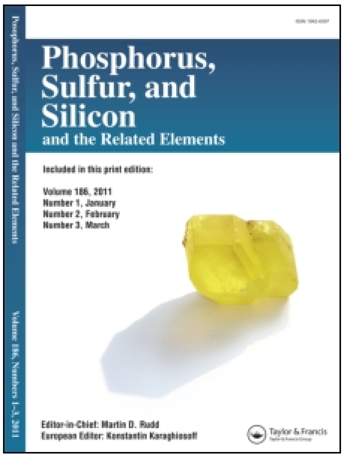

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SOME COMPLEXES OF AROMATIC *ORTHO*-BIS(METHYLTHIO)ETHERS

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SOME COMPLEXES OF AROMATIC *ORTHO*-BIS(METHYLTHIO)ETHERS

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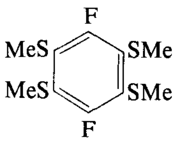
The reactions of some partially fluorinated aromatic *ortho*-bis(methylthio)ethers with various metal ions and metal carbonyls have been examined. All the complexes formed have been characterized.

INTRODUCTION

The thioethers can form complexes with various metal ions, particularly with soft acids[1] or class B[2] metal ions, as it is classified as a soft base.[1] Various complexes of mono and poly functional thioethers are known,[3] but only a few of the aromatic *ortho*-dithioethers have been studied.[4,5] Recently a number of aromatic compounds containing two methylthio groups *ortho* to each other have been prepared. Some of these are shown: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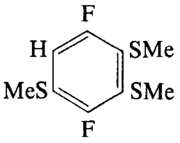
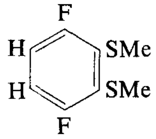

L2 (Ref. 7)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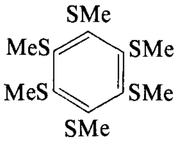
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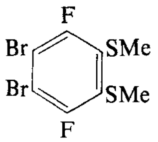
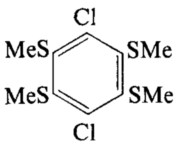

L5 (Ref. 9)

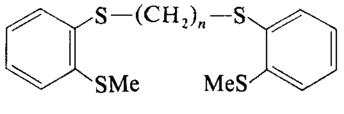

L6 (Ref. 6)

As a continuation of a study of aliphatic dithioethers as chelating agents[10] this paper describes some of the properties of these aromatic dithio ethers as chelating agents. The reactions with some metal ions and metal carbonyls have been studied.

RESULTS AND DISCUSSION

In the reaction of the methanethiolate anion with hexafluorobenzene various thioethers were isolated, $MeSC_6F_5$, p-$(MeS)_2C_6F_4$, p-$F_2C_6(SMe)_4$ (L1) and $C_6(SMe)_6$ (L6).[6] The two thioethers with isolated methylthio groups, $MeSC_6F_5$ and p-$(MeS)_2C_6F_4$, did not form any complexes with metal ions. Similarly the sulfide, $(C_6F_5)_2S$, did not form complexes with metal ions. This can probably be attributed to the electron withdrawing effect of the pentafluorophenyl or tetrafluorophenyl groups. If however the two methylthio groups are *ortho* to each other, as in L1, complexes can be formed with several metal ions. This ability to form complexes must be in part due to the chelate effect.

The metal ion complexes were prepared either by mixing solutions of the appropriate metal salt and the ligand or by Soxhlet extraction of a metal salt into a solution of the ligand. The metal ions studied included Ag(I), Hg(I), Hg(II), Cu(I), Cu(II), Pd(II), Pt(II), Pt(IV), Au(I), Au(III) and Ni(II). Products were generally obtained in the reactions with Ag(I), Hg(I) and Pd(II) and sometimes with Cu(I) and Pt(II). The products were insoluble in all common solvents and could not be recrystallized. Some were soluble in DMF, acetonitrile and DMSO but could not be reprecipitated from the solution. These products were purified by thorough washing with appropriate solvents. Somewhat similar metal complexes have been prepared using the open chain tetradentate thioethers.[5] These complexes and those


$n = 2,3,4$

of the bidentate thioethers, $RS(CH_2)_nSR$[10] could only be purified by repeated washing.

The complexes formed with chromium and molybdenum hexacarbonyl were prepared by adding a uv irradiated THF solution of the metal carbonyl, containing $M(CO)_5.THF$, to a THF solution of the ligand. These complexes could be purified by recrystallization and were of the type $[M(CO)_4 L]$. The complex $[Cr(CO)_4 L4]$ has previously been obtained as one of the products from 2,5-dithia-3-hexyne, $MeSC{\equiv}CSMe$, and $[Cr(CO)_3(MeCN)_3]$ in ether.[11]

The crystal structure of the complex $[W(CO)_4(fds)]$ (fds = *ortho*-bis(methylthio)benzene) has shown it to be monomeric with octahedral coordination around the tungsten[4] and the bis(methylthio)benzene acting as a bidentate ligand. An octahedral coordination around the metal atom and the *ortho*-bis(methylthio) compounds acting as bidentate ligands have been deduced from the infrared and nmr spectra. The infrared spectra showed CO absorptions characteristic of *cis*-$L_2M(CO)_4$ species and are tabulated in Table I.

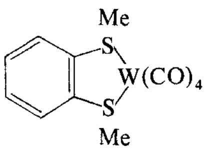


TABLE I
CO absorption in the infrared spectra

Compound	CO absorptions (cm^{-1})	
$[Cr(CO)_4(fds)]$	2025 s, 1921 m, 1906 m, 1889 s	(Ref. 4)
$[Cr(CO)_4(L1)]$	2018 m, 1925 s, 1910 s, 1898 s	
$[Cr(CO)_4(L2)]$	2020 s, 1915 s, 1900 s, 1880 s	
$[Cr(CO)_4(L3)]$	2020 s, 1925 s, 1910 s, 1890 s	
$[Cr(CO)_4(L4)]$	2020 s, 1925 s, 1910 s, 1890 s	
$[W(CO)_4(fds)]$	2027 s, 1917 m, 1904 m, 1892 s	(Ref. 4)
$[W(CO)_4(L1)]$	2018 m, 1925 m, 1907 m, 1901 m	

fds = *ortho*-bis(methylthio)benzene

The proton nmr spectra of the ligands and the carbonyl complexes are shown in Table II. The spectra were recorded rapidly as decomposition occurred in the $CDCl_3$ solvent. The spectra all show that in the complex the various methylthio groups can be differentiated. In $[Cr(CO)_4(L4)]$ the structure deduced is similar to that postulated previously[11] and shows three sets of equivalent methyl groups. It is assumed that one group is the two methylthio groups bonded to the chromium, the others the methyl groups *ortho* and *para* to these. The spectrum of $[Cr(CO)_4(L3)]$ shows that the metal protons are deshielded and the chemical shift moved to a lower value. This would be expected if the sulfur is coordinated to the metal. This was observed in all the other spectra. In the free ligands L2 and L3 the

TABLE II
Proton nmr spectra[a]

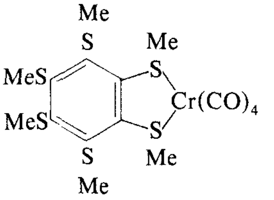
Compound	Chemical shift/p.p.m.	Relative intensity	Coupling constants/Hz	
p-$F_2C_6(SMe)_4$(L1)	2.491 T	—	$J(Me{-}F_0)$ 1.0	(Ref. 6)
$[Cr(CO)_4(L1)]$	2.586 T	1	$J(Me{-}F_0)$ 0.55	
	2.768 S	1		
$[W(CO)_4(L1)]$	2.590 S	1		
	3.022 S	1		
$HF_2C_6(SMe)_3$(L2)	2.485 D(Me)	3	$J(Me{-}F_0)$ 1.95	(Ref. 7)
	2.429 D(Me)	3	$J(Me{-}F_0)$ 1.43	
	2.444 S(Me)	3		
	6.811 Q(ArH)	1	$J(H{-}F_0)$ 9.3; $J(H{-}F_m)$ 6.4	
$[Cr(CO)_4(L2)]$	2.519 D(Me)	3	$J(Me{-}F_0)$ 2.0	
	2.467 S(Me)	6		
	6.859 Q(ArH)	1	$J(H{-}F_0)$ 9.3; $J(H{-}F_m)$ 6.5	
$H_2F_2C_6(SMe)_2$(L3)	2.469 T(Me)	3	$J(Me{-}F_0)$ 1.0	(Ref. 7)
	6.894 T(ArH)	1	$J(H{-}F)$ 6.0	
$[Cr(CO)_4(L3)]$	2.800 S(Me)	3		
	7.20 T(ArH)	1	$J(H{-}F)$ 6.0	
$C_6(SMe)_6$(L4)	2.524 S	—		
$[Cr(CO)_4(L4)]$	2.81 S	1		
	2.58 S	1		
	2.52 S	1		

[a] Measure in $CDCl_3$ with TMS as internal standard.

TABLE III
Tentative metal–sulfur infrared absorptions (cm^{-1})

Compound	Frequency (cm^{-1})	Compound	Frequency (cm^{-1})
[Ag(L1)NO$_3$]	319 w	[Pt(L3)(CN)$_2$]	325 m
[Pd(L1)(OAc)$_2$]	320 w	[Pd(L4)Cl$_2$]	320 s, 290 s
[Cu$_2$(L1)Cl$_2$]	310 w	[Co$_2$(L4)Cl$_4$]	330 m, 290 w
[Hg(L1)NO$_3$]	350 w, 310 w	[Cu$_2$(L5)Cl$_2$]	340 m
[Pt(L1)Cl$_2$]	325 w	[Pd(L5)Cl$_2$]	360 m, 325 m, 310 m
[Ag(L2)NO$_3$]	368 w, 312 w	[Pt(L5)Cl$_2$]	370 m, 335 w, 310 w
[Pd(L2)Cl$_2$]	320 w	[Cu$_2$(L6)Cl$_2$]	340 w
[Pd(L3)Cl$_2$]	335 m, 320 w		

methyl protons are split into doublets or triplets by coupling to *ortho* fluorine atoms.[7] A similar splitting is observed in L1, although this spectrum is more complex, being symmetrical.[12]



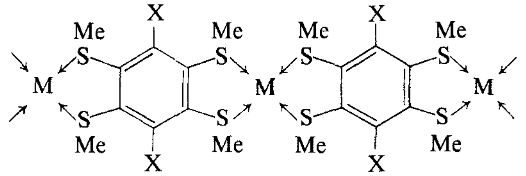
The mass spectra of the carbonyl complexes showed that decomposition had occurred and only the free ligand was detected.

Assignment of the structures of the metal ion complexes is much more difficult. The metal–sulfur stretching frequencies occur below 500 cm^{-1} in the infrared spectra[13] and are usually very weak. Some tentative assignments are shown in Table III.

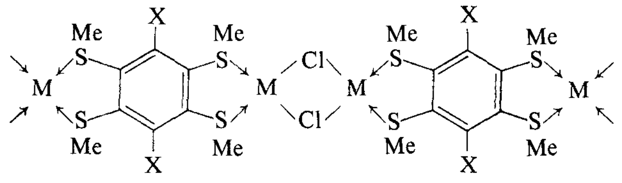
All of the metal ion complexes studied decomposed before melting. The thermal decomposition of some of the complexes in a slow stream of nitrogen was studied at 400–450°. The nature of the inorganic residue was investigated, where possible, by x-ray powder diffraction. Details are shown in Table IV. The percentage loss in weight also corresponded to the products shown. Amorphous products were obtained in the decomposition of [Pd(L1)(OAc$_2$]. [Pt(L1)(Cl$_2$)] and [Pd(L2)(Cl$_2$)]. Themogravimetric analysis of the complex [Ag(L1)-(NO$_3$)] showed 46.7% loss of weight (theoretically 47.2% loss of weight to form Ag$_2$S) at 155–255° and of the complex [Ag$_2$(L4)(NO$_3$)$_2$] showed a two stage decomposition at 220–225° and 225–350°. At 220–225° 31.6% loss of weight occurred and at 225–350° a further 19.3% loss of weight occurred, giving a total loss of 50.9% corresponding to the formation of Ag$_2$S.

These data suggest that the metal ion complexes also involve sulfur coordination. The low solubility indicates polymeric structures. Some possible structures are shown:

ML



M$_2$L



M$_2$L

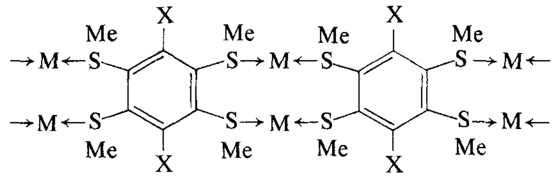


TABLE IV
Thermal decomposition studies at 400–450°

Complex	Inorganic residues
$[Cu_2(L1)Cl_2]$	$Cu_{1.98}S$, $Cu_{1.8}S$, $CuS \cdot 4Cu_2S$
$[Ni(L1)Br_2]$	$NiS_{1.03}$, NiS
$[Ag(L1)NO_3]$	Ag_2S (argentite)
$[Ag(L2)NO_3]$	Ag_2S (argentite)

Various sulfur complexes of mercury(I) are now known.[14] These complexes are probably analogous to the mercury(I) selenium complexes,[15] retaining the Hg—Hg bond with the oxygen of the anion and two sulfur atoms coordinated to each mercury.

EXPERIMENTAL

The ligands were prepared by literature methods, except L4: L1;[6] L2, L3;[7] L5.[9] Ligand L4 was prepared from C_6F_6 (60% yield) or C_6Cl_6 (89% yield) and sodium methanethiolate in DMF. The reaction procedure was similar to that described using pyridine-ethylene glycol as solvent.[6,7] Ligand L4 has been recently prepared by a somewhat different method.[8] The metal salts and carbonyls were commercially available. Chemical analyses were performed by Mikroanolytisches Laboratorium, Beller, Göttingen, West Germany or at the University of Würzburg, West Germany (Frau Ullrich). Data are shown in Table V. Infrared spectra were recorded as mulls, solutions in CCl_4, or KBr discs on a Perkin-Elmer 457 spectrophotometer. Nmr spectra were recorded in $CDCl_3$ solution with TMS as internal standard on a Varian HA 100. Mass spectra were determined on a Varian MAT CH-7 spectrometer. X-ray diffraction patterns were obtained on a Phillips Norelco x-ray powder diffractometer using FeK_α radiation with a Mn filter. The inorganic residues from the thermal decompositions were identified by comparison with standard A.S.T.M. data.

The reactions with metal ions were mainly studied by mixing solutions of the appropriate metal salt in acetone or methanol (Hg(I) reactions) with a solution of the ligand in the same solvent. After standing for 1 d. the precipitate was filtered off and washed with appropriate solvents for the metal salt and the ligand (Method 1).

Alternatively a Soxhlet extraction method was employed (Method 2). The metal salt was slowly extracted from the thimble of the extractor into the boiling acetone solution of the ligand and the complex precipitated.

TABLE V

Compound	Color	Decomposition Temp. (°C)	Calculated %			Found %			Method	Yield %
			C	H	S	C	H	S		
$C_6(SMe)_6(L6)$	White	89 (mp)	40.6	5.12	54.2	40.6	5.01	54.3	—	89
$[Cu_2(L1)Cl_2]$	Yellow	272–5	24.2	2.44	25.8	24.0	2.44	25.3	1	44
$[Ag(L1)NO_3]$	White	174–6	25.7	2.58	27.4	25.7	2.52	27.3	1	66
$[Hg(L1)NO_3]$	White	180–5	27.9	2.81	—	27.5	2.52	—	1	75
$[Ni(L1)Br_2]$	Light green	252–4	24.2	3.17	33.6	25.6	3.17	33.3	1	35
$[Pd(L1)(OAc)_2]$	Yellow	176–9	32.1	3.47	24.5	31.5	3.50	24.8	1	61
$[Pt(L1)Cl_2]$	Yellow	250–5	21.3	2.14	22.7	21.8	2.29	22.5	1	54
$[Cu(L2)Cl]$	Yellow	141–2	30.8	2.87	27.4	30.0	2.88	27.0	1	6
$[Ag(L2)NO_3]$	White	163–5	25.6	2.39	22.8	25.9	2.29	22.9	1	38
$[Hg(L2)NO_3]$	White	155–8	20.0	1.86	18.7	20.6	1.99	18.1	1	91
$[Pd(L2)Cl_2]$	Orange	210–60	25.2	2.21	22.4	25.3	2.36	22.4	1	60
$[Hg(L3)(NO_3)_2]$	White	183–5	17.8	1.49	11.9	18.0	1.39	11.4	1	9
$[Pd(L3)Cl_2]$	Yellow	>360	25.1	2.10	16.7	25.2	1.72	16.5	1	87
$[Pt(L3)(CN)_2]$	Dark green	288–90	23.8	2.50	15.9	22.4	1.72	16.3	1	62
$[Cu_2(L4)Cl_2]$	Yellow brown	220–30	26.9	3.28	—	26.9	3.09	—	1	99
$[Cu(L4)Br_2]$	Green brown	170–5	24.9	3.14	—	24.5	3.80	—	1	62
$[Ag_2(L4)(NO_3)_2]$	Light yellow	170–5	20.8	2.61	27.7	21.0	2.81	28.0	1	83
$[Ag_5(L4)(NO_3)_5]$			12.0	1.51	—	12.25	1.62	—	1	83
$[Ni(L4)Br_2]$	Yellow green	246–8	25.2	3.17	33.6	25.6	3.17	33.3	1	91
$[Pd(L4)Cl_2]$	Dark orange	252–3	27.1	3.41	36.2	27.3	3.43	35.7	1	82
$[Pt_2(L4)Cl_4]$	Gold	>300	16.3	2.05	—	16.5	1.61	—	1	78
$[Co_2(L4)Cl_4]$	Blue green	240–2	23.5	2.95	31.3	23.5	3.45	31.9	2	5
$[Pd(L5)Cl_2]$	Orange	>300	17.7	1.12	11.8	17.7	1.18	12.2	2	75
$[Pt(L5)Cl_2]$	Yellow	>300	19.3	1.21	—	19.3	0.73		2	33
$[Cu(L5)Cl]$	Light yellow	206–8	20.8	1.31	13.9	21.3	1.42	14.2	2	32
$[Ag_2(L6)(NO_3)_2]$	Pale yellow	220–2	17.9	1.80	19.1	18.5	1.92	19.8	2	45
$[Cu_2(L6)Cl_2]$	Orange yellow	>300	22.7	2.28	24.2	23.5	2.55	23.6	2	18
$[W(L1)(CO)_4]$	Yellow	>100	28.3	2.04	—	27.9	2.27	—	3	2
$[Cr(L1)(CO)_4]$	Orange red	>122	36.4	2.62	—	36.5	2.63	—	3	~20
$[Cr(L4)(CO)_4]$	Yellow	113–4	37.2	3.51	—	37.2	3.80	—	3	60

The starting materials used were $AgNO_3$, $HgNO_3.H_2O$, $Hg(NO_3)_2.\frac{1}{2}H_2O$, Cu_2O (converted to CuCl or CuBr with HCl or HBr), $Cu(NO_3)_2.3H_2O$, $CuBr_2$, $Pd(OAc)_2$, $PdCl_2$, $K_2Pt(CN)_4$, K_2PtCl_4, H_2PtCl_6, $KAu(CN)_2$, $HAuCl_4$, $Ni(NO_3)_2.6H_2O$ and $CoCl_2$. No reaction was observed between C_6F_5SMe or p-$(MeS)_2C_6F_4$ and Ag(I), Hg(I), Hg(II), Cu(I), Cu(II), Pd(II), Pt(II), Pt(IV), Au(I), Au(III), Pb(II), Cd(II), Cr(III) or Ni(II); Hg(II), Cu(II), Au(I), Au(III) and L1, L2 or L3; Cu(I) and Ni(II) and L2 or L3; Pt(II) and L2; L5 and Ag(I) or Ni(II). No stoichiometric products were obtained from Ag(I), Hg(I) and Pt(II) and L3.

In the reactions with metal carbonyls the method used (Method 3) has been described previously.[16] THF solutions of the chromium or tungsten hexacarbonyl were irradiated with uv light until the ir spectra showed that at least 80% $M(CO)_5$ THF had been formed. These solutions were added to THF solutions of the appropriate ligand. The solvent was removed and the residue extracted with 50/70 pet. ether, and filtered. The product precipitated on cooling. Excess hexacarbonyl was removed by warming to 40–50° in vacuo. The complexes $[Cr(CO)_4(L1)]$ and $[W(CO)_4(L1)]$ were analysed immediately after preparation at the University of Würzburg, but samples $[Cr(CO)_4(L2)[$ and $[Cr(CO)_4(L3)]$ decomposed when mailed for analysis.

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