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METAL DERIVATIVES OF PENTACHLOROTHIOPHENOL

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Knowledge of the derivatives of pentafluorothiophenol is increasing rapidly (1-4) but few studies of the pentachlorophenylthio analogs have been reported. We have prepared several mercaptides (Table I) and a few complex ions (Table II) containing the pentachlorophenylthio group.

The metal mercaptides were prepared by a variety of methods. The sodium and potassium derivatives were prepared by mixing an alcoholic solution of the thiophenol with an equivalent amount of an alcoholic solution of the appropriate hydroxide. The rubidium, cesium, mercuric, lead and palladium mercaptides were formed by shaking together an aqueous solution of the metal salt and a benzene solution of the thiophenol. The rubidium and cesium mercaptides were synthesized under nitrogen; in the presence of these ions air caused rapid oxidation of the thiophenol. The nickel compound was prepared in absolute ethanol, dry ammonia being bubbled through the stirred mixture. Suspensions of pentachlorothiophenol and solutions of a number of other metal salts in 95% ethanol were stirred at room temperature for varying periods. Most of the resulting mercaptides were sparingly soluble in common organic solvents. The silver mercaptide was light-sensitive.

TABLE I

Pentachlorophenylthiometcaptides

Reaction of C_6Cl_5SH with	Compound Formed	Colour	Melting Pt. °C.
NaOH	$NaSC_6Cl_5$	white	>300
KOH	KSC_6Cl_5	white	>300
Rb_2CO_3	$RbSC_6Cl_5$	white	>300
Cs_2CO_3	$CsSC_6CL_5$	white	>300
$Ni(NO_3)_2 \cdot 6H_2O$	$Ni(SC_6Cl_5)_2$	black	282d
$PdCl_2$	$Pd(SC_6Cl_5)_2$	red-brown	>300
$AgNO_3$	$AgSC_6Cl_5$	yellow	>300
$HAuCl_4 \cdot 3H_2O$	$AuSC_6Cl_5$	brown	265d
	$+(C_6Cl_5S)_2$	orange	234-235
$Cd(NO_3)_2 \cdot 4H_2O$	$Cd(SC_6Cl_5)_2$	white	>300
$Hg(NO_3)_2 \cdot H_2O$	$Hg(SC_6Cl_5)_2$	white	>300
$TlNO_3$	$TlSC_6Cl_5$	yellow	>300
$(C_6H_5)_3SnCl$	$(C_6H_5)_3SnSC_6Cl_5$	white	218
$Pb(C_2H_3O_2)_2$	$Pb(SC_6Cl_5)_2$	yellow	>300
$(C_6H_5)_3PbCl$	$(C_6H_5)_3PbSC_6Cl_5$	white	214d
ZnO	$Zn(SC_6Cl_5)_2$	white	>300
$(\underline{n}-C_4H_9)_2SnO$	$(n-C_4H_9)_2Sn(SC_6Cl_5)_2$	white	105
$[(n-C_4H_9)_3Sn]_2O$	$(n-C_4H_9)_3SnSC_6Cl_5$	colourless	b.p. 195/0.4 mm.
PbO	$Pb(SC_6Cl_5)_2$	yellow	>300
PbO_2	$Pb(SC_6Cl_5)_2$	yellow	>300
	$+(C_6Cl_5S)_2$	orange	234-235
$(C_6H_5)_4AsCl$	$[(C_6H_5)_4As][SC_6Cl_5]$	orange	>300
$(C_2H_5)_3N$	$[(C_2H_5)_3NH][SC_6Cl_5]$	orange	89d

TABLE II

Pentachlorophenylthio-Metal Complexes

Reaction of $NaSC_6Cl_5$ with	Compound Formed	Colour	Melting Pt. °C.
$Ni(NO_3)_2.6H_2O$	$[(C_6H_5)_4As]_2\ [Ni(SC_6Cl_5)_4]$	black	258d
$PdCl_2$	$[(C_6H_5)_4As]_2\ [Pd(SC_6Cl_5)_4]$	red-brown	242d
$ZnSO_4.7H_2O$	$[(C_6H_5)_4As]_2\ [Zn(SC_6Cl_5)_4]$	white	172d
$Hg(NO_3)_2.H_2O$	$[(C_6H_5)_4As]_2\ [Hg(SC_6Cl_5)_4]$	yellow	153d

Salts of beryllium, magnesium, calcium, strontium, barium, titanium (III) and (IV), vanadium (III), chromium (III), maganese (II), iron (II) and (III), aluminium, germanium, tin (IV) and bismuth did not form mercaptides either under the conditions described or in anhydrous media.

Iron (III) and gold (III) salts were reduced to iron (II) and gold (I); the latter formed $Au(SC_6Cl_5)$ and the thiol was oxidized to the disulphide.

$$2Au^{3+} + 6C_6Cl_5SH \rightarrow 2AuSC_6Cl_5 + 2(C_6Cl_5S)_2 + 6H^+$$

Mercaptides were prepared from several metal oxides and alkylmetal oxides by stirring alcoholic suspensions of the oxide and the thiophenol at room temperature. Tri-n-butyltin mercaptide, a colourless oil, was formed in solution by stirring tri-n-butyltin oxide with pertachlorothiophenol in benzene Lead dioxide was reduced to its monoxide, the thiophenol being oxidized to the disulphide and lead (II) oxide then forming plumbous mercaptide.

A few complex ions of the type $[M(SC_6Cl_5)_4]^{2-}$ (see Table II) have been formed using the pentachlorophenylthio anion as a ligand. These were prepared by adding an aqueous solution of a metal salt to an aqueous, alkaline solution of pentachlorothiophenol. After filtration, an aqueous solution of tetraphenylarsonium chloride was added to the filtrate to precipitate the complex ion as its tetraphenylarsonium salt. The tetrakis (pentachlorophenylthio) zincate ion decomposed slowly under nitrogen.

The formulas presented for the compounds listed in the tables are supported by elemental analysis. Infra-red spectra of all these compounds show characteristic bands in the following regions: doublets between 1308 and 1336 cm^{-1} and between 1227 and 1304 cm^{-1} (C-C ring), a singlet between 860 and 870 cm^{-1} (C-S stretch) and a third doublet between 668 and 694 cm^{-1} (C-Cl vibration).

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