by drying in vacuo over P₂O₅ at room temperature, but thermogravimetric analysis showed the loss of 2.3 ± 0.1 moles of water per mole of thiol at $203 \pm 5^{\circ}$.

The MSC₆Cl₅ was obtained either from the thiol and the hydroxide in ethanol (Na, K) and isolated on removal of the solvent, or precipitated on shaking a saturated aqueous carbonate solution (Rb, Cs) in a nitrogen atmosphere with the thiol in benzene. On standing in air the alkali metal mercaptides slowly decomposed to the hydroxide and the disulfide.

Precipitation of Mercaptides

Various insoluble metal mercaptides were formed by mixing ethanol solutions of the thiol and a metal salt (Tl(I), Ag(I), Pb(II), Cd(II), Pt(IV) (10% in 1 M HCl \rightarrow $Pt(SC_6Cl_5)_3Cl)$, Ph_3M (M = Sn, Pb, from Ph_3MCl)). Oxidation occurred and precipitation of the metal in its lower valence state as its mercaptide with $Cu(II) \rightarrow Cu(I)$, $Au(III) \rightarrow Au(I)$; Fe(III) was reduced to Fe(II), but no mercaptide formed. No reaction was observed with salts of the metals Mg, Ca, Sr, Ba, Al, Cr(III), Mn(II) and Be (in C₆H₆). A product of uncertain composition was obtained from Ph₂PbCl₂; the compounds Ph₂Pb(SR)₂ are known to be unstable (22), decomposing to Pb(SR)₂, RSSR, and Ph₃PbSR.

Two somewhat different Ni mercaptides were obtained from Ni(II) in ethanol through which dry NH₃ was bubbled, or in ethanol to which aqueous NH₃ had been added; on evaporation of the solvent black crystals were recovered in each case. Under similar conditions Fe(II) did not react, but Co(II) gave an impure green product.

Reactions Using Pb(SC₆Cl₅)₂

The reaction of a non-metallic chloride, MCl_x, with suspension of Pb(SC₆Cl₅)₂ in refluxing benzene formed PbCl₂ and M(SC₆Cl₅)_x (M = P(III) (from PCl₃, or PCl₅ \rightarrow P(SC₆Cl₅)₃ + (C₆Cl₅S)₂), PhP(III), As(III), and Sb(III)). With BCl₃ in a sealed tube with no solvent a very hydrolytically sensitive white product was extracted with CCl₄; analysis for boron, after complete hydrolysis, via the mannitol method, was about half that required for B(SC₆Cl₅)₃. No reaction was observed with Me₃SiCl, SnCl₂, or SnCl₄.

Reactions Involving Triethylamine

12

A chloride (MCl_x) was reacted with the thiol in a suitable solvent to which Et₃N had been added, forming Et₃NHCl (removed by washing with HCCl₃) and $M(SC_6Cl_5)$, (M = Ge(IV), Sn(II) (from Sn(IV)), and Sb(III)). The BiO(SC₆Cl₅) formed using BiCl₃ and TiCl₄ gave an extremely air and water sensitive red product, m.p. about 184°. No reaction was observed when M = Al, PO, V(III), and Ti(III).

Miscellaneous Preparations

Hydrolytically sensitive $Ge(SC_6Cl_5)_4$ precipitated from a mixture of GeCl₄ and n-Bu₂Sn(SC₆Cl₅)₂ in ether, but no reaction occurred using SiCl₄ in place of the GeCl₄.

No reaction occurred between (Me₃Si)₂NH and C₆Cl₅SH in refluxing benzene, or Sn and (C₆Cl₅S)₂ in benzene through which HCl gas was bubbled (a standard technique for the preparation of $Sn(SR)_2$ (23)). The Ph₃Sb did not react with the thiol in refluxing benzene, but partial reaction occurred with Ph₃Bi.

The $M(SC_6Cl_5)$ (M = Ph₄As⁺, Et₃NH⁺) precipitated on addition of Ph₄AsCl or Et₃N to a solution of the thiol in aqueous base or benzene respectively.

Infrared Data

The i.r. absorption peaks in the region 4000 to 250 cm⁻¹ of a selection of compounds are listed below:

C₆Cl₅SH: 2582 w, 2573 w, 1338 s, 1288 m, 1229 w, 1100 w, 945 w, 934 w, 921 w, 872 w, 688 s, 679 s, 608 w, 390 vw, 375 vw

C₆Cl₅SSC₆Cl₅: 1510 m, 1330 s, 1308 s, 1215 w, 1205 w, 1170 m, 1100 s, 870 m, 688 s, 672 m, 599 w, 399 w, 319 w.

KSC₆Cl₅: 1505 w, 1470 w, 1320 s, 1288 s, 1278 m, 1202 s, 1170 m, 1085 vw, 969 vw, 920 vw, 872 vw, 688 s, 394 vw, 370 vw, 320 w.

Ge(SC₆Cl₅)₄: 1508 w, 1335 s, 1306 s, 1210 vw, 1180 w, 1120 vw, 1100 m, 692 s, 681 s, 422 m, 400 w, 348 w, 318 w

Sn(SC₆Cl₅)₂: 1330 s, 1300 m, 688 m, 679 m, 385 w, 335 w, 309 vw.

As(SC₆Cl₅)₃: 1505 vw, 1330 s, 1299 s, 1210 vw, 1170 vw, 1095 w, 965 vw, 935 vw, 870 w, 688 s, 678 s, 590 vw, 380 m, 338 m, 312 m.

CuSC₆Cl₅: 1328 s, 1318 vw, 1290 s, 870 vw, 688 m, 678 m. 590 vw.

 $[(C_6H_5)_4A_8]_2[Cd(SC_6Cl_5)_3Cl]$ (1): 3045 w, 1505 w, 1479 m, 1435 s, 1322 s, 1290 s, 1210 m, 1181 w, 1160 w, 1080 s, 1020 w, 995 s, 930 vw, 870 w, 835 w, 740 s, 680 s, 610 vw, 478 m, 460 m, 395 vw, 350 m, 320 w.

Mass Spectra

In the mass spectra the ions with relative abundance

In the mass spectra the ions with relative abundance greater than 5% are: $C_6Cl_5SH: C_6Cl_5SH^+, C_6Cl_5S^+, C_6Cl_5H^+, C_6Cl_5^+, C_6Cl_4SH^+, C_6Cl_4SH^+, C_6Cl_4SH^+, C_6Cl_2SH^+, C_6Cl_2S^+, C_5Cl_3^+, C_6Cl_2H^+, C_6Cl_2^+, C_6Cl_6^{2+}, C_6Cl_5SH^+, C_6Cl_2S^+, C_5Cl_2H^+, C_5Cl_2^+, C_5Cl_5SH^+, C_6Cl_4SH^{2+}, C_6Cl_4SH^{2+}, C_6Cl_4SH^{2+}, C_6Cl_4SH^{2+}, C_6Cl_4SH^{2+}, C_6Cl_2S^{2+}, C_6Cl_4SH^{2+}, C_6Cl_2S^+, C_3Cl_2S^+, C_5Cl_1S^+, C_5Cl_1S^+, C_5Cl_2S^+, C_6Cl_2S^{2+}, CCl_2S^+, C_3Cl_2S^+, C_3SH^+, C_5S^+, C_6Cl_2S^{2+}, CCl_2S^+, C_3Cl^+, C_3S^+, C_5^+, Ccl^+, (C_6Cl_5S)_2: C_{12}Cl_{10}S_2^+, C_{12}Cl_{18}S^+, C_{12}Cl_4S^+, C_6Cl_6S^+,$

 $\begin{array}{l} C_6Cl_6^+,\, C_6Cl_5S^+,\, C_6Cl_4S^+,\, C_6Cl_3S_2^+,\, C_5Cl_5^+,\, C_6Cl_4^+,\\ C_6Cl_3S^+,\, C_6Cl_3^+,\, C_6Cl_2S^+,\, C_5Cl_3^+,\, C_6Cl_2^+,\, C_3Cl_3^+,\\ C_6ClS^+,\, C_5ClS^+,\, C_6Cl_4S^{2+},\, C_4ClS^+,\, C_6Cl^+,\, C_3Cl_2^+,\\ C_3ClS^+,\, C_5Cl^+,\, C_3Cl^+. \end{array}$

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