Interaction of Tin Chlorides with Iron, Chromium and Vanadium Chlorides in Tetrahydrofuran. Crystal Structures of $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$, $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ and *trans*-$[CrCl_2(thf)_4][SnCl_5(thf)]$ †

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The reaction of $FeCl_3$ with $SnCl_2$ in tetrahydrofuran (thf) yields the salt $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ **1**. In the $[Fe_2(\mu\text{-}Cl)_3(thf)_6]^+$ cation, two six-co-ordinate Fe^{2+} ions separated by an Fe···Fe distance of 3.086(2) Å are bonded through three bridging Cl atoms. Compound **1** undergoes partial decomposition under reflux in thf to give $[Fe_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$ **2** and $[SnCl_4(thf)_2]$. The compound $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ **3** is formed under the influence of moisture during the crystallization of $[SnCl_4(thf)_2]$. It is a dimeric complex of Sn^{IV} in which each tin atom is surrounded octahedrally by three chlorine atoms, one thf molecule and two bridging hydroxide groups. An additional two thf molecules are hydrogen-bonded to the oxygen atoms of the hydroxide groups. By contrast with $FeCl_3$, the reactions of $[SnCl_4(thf)_2]$ with $[MCl_3(thf)_3]$ (M = V or Cr) in thf give tin(IV) salts of the type *trans*-$[MCl_2(thf)_4][SnCl_5(thf)]$.

Halide transfer between transition and main-group metals leads to the formation of new salts, for example the dimeric cations $[V_2(\mu\text{-}Cl)_3(thf)_6]^+$ and $[Mg_2(\mu\text{-}Cl)_3(thf)_6]^+$ are formed in reactions (1) and (2) in tetrahydrofuran (thf).[1,2] Each of these

$$4[VCl_3(thf)_3] + 2Zn \longrightarrow [V_2(\mu\text{-}Cl)_3(thf)_6]_2[Zn_2(\mu\text{-}Cl)_2Cl_4] \quad (1)$$

$$2[MgCl_2(thf)_2] + [TiCl_4(thf)_2] \longrightarrow [Mg_2(\mu\text{-}Cl)_3(thf)_6][TiCl_5(thf)] \quad (2)$$

cations consists of two distorted octahedra sharing a Cl_3 triangular face.

Alternatively mononuclear cationic species such as $[VCl_2(thf)_4]^+$, $[Mg(thf)_6]^{2+}$ or $[MgCl(thf)_5]^+$ can also be isolated, depending on the halide abstracting agent.[3–5]

To extend this chemistry we are attempting to utilize the halide abstraction ability of Sn^{II} and Sn^{IV} with covalent metal halides as a convenient and direct route to reactive cationic species. In a previous paper we described the formation and crystal structure of *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$, which was obtained from a $TiCl_3$–$SnCl_4$ or $TiCl_4$–$SnCl_2$ system in thf.[6] Tin(II) chloride can also act as a non-redox halide acceptor towards metal(II) halides and CuCl.[7]

Herein, we report on the reactions of several covalent metal chlorides with Sn^{II} and Sn^{IV} chlorides. The crystal structures of $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$, $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ and *trans*-$[CrCl_2(thf)_4][SnCl_5(thf)]$ have been determined.

Results and Discussion

Synthesis and Structure of $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$.—The reaction between $FeCl_3$ and $SnCl_2$ in a 2:1 molar ratio in thf at room temperature gives air-sensitive, bright yellow crystals of composition $2FeCl_2\cdot SnCl_4\cdot 7thf$ **1**, which can be stored under dinitrogen.

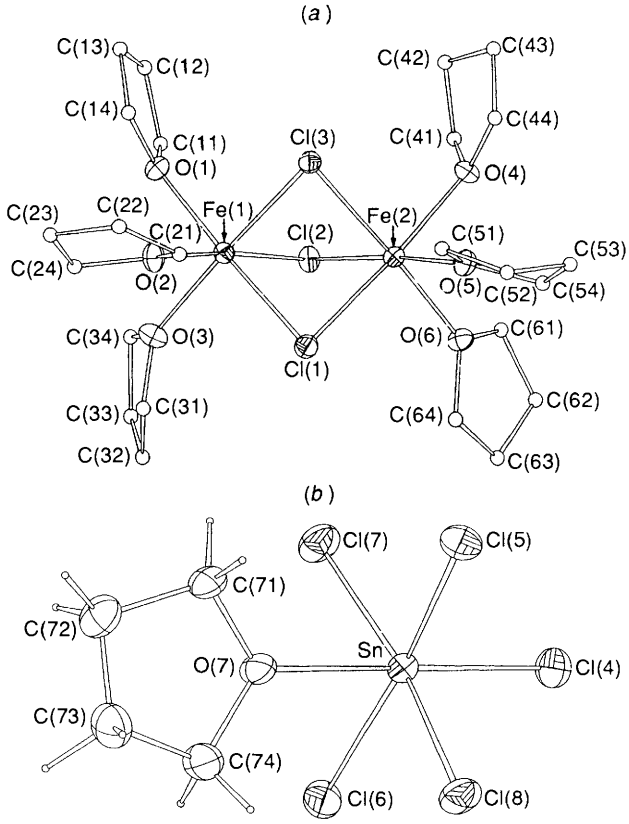

Fig. 1 Structures of (*a*) the $[Fe_2(\mu\text{-}Cl)_3(thf)_6]^+$ cation and (*b*) the $[SnCl_5(thf)]^-$ anion in $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ **1**

The IR spectrum of compound **1** shows a band at 240s cm^{-1} assigned to Fe–Cl vibrations, and characteristic modes at 296m and 322s cm^{-1} which are due to ν(Sn–Cl) of the $[SnCl_5(thf)]^-$ anion by comparison with *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$.[6] The complex as a solid shows a band at 9090 cm^{-1} in its diffuse

† Tri-μ-chlorohexakis(tetrahydrofuran)diiron(II) pentachloro(tetrahydrofuran)stannate(IV), di-μ-hydroxo-bis[trichloro(tetrahydrofuran)tin(IV)]-tetrahydrofuran(1/2) and *trans*-dichlorotetrakis(tetrahydrofuran)chromium(III) pentachloro(tetrahydrofuran)stannate(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and angles (°) for $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ **1**

Fe(1)···Fe(2)	3.086(2)	Fe(1)–O(2)	2.131(7)	Fe(2)–Cl(1)	2.503(3)	Fe(2)–O(6)	2.134(7)
Fe(1)–Cl(1)	2.485(3)	Fe(1)–O(3)	2.159(7)	Fe(2)–Cl(2)	2.479(3)	Sn–Cl(7)	2.395(3)
Fe(1)–Cl(2)	2.486(3)	Sn–Cl(4)	2.378(3)	Fe(2)–Cl(3)	2.499(3)	Sn–Cl(8)	2.411(3)
Fe(1)–Cl(3)	2.477(3)	Sn–Cl(5)	2.390(3)	Fe(2)–O(4)	2.181(6)	Sn–O(7)	2.272(6)
Fe(1)–O(1)	2.127(7)	Sn–Cl(6)	2.398(3)	Fe(2)–O(5)	2.093(7)		
Cl(1)–Fe(1)–Cl(2)	85.2(1)	O(2)–Fe(1)–O(1)	89.0(3)	Cl(1)–Fe(2)–Cl(2)	85.0(1)	O(5)–Fe(2)–O(4)	86.0(3)
Cl(1)–Fe(1)–Cl(3)	86.1(1)	O(3)–Fe(1)–O(1)	91.6(3)	Cl(1)–Fe(2)–Cl(3)	85.2(1)	O(6)–Fe(2)–O(4)	91.7(3)
Cl(2)–Fe(1)–Cl(3)	86.2(1)	O(3)–Fe(1)–O(2)	85.1(3)	Cl(2)–Fe(2)–Cl(3)	85.9(1)	O(6)–Fe(2)–O(5)	87.1(3)
O(1)–Fe(1)–Cl(1)	176.2(2)	Fe(1)–Cl(1)–Fe(2)	76.4(1)	O(4)–Fe(2)–Cl(1)	173.8(2)	Fe(1)–Cl(2)–Fe(2)	76.9(1)
O(1)–Fe(1)–Cl(2)	95.5(2)	Fe(1)–Cl(3)–Fe(2)	76.7(1)	O(4)–Fe(2)–Cl(2)	97.5(2)	Cl(5)–Sn–Cl(4)	95.3(1)
O(1)–Fe(1)–Cl(3)	90.3(2)	Cl(6)–Sn–Cl(4)	93.8(1)	O(4)–Fe(2)–Cl(3)	89.3(2)	Cl(8)–Sn–Cl(6)	89.0(1)
O(2)–Fe(1)–Cl(1)	90.5(2)	Cl(6)–Sn–Cl(5)	170.9(1)	O(5)–Fe(2)–Cl(1)	91.8(2)	Cl(8)–Sn–Cl(7)	169.9(1)
O(2)–Fe(1)–Cl(2)	174.8(3)	Cl(7)–Sn–Cl(4)	94.2(1)	O(5)–Fe(2)–Cl(2)	175.8(2)	O(7)–Sn–Cl(4)	178.8(2)
O(2)–Fe(1)–Cl(3)	96.3(2)	Cl(7)–Sn–Cl(5)	90.1(1)	O(5)–Fe(2)–Cl(3)	96.5(2)	O(7)–Sn–Cl(5)	85.7(2)
O(3)–Fe(1)–Cl(1)	92.0(3)	Cl(7)–Sn–Cl(6)	90.2(1)	O(6)–Fe(2)–Cl(1)	93.9(2)	O(7)–Sn–Cl(6)	85.2(2)
O(3)–Fe(1)–Cl(2)	92.2(3)	Cl(8)–Sn–Cl(4)	95.9(1)	O(6)–Fe(2)–Cl(2)	90.5(2)	O(7)–Sn–Cl(7)	85.3(2)
O(3)–Fe(1)–Cl(3)	177.6(3)	Cl(8)–Sn–Cl(5)	89.2(1)	O(6)–Fe(2)–Cl(3)	176.3(2)	O(7)–Sn–Cl(8)	84.6(2)

Table 2 Selected bond lengths (Å) and angles (°) for $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ **3***

Sn···Sn′	3.338(3)	Sn–O(1)	2.073(5)
Sn–Cl(1)	2.356(3)	Sn–O(1′)	2.070(4)
Sn–Cl(2)	2.359(3)	Sn–O(2)	2.206(5)
Sn–Cl(3)	2.353(3)	H(01)···O(3)	1.59(7)
O(1)···O(3)	2.548(7)		
Cl(1)–Sn–Cl(2)	99.4(1)	O(1′)–Sn–Cl(3)	94.9(2)
Cl(1)–Sn–Cl(3)	94.5(1)	O(2)–Sn–Cl(1)	86.7(2)
Cl(2)–Sn–Cl(3)	92.8(1)	O(2)–Sn–Cl(2)	85.4(2)
O(1)–Sn–Cl(1)	92.1(2)	O(2)–Sn–Cl(3)	177.9(2)
O(1)–Sn–Cl(2)	165.1(2)	O(2)–Sn–O(1)	85.9(2)
O(1)–Sn–Cl(3)	95.7(2)	O(2)–Sn–O(1′)	84.3(2)
O(1′)–Sn–Cl(1)	162.8(2)	O(1)–Sn–O(1′)	72.6(2)
O(1′)–Sn–Cl(2)	94.5(2)	Sn–O(1)–Sn′	107.4(2)
O(1)–H(01)···O(3)	171(6)		

* Primed atoms related to unprimed atoms by $1-x, -y, -z$.

reflectance spectrum which is close to the value of 8695 cm^{-1} observed for the compound in solution. This band can be assigned to the $^5T_{2g} \longrightarrow {}^5E_g$ transition for an octahedrally co-ordinated high-spin d^6 species. The electronic spectra suggest that the compound has similar solution and solid-state structures.

Compound **1** shows a temperature-dependent magnetic moment with μ_{eff} per Fe atom varying from 5.46 at 289 K to 1.91 at 4.2 K. The magnetic susceptibility data were readily fitted using the Heisenberg model, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$, where $S_1 = S_2 = 2$ and $g = 2.4$. The spin-exchange coupling constant (J) of -3 cm^{-1} indicates very weak antiferromagnetic behaviour.

Identification of the $[SnCl_5(thf)]^-$ anion by IR spectroscopy coupled with the antiferromagnetism, electronic spectra and stoichiometry suggested that compound **1** was a stannate(IV) salt containing a dinuclear cationic Fe^{II} species [equation (3)].

$$2FeCl_3 + SnCl_2 \xrightarrow{thf} \underset{\mathbf{1}}{[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]} \quad (3)$$

This formulation was confirmed by an X-ray structural study. The results are presented in Table 1 and Fig. 1. Crystals of **1** consist of $[Fe_2(\mu\text{-}Cl)_3(thf)_6]^+$ cations and $[SnCl_5(thf)]^-$ anions in a 1:1 ratio. The cation consists of two *fac*-$FeCl_3O_3$ octahedra sharing a Cl_3 triangular face. The observed Fe···Fe distance of 3.086(2) Å is distinctly shorter than the average distance of 3.695(2) Å found in $[Fe_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$[8] but 0.03 Å longer than the corresponding bond length for the diamagnetic complex $[Fe_2(\mu\text{-}I)_2(NO)_4]$.[9] The average Fe–Cl distance, 2.488(9) Å, is close to the corresponding values found in the tetrameric complex $[Fe_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$ [2.475(3) Å][8] and the trimeric anion $[Fe_3(\mu\text{-}Cl)_4Cl_4(thf)_2]^{2-}$ [2.441(2) Å].[10] The Fe–O distances [average value 2.14(2) Å] are close to the sum of the covalent radii of iron and oxygen. The O–Fe–O angles range from 85.1(3) to 91.7(3)°, and Cl–Fe–Cl from 85.0(1) to 86.2(1)°. Of the six independent thf rings, two are in the envelope conformation [containing O(1) and O(2)], three are in the twist conformation [containing O(3), O(5) and O(6)] and the thf ring with O(4) adopts a conformation intermediate between these. The conformations of the co-ordinated thf molecules differ from those observed in the analogous $[V_2(\mu\text{-}Cl)_3(thf)_6]^+$ cation.[1] It seems that packing conditions are mainly responsible for the conformational variations of the thf rings, these being the most flexible part of the structure.

The structure of the $[SnCl_5(thf)]^-$ anion is shown in Fig. 1(*b*) and is similar to that observed in the structure of *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$.[6]

Synthesis and Structure of $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$.—Under reflux in thf compound **1** undergoes partial decomposition to a white microcrystalline solid of composition $4FeCl_2\cdot 6thf$ **2**, identified as the well known tetrameric complex $[Fe_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]$[8] [equation (4)].

$$2\underset{\mathbf{1}}{[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]} \xrightarrow[thf]{reflux} \underset{\mathbf{2}}{[Fe_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_2(thf)_6]} + 2[SnCl_4(thf)_2] \quad (4)$$

Unexpectedly, a dimeric complex, $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ **3** [equation (5)], was isolated from the filtrate instead of the expected $[SnCl_4(thf)_2]$. Although the crystallization had been carried out under dinitrogen, moisture had inadvertently entered the vessel because the grease on the stopper had been washed away by solvent.

$$2[SnCl_4(thf)_2] + 2H_2O \xrightarrow{thf} \underset{\mathbf{3}}{[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf} + 2HCl \quad (5)$$

Crystals of compound **3** consist of centrosymmetric $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]$ molecules in which the tin atoms have a distorted octahedral arrangement formed by three chlorine atoms at neighbouring vertices, two hydroxy oxygen bridges and one thf molecule. A further two thf molecules are hydrogen-bonded to the hydroxyl oxygen atoms of the μ-OH bridges. The

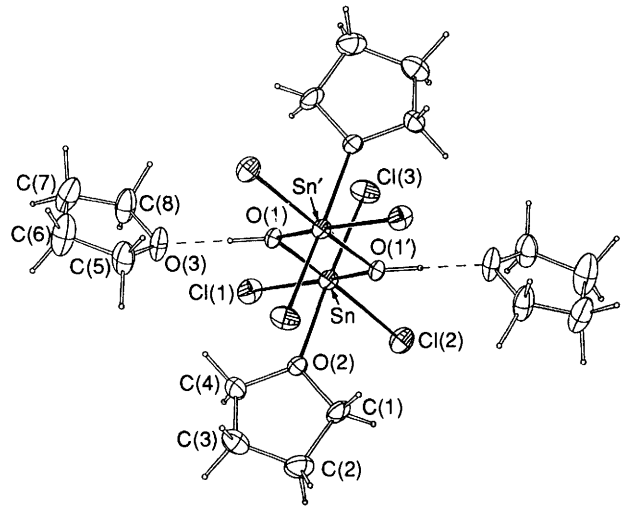

Fig. 2 Structure and numbering scheme of $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ **3**

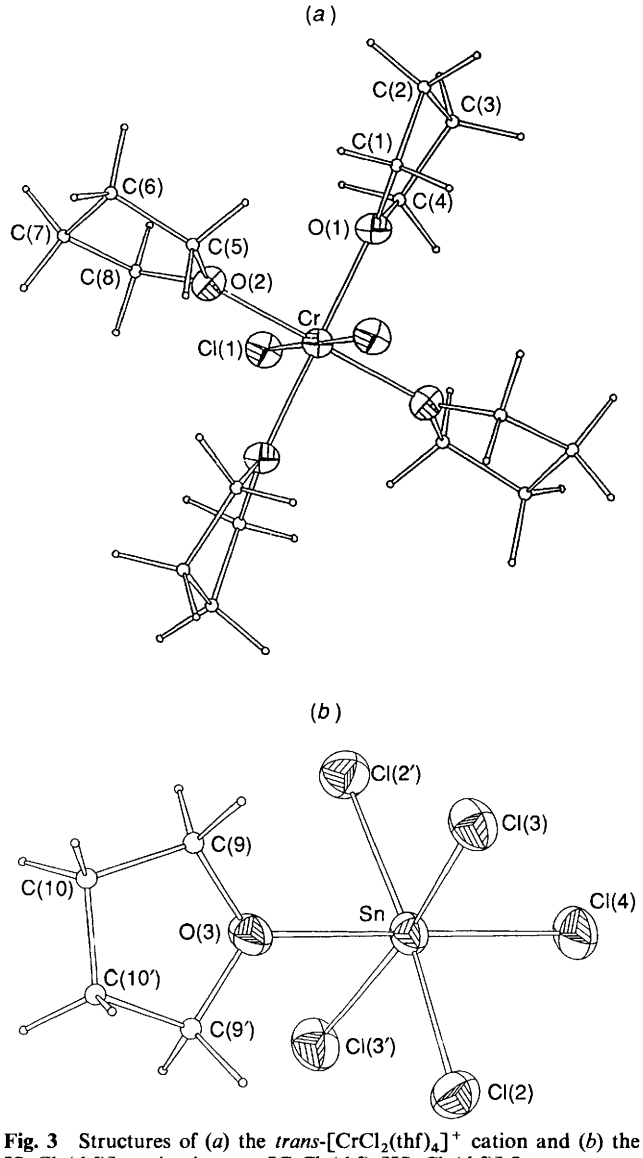

Fig. 3 Structures of (*a*) the *trans*-$[CrCl_2(thf)_4]^+$ cation and (*b*) the $[SnCl_5(thf)]^-$ anion in *trans*-$[CrCl_2(thf)_4][SnCl_5(thf)]$ **5**

angles subtended at tin in the Sn_2O_2 four-membered ring [72.6(2)°] are very acute with more open angles of 107.4(2)° at oxygen. The structure of compound **3** is shown in Fig. 2, while selected bond lengths and angles are summarized in Table 2.

Table 3 Selected bond lengths (Å) and angles (°) for *trans*-$[CrCl_2(thf)_4][SnCl_5(thf)]$ **5***

Cr–Cl(1)	2.288(3)	Sn–Cl(2)	2.396(3)
Cr–O(1)	2.011(6)	Sn–Cl(3)	2.397(3)
Cr–O(2)	2.029(6)	Sn–Cl(4)	2.368(4)
		Sn–O(3)	2.257(7)
Cl(1)–Cr–O(1)	89.6(2)	Cl(2')–Sn–Cl(3)	89.2(1)
Cl(1)–Cr–O(2)	90.0(2)	Cl(3)–Sn–Cl(3')	169.7(1)
O(2)–Cr–O(1)	91.2(3)	Cl(3)–Sn–Cl(4)	95.1(1)
Cl(2)–Sn–Cl(2')	173.6(2)	O(3)–Sn–Cl(2)	86.8(2)
Cl(2)–Sn–Cl(3)	90.2(1)	O(3)–Sn–Cl(3)	84.9(2)
Cl(2)–Sn–Cl(4)	93.2(1)		

* Primed atoms related to unprimed atoms by $-x, y, 0.5 - z$.

In a recent paper,[11] a compound of the same formula was described as a complex of tin(II) although it was obtained *via* mild hydrolysis of a thf solution of $SnCl_4$. (In this instance considerably higher thermal parameters and final residuals *R* were obtained in a crystallographic study. This led to the failure to locate the hydrogen atoms of the μ-hydroxy groups.)

The formation of **3** shows that the reaction of $SnCl_4$ with traces of H_2O in thf ceases upon formation of the dimeric tin(IV) complex with further substitution of Cl not being observed. A similar situation resulted from the interaction of $SnCl_4$ with MeOH which gave $[Sn_2(\mu\text{-}OMe)_2Cl_6(MeOH)_2]$.[12] Therefore, it seems that dimeric tin(IV) complexes with OH bridges are exceptionally stable.

Synthesis and Structure of trans-$[CrCl_2(thf)_4][SnCl_5(thf)]$.—We have also tried to apply the reductive ability of $SnCl_2$ to prepare compounds with dinuclear cations similar to that found in **1** using $[MCl_3(thf)_3]$ (M = V or Cr) as a substrate. However neither of these chlorides undergoes reduction perhaps owing to the low oxidation potential of V^{III} and Cr^{III}. Instead, as for Ti^{III} and Ti^{IV},[6] $[VCl_3(thf)_3]$ and $[CrCl_3(thf)_3]$ interact with $[SnCl_4(thf)_2]$ in thf to give green or violet crystalline solids respectively of composition $MCl_3\cdot SnCl_4\cdot 5thf$ (M = V, **4**; M = Cr, **5**). These compounds are air and moisture sensitive but are stable under dinitrogen. They are readily soluble in CH_2Cl_2.

The IR spectra of compounds **4** and **5** contain M–Cl vibrations at 385s and 405s cm^{-1}, respectively and two modes at 310s and 290m cm^{-1} due to ν(Sn–Cl).

The electronic spectrum of the vanadium compound **4** shows bands at 13 089 and 20 408 cm^{-1} which can be assigned to $^3T_{1g}(F) \longrightarrow {}^3T_{2g}(F)$ and $^3T_{1g}(F) \longrightarrow {}^3T_{1g}(P)$ transitions respectively for co-ordinated d^2 species, *cf.* $[VCl_2(H_2O)_4]Cl$,[13] $[VCl_2(ROH)_4]Cl$[14] (R = alkyl) and $[VCl_2(MeCN)_4]SbCl_6$.[15] For complex **5** bands at 14 492 cm^{-1} ($^4A_{2g} \longrightarrow {}^4T_{2g}$) and 21 186 cm^{-1} [$^4A_{2g} \longrightarrow {}^4T_{1g}(F)$] are similar to those observed for *trans*-$[CrCl_2(H_2O)_4]Cl$[16] and *trans*-$[CrCl_2(MeCN)_4]SbCl_6$.[17] Compounds **4** and **5** are paramagnetic with μ_{eff} values 2.57 and 3.71, respectively. The above data indicate that **4** and **5** are probably salts of formula $[MCl_2(thf)_4][SnCl_5(thf)]$ analogous to *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$.[6] This conclusion was confirmed for **5** by X-ray crystallography. Crystals of **5** consist of *trans*-$[CrCl_2(thf)_4]^+$ cations and $[SnCl_5(thf)]^-$ anions. The chromium atom occupies a centre of symmetry and is surrounded octahedrally by two chlorine atoms and four *thf* molecules. The structure of the *trans*-$[CrCl_2(thf)_4]^+$ cation is shown in Fig. 3(*a*) while selected bond lengths and angles are summarized in Table 3. The Cr–Cl distances of 2.288(3) Å in **5** are similar to the corresponding average values of 2.300(2) Å in *mer*-$[CrCl_3(thf)_3]$[18] and 2.289(1) Å in the *trans*-$[CrCl_2(H_2O)_4]^+$ cation.[19] The average Cr–O bond length of 2.020(9) Å in **5** is comparable to the value of 2.010(4) Å found in *mer*-$[CrCl_3(thf)_3]$.[18]

The structure of the octahedral $[SnCl_5(thf)]^-$ anion is shown in Fig. 3(*b*). The anion lies on a two-fold axis of symmetry so that the Sn, Cl(4) and O(3) atoms are located on this axis. The $[SnCl_5(thf)]^-$ anion in crystals of *trans*-$[TiCl_2(thf)_4][SnCl_5(thf)]$[6] lies on a symmetry plane while in $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ there is only C_1 point symmetry. In all three cases, however, the bond lengths and angles are comparable (differences $\leqslant$ 3 standard deviations).

The formation of *trans*-$[MCl_2(thf)_4][SnCl_5(thf)]$ salts in thf for M = Ti, V or Cr indicates that $SnCl_4$ behaves as a halide-abstracting reagent toward MCl_3 yielding the $[SnCl_5(thf)]^-$ anion [equation (6)]. This behaviour is observed to be inde-

$$[MCl_3(thf)_3] + [SnCl_4(thf)_2] \xrightarrow{thf} trans\text{-}[MCl_2(thf)_4][SnCl_5(thf)] \quad (6)$$

pendent of the substrate molar ratio, with the $[SnCl_5(thf)]^-$ anion always being formed. This is in contrast to the PCl_5–$SnCl_5$ system for which the formation of $[SnCl_5]^-$, $[SnCl_6]^{2-}$ and $[Sn_2Cl_{10}]^{2-}$ anions are observed.[20] The equilibrium attained in equation (6) would depend upon the least soluble species formed in the solution. From the data presented here and previously,[2,6,21] it follows that the $[MCl_5(thf)]^-$ anion (M = Ti, Zr, Hf or Sn) gives the least soluble salts which precipitate preferentially so driving the equilibria to their formation.

Recent studies[22] have revealed that the formation of ionic or molecular species in thf depends on the oxidation state of the metal M^{n+}. When $n \geqslant 3$, formation of the salts is always promoted, but when $n = 2$ chloride-bridged cations, *e.g.* $[M_2(\mu\text{-}Cl)_3(thf)_6]^+$, or molecular compounds such as $[(thf)_4Mg(\mu\text{-}Cl)_2FeCl_2]$[23] or $[(thf)_4V(\mu\text{-}Cl)_2ZnCl_2]$[24] are formed.

Experimental

All manipulations were carried out under an inert atmosphere by use of a standard Schlenk system and a vacuum line. Iron trichloride and tin tetrachloride were commercial materials. The compounds $SnCl_2$,[25] $[VCl_3(thf)_3]$[26] and $[CrCl_3(thf)_3]$[27] were prepared by reported procedures. Solvents were dried and purified by standard techniques. Magnetic susceptibilities were measured by the Faraday method within the temperature range 4.2–293 K. Corrections for diamagnetism were made with Pascal's constants.[28] The following spectrometers were used: Specord Perkin-Elmer 180 for IR and Beckman UV 5240 for UV/VIS spectroscopy.

Syntheses.—*Tri-μ-chlorohexakis(tetrahydrofuran)diiron*(II) *pentachloro(tetrahydrofuran)stannate*(IV) **1**.—To a solution of $FeCl_3$ (1.61 g, 9.9 mmol) in thf (50 cm^3), $SnCl_2$ (0.94 g, 4.9 mmol) was added. The solution was stirred for 0.5 h at room temperature and filtered through Celite 501. After 24 h bright yellow X-ray quality needles of $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ were formed. They were filtered off, washed with thf (3 × 5 cm^3) and vacuum dried. Yield 2.62 g (52%), which can be increased by concentration of the filtrate (Found: Cl, 26.95; Fe, 10.5; Sn, 11.70. $C_{28}H_{56}Cl_8Fe_2O_7Sn$ requires Cl, 27.85; Fe, 10.95; Sn, 11.65%); μ_{eff} = 5.46 per Fe at 289 K. IR (Nujol): ν(Fe–Cl) 240s; ν(Sn–Cl) 322s, 296m; other 1030s, 955m, 920m and 860s cm^{-1}. UV/VIS in thf: 8695 cm^{-1}. Reflectance spectrum: 9090 cm^{-1}.

Di-μ-hydroxo-bis[trichloro(tetrahydrofuran)tin(IV)] **3**. A solution of compound **1** (0.5 g, 0.5 mmol) in thf (25 cm^3) was refluxed for 2 h. A white solid, **2**, was formed, which was filtered off from the hot solution, washed with thf (3 × 5 cm^3) and vacuum dried (Found: Cl, 29.00; Fe, 24.4. $C_{24}H_{48}Cl_8Fe_4O_6$ requires Cl, 29.80; Fe, 24.75%), μ_{eff} = 6.24 per Fe at 292 K.

The yellow filtrate was cooled to 278 K to give bright yellow crystals of **1**. After separation of **1** the filtrate was concentrated to 10 cm^3 and left to crystallize at room temperature. A small amount of white almost cubic crystals was formed after 2 weeks. These were identified by X-ray diffraction as the dimer $[Sn_2(\mu\text{-}OH)_2Cl_6(thf)_2]\cdot 2thf$ **3**.

Dichlorotetrakis(tetrahydrofuran)vanadium(III) *pentachloro-(tetrahydrofuran)stannate*(IV) **4**. A solution of $[VCl_3(thf)_3]$ (1.80 g, 4.8 mmol) in thf (50 cm^3) and $[SnCl_4(thf)_2]$ (1.95 g, 4.8 mmol) in thf (30 cm^3) were mixed and stirred during 2 h. A bright green solid which settled down from an orange-pink reaction mixture was filtered off, washed with thf (3 × 5 cm^3) and dried in vacuum.

The compound was recrystallized by slow diffusion of thf into a CH_2Cl_2 solution of **4** (Found: Cl, 30.30, Sn, 14.90; V, 7.00. $C_{20}H_{40}Cl_7O_5SnV$ requires Cl, 31.90, Sn, 15.25; V, 6.55%), μ_{eff} = 2.57 at 293 K. IR (Nujol): ν(V–Cl) 385s; ν(Sn–Cl) 320s and 290m; other 998s, 960w, 928m and 834s cm^{-1}. UV/VIS (thf–CH_2Cl_2): 20 408 and 13 089 cm^{-1}.

trans-*Dichlorotetrakis(tetrahydrofuran)chromium*(III) *pentachloro(tetrahydrofuran)stannate*(IV) **5**. To a stirred solution of $[CrCl_3(thf)_3]$ (2.06 g, 5.5 mmol) in thf (20 cm^3) was added $[SnCl_4(thf)_2]$ (2.22 g, 5.5 mmol) dissolved in thf (30 cm^3). Immediately, a bright violet solid precipitated and after stirring for 1 h the product was filtered off, washed with thf (3 × 5 cm^3) and dried in vacuum.

Recrystallization by slow diffusion of thf into a solution of **5** in CH_2Cl_2 yielded violet crystals suitable for an X-ray crystal structure analysis (Found: Cl, 31.20; Cr, 6.95; Sn, 14.55. $C_{20}H_{40}Cl_7CrO_5Sn$ requires Cl, 31.85; Cr, 6.65; Sn, 15.20%), μ_{eff} = 3.71 at 298 K. IR (Nujol): ν(Cr–Cl) 405s; ν(Sn–Cl) 320s and 290m; other 1002s, 960w, 930m and 840s cm^{-1}. UV/VIS (thf–CH_2Cl_2): 21 186 and 14 492 cm^{-1}.

Crystallography.—*Crystal data* for **1**. Bright yellow crystals, $C_{28}H_{56}Cl_8Fe_2O_7Sn$, M = 1018.8, monoclinic, space group $P2_1/c$, a = 17.220(7), b = 12.876(4), c = 20.973(8) Å, β = 113.0(4)°, U = 4280(3) $Å^3$, Z = 4, D_c = 1.581(2) g cm^{-3}, D_m = 1.62 g cm^{-3}, $F(000)$ = 2072, T = 297(2) K, μ(Mo-Kα) = 18.0 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Crystal data for **3**. Colourless crystals, $C_8H_{18}Cl_6O_4Sn_2\cdot 2C_4H_8O$, M = 772.5, monoclinic, space group $P2_1/c$, a = 9.696(8), b = 15.674(13), c = 9.885(7) Å, β = 109.22(6)°, U = 1419(2) $Å^3$, Z = 2, D_c = 1.809(3) g cm^{-3}, D_m = 1.84 g cm^{-3}, $F(000)$ = 760, T = 302(2) K, μ(Mo-Kα) = 23.6 cm^{-1}.

Crystal data for **5**. Bright violet crystals, $C_{20}H_{40}Cl_7CrO_5Sn$, M = 779.4, monoclinic, space group $C2/c$, a = 13.888(12), b = 10.399(7), c = 23.354(21) Å, β = 108.82(7)°, U = 3192(5) $Å^3$, Z = 4, D_c = 1.621(3) g cm^{-3}, D_m = 1.63 g cm^{-3}, $F(000)$ = 1572, T = 300(1) K, μ(Mo-Kα) = 17.5 cm^{-1}.

Data collections and processing. All crystals were sealed in glass capillaries. Preliminary data were recorded by photographic methods. Intensities were collected with a Syntex $P2_1$ four-circle diffractometer in the ω–2θ mode (with crystals of dimensions 0.5 × 0.8 × 0.5 mm for **1**, 0.7 × 0.5 × 0.9 mm for **3** and 0.6 × 0.9 × 0.5 mm for **5**) and Mo-Kα radiation; 4885 ($4 < 2\theta < 52°$), 2257 ($4 < 2\theta < 52°$) and 4463 ($4 < 2\theta < 60°$) reflections were measured for **1**, **3** and **5**, respectively, from which 3707 (**1**), 2040 (**3**) and 2741 (**5**) with $I > 3.0\ \sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELX 76.[29] Atomic scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 30. The carbon-bonded hydrogen atoms were included in geometrically calculated positions with d(C–H) = 1.08 Å. The hydrogen atom from the hydroxyl group in **3** was found from a difference map and refined with the constraint d(O–H) = 0.97 Å. The C–C distances of the thf molecules in the *trans*-$[CrCl_2(thf)_4]^+$ cation of **5** were unrealistically short, probably because of partial disorder and therefore these bond lengths were constrained as in ref. 31. A weighting scheme of the form $w = 1/\sigma^2(F_o)$ was applied for all the structures. Final R $\{= (\Sigma\|F_o| - |F_c\|)/\Sigma|F_o|\}$ and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ values are 0.0389 and 0.0451 for **1**, 0.0346 and 0.0413 for **3**, and

Table 4 Fractional atomic coordinates for complex **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	0.565 48(4)	0.723 49(5)	0.116 30(3)	C(22)	0.869 1(9)	0.410 5(10)	0.063 8(8)
Fe(1)	0.996 88(8)	0.693 24(9)	0.157 93(6)	C(23)	0.792 1(9)	0.475 8(10)	0.051 8(8)
Fe(2)	1.191 20(8)	0.691 88(9)	0.211 21(6)	C(24)	0.821 2(8)	0.584 2(10)	0.061 1(7)
Cl(1)	1.085 43(15)	0.676 09(20)	0.089 14(12)	C(31)	0.898 5(13)	0.812 9(13)	0.015 0(7)
Cl(2)	1.097 97(15)	0.831 73(17)	0.221 71(13)	C(32)	0.897 7(17)	0.911 2(16)	−0.002 2(11)
Cl(3)	1.096 84(15)	0.570 15(17)	0.240 30(13)	C(33)	0.888 3(16)	0.973 2(13)	0.050 8(10)
Cl(4)	0.562 11(20)	0.709 80(22)	0.228 27(13)	C(34)	0.890 4(8)	0.901 6(10)	0.105 6(6)
Cl(5)	0.626 27(19)	0.555 91(19)	0.118 62(15)	C(41)	1.268 6(7)	0.759 9(8)	0.369 4(5)
Cl(6)	0.507 17(17)	0.895 32(20)	0.096 91(14)	C(42)	1.260 1(9)	0.691 5(10)	0.421 7(6)
Cl(7)	0.427 34(16)	0.651 59(23)	0.058 01(14)	C(43)	1.313 5(9)	0.598 6(10)	0.423 6(6)
Cl(8)	0.704 03(16)	0.798 29(21)	0.154 73(15)	C(44)	1.311 3(7)	0.590 0(8)	0.353 0(5)
O(1)	0.925 1(4)	0.699 1(5)	0.220 5(4)	C(51)	1.240 0(7)	0.473 4(8)	0.170 7(6)
O(2)	0.912 0(5)	0.578 7(6)	0.095 1(4)	C(52)	1.312 2(8)	0.427 8(10)	0.155 7(7)
O(3)	0.914 1(5)	0.803 4(6)	0.085 5(4)	C(53)	1.387 1(8)	0.485 6(10)	0.202 4(7)
O(4)	1.279 1(4)	0.689 0(5)	0.319 4(3)	C(54)	1.357 8(7)	0.591 9(9)	0.206 2(7)
O(5)	1.268 1(4)	0.577 8(5)	0.195 0(4)	C(61)	1.315 4(8)	0.881 8(9)	0.232 5(6)
O(6)	1.266 0(4)	0.803 6(5)	0.185 7(4)	C(62)	1.353 9(12)	0.940 7(12)	0.194 9(8)
O(7)	0.566 4(5)	0.738 7(5)	0.008 7(3)	C(63)	1.305 2(9)	0.923 3(12)	0.121 0(7)
C(11)	0.932 5(8)	0.779 4(9)	0.270 0(6)	C(64)	1.256 9(10)	0.833 0(11)	0.116 7(6)
C(12)	0.916 6(11)	0.732 5(11)	0.326 0(7)	C(71)	0.546 1(7)	0.657 7(8)	−0.042 7(5)
C(13)	0.886 3(11)	0.629 6(12)	0.305 0(8)	C(72)	0.522 4(7)	0.715 5(10)	−0.109 8(6)
C(14)	0.892 0(9)	0.607 1(9)	0.238 4(7)	C(73)	0.577 7(8)	0.810 2(10)	−0.090 5(6)
C(21)	0.939 4(8)	0.482 4(8)	0.078 5(6)	C(74)	0.589 4(9)	0.833 9(9)	0.017 6(6)

Table 5 Fractional atomic coordinates for complex **3**

Atom	*x*	*y*	*z*
Sn	0.410 08(5)	0.040 20(3)	0.103 28(5)
Cl(1)	0.466 63(24)	0.163 45(11)	0.247 50(22)
Cl(2)	0.243 94(23)	−0.024 94(14)	0.199 91(24)
Cl(3)	0.222 26(23)	0.105 89(15)	−0.082 14(22)
O(1)	0.574 0(5)	0.065 1(3)	0.017 1(5)
O(2)	0.580 6(5)	−0.025 0(3)	0.277 4(5)
O(3)	0.789 5(6)	0.164 3(4)	0.130 1(8)
C(1)	0.570 9(10)	−0.115 3(5)	0.317 1(10)
C(2)	0.698 8(11)	−0.128 9(7)	0.453 4(10)
C(3)	0.801 4(10)	−0.054 3(6)	0.458 9(10)
C(4)	0.708 1(9)	0.016 4(6)	0.378 8(9)
C(5)	0.937 1(9)	0.142 0(7)	0.151 9(13)
C(6)	1.018 1(12)	0.220 5(7)	0.162 0(16)
C(7)	0.908 9(11)	0.288 6(7)	0.112 6(14)
C(8)	0.769 1(10)	0.253 7(5)	0.107 0(13)
H(O1)	0.662(5)	0.099(5)	0.057(8)

Table 6 Fractional atomic coordinates for complex **5**

Atom	*x*	*y*	*z*
Sn	0	0.069 92(8)	0.25
Cr	0	0.5	0
Cl(1)	−0.098 7(3)	0.485 0(3)	0.061 5(2)
Cl(2)	−0.173 0(3)	0.082 8(3)	0.248 5(2)
Cl(3)	0.057 7(3)	0.090 6(3)	0.358 0(2)
Cl(4)	0	−0.157 8(4)	0.25
O(1)	0.107 4(5)	0.393 0(7)	0.059 2(3)
O(2)	0.063 1(5)	0.664 3(6)	0.042 6(3)
O(3)	0	0.287 0(7)	0.25
C(1)	0.121 1(12)	0.380 1(16)	0.121 8(4)
C(2)	0.218 4(12)	0.308 6(17)	0.150 8(4)
C(3)	0.232 6(14)	0.233 4(17)	0.099 3(7)
C(4)	0.180 8(12)	0.315 1(18)	0.045 2(5)
C(5)	0.051 2(14)	0.719 5(13)	0.095 6(6)
C(6)	0.127 9(15)	0.825 2(14)	0.116 8(7)
C(7)	0.149 4(15)	0.864 1(11)	0.060 2(9)
C(8)	0.130 7(13)	0.742 7(14)	0.023 5(7)
C(9)	0.083 3(5)	0.366 6(7)	0.281 6(5)
C(10)	0.054 4(9)	0.504 0(7)	0.265 2(7)

0.0733 and 0.0827 for **5**. The isotropic thermal factors for hydrogen atoms were fixed. All non-hydrogen atoms were refined anisotropically. 415 Parameters were refined for **1**, 139 for **3** and 157 for **5**. For the last cycle of the refinement the maximum value of the ratio Δ/σ was 0.11 for **1**, 0.17 for **3** and 0.10 for **5** and the final difference maps showed a general background within −0.41 and 0.65, −0.65 and 0.76, and −0.70 and 1.45 e Å^{-3} for **1**, **3** and **5** respectively. The final positional parameters for the non-hydrogen atoms are given in Tables 4–6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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