Tetrafluorobenzene 1,2-Dithiolene Complexes of the Transition Metals

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A NEW chelate ligand, tetrafluorobenzene-1,2-dithiol (H_2tfdt) (I), has been synthesised; it reacts readily with most first-row transition metals and its complexes with these and with Mo and Pt have been studied.

Magnetic measurements suggest a trigonal prismatic structure for the Mo^{IV} complex.

As part of our studies of the structure of metal complexes of various fluoro-ligands[1-3] we have prepared (I) from 1,2,3,4-tetrafluorobenzene. The monothiol was first prepared[4] by lithiation with n-butyl-lithium followed by treatment with sulphur and then hydrochloric acid. Repetition of this process with the monothiol yielded the dithiol† as an high-boiling oil which is reasonably acidic (p$K \sim 5$).

Surprising reactivity is shown towards the free first-row transition metals; thus the dithiol reacts rapidly in methanol with all these metals to form deeply coloured solutions, except in the cases of titanium and nickel where the reaction is much slower. With finely powdered metals, dissolution is complete in 1 hr.; with manganese rapid evolution of a gas (hydrogen, confirmed by mass spectrometry), is observed. Crystalline complex salts are obtained by adding the $[Bu_4N]^+$ cation. The compounds $[Bu_4N][Cu^{III}tfdt_2]$, $[Bu_4N][Cr^{III}tfdt_2]$ and similar Mn, Fe, Co, and Ni derivatives have been prepared in this way. The metals react in nitrogen or air but in the latter case $[C_6F_4S_2]_n$, $n \simeq 4$, is obtained as a by-product; this is presumably a polymeric disulphide and may involve a large ring.

The magnetic properties of $[Bu_4N][M^{III}\ tfdt_2]$, M = Fe, Co, and Ni, have been studied over a temperature range (see Table 1). The results indicate substantial antiferromagnetic interaction for the Fe and Co complexes but less so for the nickel one. Similar interaction[5,6] has been reported previously in complexes of (II) and (III). The

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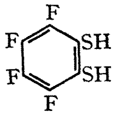
residual paramagnetism of the Co^{III} complex is in marked contrast with the diamagnetism of the corresponding dimeric tetrachloro-dithiol derivative.[7]

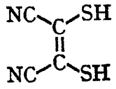
TABLE 1

Magnetic susceptibilities of Fe^{III}, Ni^{III}, *and* Co^{III} *dithiolenes*

			μ_{eff} at		
			100° K	200° K	300° K
$Bu_4N[Fe(C_6F_4S_2)_2]$	(d^5)	..	0·94	1·58	1·96
$Bu_4N[Co(C_6F_4S_2)_2]$	(d^6)	..	0·56	0·85	1·15
$Bu_4N[Ni(C_6F_4S_2)_2]$	(d^7)	..	1·58	1·75	1·80

With heavier transition-metals the formation of tris-chelate complexes is observed. Thus $[Et_4N]_2[Mo^{IV}\ tfdt_3]$ and $[Bu_4N]_2(Pt^{IV}\ tfdt_3]$ are readily prepared from Mo^{II} acetate and K_2PtCl_4, respectively. The diamagnetism of the Mo^{IV} complex suggests a trigonal prismatic structure similar to that observed for various *neutral* complexes.[8] An *X*-ray investigation is in progress to determine this. As shown in Table 2, the molecular conductivity of 10^{-3}M indicates *two* ions for the Fe, Co, and Ni complexes, and *three* for the Mo and Pt derivatives.


(I)


(II)

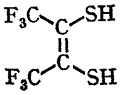

(III)

TABLE 2

Complex	Colour	m.p.	Molec.[a] conduct. (ohm^{-1})
$[Bu_4N]Fe\ tfdt_2$	dark red-black	230°	79
$[Bu_4N]Co\ tfdt_2$	dark blue-black	170°	70
$[Bu_4N]Ni\ tfdt_2$	black	144°	74
$[Et_4N]_2Mo\ tfdt_3$	blue	242°	159
$[Bu_4N]_2Pt\ tfdt_3$	red	246°	133

[a] 10^{-3}M in $MeNO_2$ (1 : 1 electrolyte ~70 ohm^{-1}). Satisfactory analyses have been obtained in all cases and agree with the formulae assigned.

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