Charge-transfer Interactions between Transition-metal Fluorides and Compounds of Group IV Elements

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Summary Charge-transfer interactions have been observed between NbF_5, MoF_6, WF_6, and WF_5OMe, and the Group IV compounds MX_4 (M = Si, Ge, Sn, X = alkyl; M = C, Si, Sn, X = Cl).

IT is considered that the colours observed when high oxidation state halides, oxohalides, and oxides are mixed with π-donors such as mesitylene and hexafluorobenzene are due to charge-transfer interactions.[1] We report that similar interactions can occur between NbF_5, MoF_6, WF_6, WF_5OMe, and some Group IV compounds: the presence of an aromatic system to act as a donor is unnecessary. Solutions of the fluorides in tetra-alkyl-silicon, -germanium, and -tin compounds are characterised by broad absorptions ($\epsilon_{molar} = 5 \times 10^4$—$10^5$) in the near u.v. region. NbF_5 solutions are yellow and those of MoF_6, WF_6, and WF_5OMe are yellow when dilute and become red with increasing concentration. The observed colours are due to the u.v. bands 'tailing' into the visible region. The colours of the MoF_6, WF_6, and WF_5OMe solutions almost disappear when they are frozen as has been observed for other weak complexes of this type;[1,2] the NbF_5 solutions were too dilute for colour changes to be detected. Similar bands are observed in the colourless mixtures of WF_6 with carbon, silicon, and tin tetrachlorides and for WF_5OMe in CCl_4.

The variation of absorbance with concentration[3] in WF_6, Bu^n_4Sn solutions is consistent with the presence of 1 : 1 complexes with near-zero equilibrium constants as has been observed for MoF_6 and WF_6 with π-donors.[1,4] The order of ionisation potentials for Me_4M is Si $\geqslant$ Ge > Sn[5] and the electron affinity of MoF_6 is probably greater than that of WF_6[6] but the ν_{max} values (Table) indicate that there is no simple dependence on these terms. Different spectra are obtained in the systems WF_6, R_4Sn when R is varied, so that the energies of the transitions depend upon electronic factors influenced by R and on the size of the tetra-alkyltin molecule. It is not possible to assign the observed bands to particular transitions as the model for the bonding is not known. $SiCl_4$, $SnCl_4$, and the fluorides are known to behave as conventional acceptors but it is considered that the observed spectra are the result of more than one electronic transition and that the model required to explain the bonding is complex.

Electronic spectra ($\nu_{max} \times 10^{-3}$ cm^{-1})

Solution	NbF_5	WF_6	MoF_6	WF_5OMe
Me_4Si	43·5, 37·9sh	40·3	27·9	40·3
Me_4Ge	42·9	34·8	43·4	
Me_4Sn	36·3	29·8	Reaction	
Pr^n_4Sn		43·7, 34·5sh		
Bu^n_4Sn		41·3, 31·7		
CCl_4		37·2	Reaction	37·2
$SiCl_4$		41·8	Reaction	
$SnCl_4$		42·9		

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