Labile adducts of TiCl₄ with thionyl chloride structurally characterized at low temperature: a comparison with the zirconium and hafnium analogues, [MCl₄(SOCl₂)]₂

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The thermally unstable (decomp. *ca.* −30 °C) titanium derivative [TiCl₄(SOCl₂)]₂, prepared from TiCl₄ and SOCl₂, forms three crystalline modifications (I–III) in the temperature range between 220 and 234 K; these modifications differ in the orientation of the SOCl₂ ligand with respect to the titanium-containing fragment within the dinuclear molecule and in the packing modes due to intermolecular S···Cl interactions at distances between 3.25 and 3.82 Å.

Thionyl chloride, a reagent frequently used for the preparation of anhydrous metal chlorides,[1] is a poor electron donor, as denoted by its low donor number (DN = 0.4).[2] As far as metal chlorides of Group 4 are concerned, high solubility (HfCl₄, mp 705 K), partial or complete miscibility (TiCl₄, mp 284 K) with SOCl₂ at room temperature were observed in our Laboratories. Moreover, in an early study on the TiCl₄/SOCl₂ system,[3] a smooth maximum on the freezing point diagram was found at *ca.* 243 K, in the range of SOCl₂ composition between about 40 and 70 mol%, which was attributed to the formation of a 1:1 adduct. This prompted us to investigate the molecular basis of these phenomena; further interest in this project came from the paucity of data concerning MClₙ/SOCl₂ adducts.[3a,4] We wish to report that while HfCl₄ forms a binuclear complex with thionyl chloride of composition [HfCl₄(SOCl₂)]₂ which is stable at room temperature, similar to that already reported in the literature for ZrCl₄,[5] the corresponding adduct with TiCl₄ of the identical molecular composition [TiCl₄(SOCl₂)]₂ and structure, is stable at low temperature only, according to both spectrophotometric and X-ray diffractometric experiments.†

Titanium tetrachloride dissolves in SOCl₂ to give a colorless solution which affords large yellow crystals at dry ice temperature. At about 243 K, the solid converts into a liquid. The room temperature IR spectrum of TiCl₄ dissolved in SOCl₂ shows the absorption due to uncoordinated SOCl₂ only at 1230 cm⁻¹. For comparison, solutions of MCl₄ (M = Zr, Hf) in SOCl₂, containing the thionyl chloride complex [MCl₄(SOCl₂)]₂, show a strong absorption at 1151 cm⁻¹ (M = Zr) or at 1145 cm⁻¹ (M = Hf) due to the S=O stretching vibration of coordinated SOCl₂.

The X-ray crystallographic study of the materials obtained by cooling the TiCl₄/SOCl₂ solutions established the existence of three crystalline modifications of the 1:1 adduct. By repeated cycles of heating and cooling of the solutions, a single crystal of the dinuclear, chloride-bridged 1:1 adduct of TiCl₄ with SOCl₂, [TiCl₄(SOCl₂)]₂, was obtained, hereinafter indicated as **I**, see Fig. 1, which is isotypic with the zirconium derivative[5] isolated by Collins and Drew at room temperature.

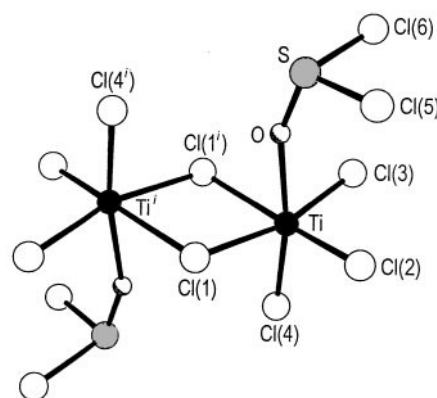The titanium atom of **I**, see Fig. 1, is hexacoordinated to five

Fig. 1 The centrosymmetric molecule of [TiCl₄(SOCl₂)]₂ **I**. Main distances [Å]: Ti–Cl(1), 2.465(1); Ti–Cl(1'), 2.450(1); Ti–Cl(2), 2.229(1); Ti–Cl(3), 2.210(1); Ti–Cl(4), 2.195(1); Ti–O, 2.196(3); S–O, 1.463(3); S–Cl(5), 2.043(1); S–Cl(6), 2.038(1).

chlorine atoms and to the oxygen atom of the thionyl chloride ligand in an approximately octahedral coordination. The molecule is centrosymmetric. The mean Ti–Clₜ bond length is 2.221 Å, whereas the mean Ti–Cl_b (Cl_b, bridging chloride; Clₜ, terminal chloride) bond distance of 2.457 Å is appreciably longer. In [TiCl₄(POCl₃)]₂,[9] the mean Ti–Clₜ and Ti–Cl_b bond distances are 2.23 and 2.49 Å, respectively. The Ti–Cl(4) bond distance of 2.195 Å, *trans* to the Ti–O bond (2.196 Å), is the shortest of the three Ti–Clₜ bond distances. The O–Ti–Cl(4) bond angle is 171.0° and the mean values of the O–Ti–Clₜ (equatorial) and O–Ti–Cl_b bond angles are 87.7 and 80.4°, respectively, both below 90°.

In the course of the freezing/melting cycles, single crystals of two additional crystalline modifications of [TiCl₄(SOCl₂)]₂ were obtained. These crystalline modifications, hereinafter denoted as **II** and **III**, are stable over several hours below 220 K. Near their melting point (234 ± 2 K), they convert into **I**, whose melting point is 2–3 °C higher.

Modifications **I**–**III** contain the same Ti₂Cl₈O₂ frame, the only pronounced difference concerns the coordinated SOCl₂ ligands. The Ti–O–S bond angle in **I** (154.7°) decreases to 148.8° and 148.6° in **II** and **III**, respectively. Moreover, the three modifications of [TiCl₄(SOCl₂)]₂ differ in the dihedral angle φ between the pseudosymmetry plane of the SOCl₂ moiety (passing through the atoms S and O and bisecting the Cl–S–Cl angle) and the pseudosymmetry plane of the Ti₂Cl₈ moiety (passing through the titanium atoms and the two Cl(4) atoms). The φ angle amounts, in fact, to 2.4, 57.4, and 50.4° in **I**, **II**, and **III**, respectively. The smaller angle φ found in **I** reflects its
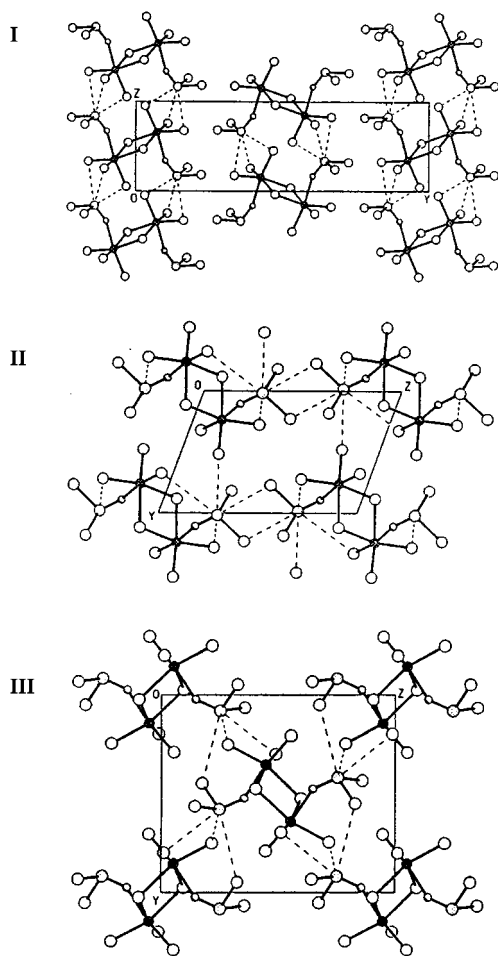
Fig. 2 Crystal packing of [TiCl$_4$(SOCl$_2$)]$_2$, **I–III**, along the x axis.

more symmetrical shape. This feature is associated with a closer packing of **I**, the V/Z ratio of 437.5Å^3 being compared with 440.5 Å^3 for **II**, both measured at 140 K. Phase **III** at 220 K shows a V/Z ratio of 451.6 Å^3.

Intermolecular S$\cdots$Cl interactions are important for both the crystal packing of **I–III** and for allowing the chalcogen atom to achieve hexacoordination, a situation frequently encountered in derivatives of sulfur(IV), such as (SCl$_3$)(AlCl$_4$),[10] (SCl$_3$)(Ti$_2$Cl$_9$),[11] or SOCl$_2$ itself.[12] Although the S–O and S–Cl bond distances are similar within the three modifications, the sulfur environments and interaction distances are significantly different. For example, in **I**, see Fig. 2, there are additional S$\cdots$Cl interactions with the chlorine atoms of two different binuclear units, *i.e.*, Cl(2^{ii}) (S$\cdots$Cl = 3.464 Å), Cl(3^{iii}) (3.392 Å), and Cl(4^{ii}) (3.247 Å), where $ii = x - 1, y, z - 1$; $iii = x, y, z - 1$. In **II**, see Fig. 2, the interactions involve the S-atom and the chlorine atoms of four different binuclear units, *i.e.*, Cl(2^{iv}) (S$\cdots$Cl = 3.747 Å), Cl(3^{v}) (3.420 Å), Cl(4^{vi}) (3.791 Å), and Cl(5^{vii}) (S$\cdots$Cl = 3.760 Å) where $iv = x, y - 1, z$; $v = x + 1, y, z$; $vi = -x, -y, -z$; $vii = x + 1, y, z + 1$. As far as **III** is concerned, the interactions involve the sulfur and three chlorine atoms within the same adjacent binuclear unit at distances ranging from 3.486 to 3.820 Å, Thus, the tendency of sulfur(IV) to interact with atoms of the adjacent binuclear unit(s) substantially contributes to the stability of the observed three crystalline modifications of [TiCl$_4$(SOCl$_2$)]$_2$.

At variance with titanium and similar to zirconium,[5] HfCl$_4$ dissolves in SOCl$_2$ to give a colorless adduct stable at room temperature. An X-ray diffractometric experiment † has shown the hafnium derivative to be isotypic with both the corresponding zirconium compound ‡ and **I**, the metal–ligand bond distances changing according to the ionic radii of the hexacoordinated central metal atom: Ti (0.605 Å), Zr (0.72 Å), and Hf (0.71 Å).[13] In the hafnium compound, the sulfur atoms also achieve hexacoordination by interaction with three chlorine

atoms of two different binuclear units, *i.e.*, S$\cdots$Cl(2^{ii}) (3.609 Å), S$\cdots$Cl(3^{iii}) (3.443 Å), and S$\cdots$Cl(4^{ii}) (3.316 Å): most of these distances are shorter than the sum of the van der Waals radii (3.55 Å).[14]

It is noteworthy that the 1:1 MCl$_4$/SOCl$_2$ adducts were isolated in the presence of a large excess of the ligand; in particular, crystals of [TiCl$_4$(SOCl$_2$)]$_2$ were obtained even with SOCl$_2$ to TiCl$_4$ molar ratios as high as 8:1, thus suggesting that the 2:1 adducts, which are typical of MCl$_4$ with more basic ligands containing oxygen or nitrogen donor atoms,[15] are not stable under these experimental conditions. The low stability of the titanium derivative at room temperature is consistent with the observation that tetracoordination of the titanium atom is the preferred one for TiCl$_4$,[16] both in the liquid and in the solid state, while in ZrCl$_4$ and HfCl$_4$ the metal is octahedrally coordinated [17] to form polynuclear chloride-bridged aggregates.

Apparently, the existence of [TiCl$_4$(SOCl$_2$)]$_2$ is due to relatively weak Ti–O covalent bonds supported by additional S$\cdots$Cl interactions. The increase of the M–O bond enthalpy on descending the group Ti–Hf explains the higher stability of the zirconium and hafnium analogs up to at least room temperature.

These results are complementary to those reported years ago by Floriani and co-workers,[18] who isolated labile adducts of TiCl$_4$ with benzene or 1,2,4,5-tetramethylbenzene and SO$_2$ of formula [(TiCl$_4$)$_2$(SO$_2$)$_2$(C$_6$H$_2$R$_4$)$_2$], R = H, Me; in the case of the benzene derivative, S$\cdots$C weak interactions were suggested to be important in stabilizing the adduct. The less unfavourable entropic contribution in our case (SO$_2$, bp 263 K; SOCl$_2$, bp 349 K) also explains our successful isolation of the thionyl chloride adduct.

In conclusion, we have shown that: i) the maximum at about 243 K in the freezing point diagram of the TiCl$_4$/SOCl$_2$ system corresponds to the formation of at least three different 1:1 crystalline modifications; ii) non-isolable, presumably less stable, 1:2 modifications may exist, at higher SOCl$_2$ mol% compositions; iii) the formation of the Ti–O coordinated bond in the 1:1 adducts requires some further intermolecular interaction to stabilize the system, namely S$\cdots$Cl contacts.

Acknowledgements

Notes and references

† [TiCl$_4$(SOCl$_2$)]$_2$: A solution of TiCl$_4$ (4.4 ml, 40.0 mmol) in SOCl$_2$ (15 ml, 205.4 mmol) was cooled at dry-ice temperature. From the colorless solution, the light yellow adduct was collected by filtration at low temperature. Attempts to dry the substance *in vacuo* resulted in decomposition, the volatile components recombining in the cold trap (77 K). For X-ray diffractometry, single crystals of phases **I**, **II** and **III** of [TiCl$_4$(SOCl$_2$)]$_2$ were obtained by repeated cooling and heating cycles of TiCl$_4$/SOCl$_2$ mixtures sealed in capillaries directly mounted on the diffractometer. The capillaries were firstly cooled (215–220 K) until the solution froze to a polycrystalline solid; they were then slowly heated until the major part of the solid melted. The temperature was then slowly lowered (0.5 °C min^{-1}) causing the growth of the crystal seeds. The melting–freezing procedure was repeated until single crystals of the appropriate quality were obtained. Modification **I** (mp 234 K) was obtained as a stable phase when the crystal growth occurred between 230 and 234 K. The first cycles of crystal growth gave modifications **II** and **III** from mixtures containing SOCl$_2$ and TiCl$_4$ in molar ratios ranging between 2.2 and 4.0. Crystal data: **I**, STADI-4(Stoe) diffractometer; M, 617.32; crystal size $0.4 \times 0.3 \times 0.3$ mm; $T = 140(2)$ K; monoclinic, $P2_1/c$; $a = 6.442(1)$, $b = 21.148(4)$, $c = 7.065(1)$ Å; $\beta = 114.63(3)°$; $V = 874.9$ Å^3; $Z = 2$; $D_{calc} = 2.343$ g cm^{-3}; $\mu = 2.968$ mm^{-1}; reflections: 1911 (collected), 1911 (unique); $R_1 = 0.037$. **II**, STADI-4 (Stoe) diffractometer; crystal size, $0.5 \times 0.35 \times 0.3$ mm; $T = 140(2)$ K; triclinic, $P\bar{1}$; $a = 6.179(1)$, $b = 7.679(2)$, $c = 10.715(2)$ Å; $\alpha = 107.74(3)°$, $\beta = 91.33(3)°$ $\gamma = 112.81(3)°$ $V = 440.54$ Å^3; $Z = 1$; $D_{calc} = 2.327$ g cm^{-3}; $\mu = 2.948$ mm^{-1}; reflections: 1827 (collected), 1827 (unique); $R_1 = 0.036$. **III**, IPDS (Stoe) diffractometer; crystal size, $0.4 \times 0.3 \times 0.3$ mm; $T = 220(2)$ K; monoclinic, $P2_1/c$; $a = 7.563(2)$, $b = 10.074(3)$, $c =$

12.235(4) Å; $\beta = 103.36(3)°$; $V = 903.7$ Å^3; $Z = 2$; $D_{calc} = 2.269$ g cm^{-3}; $\mu = 2.874$ mm^{-1}; reflections: 7852 (collected), 2032 (unique); $R_1 = 0.044$. The structures were solved by using direct methods (SHELXS-86[6]) and refined anisotropically using SHELXL-93.[7] [HfCl$_4$(SOCl$_2$)]$_2$·HfCl$_4$ (1.964 g, 6.1 mmol) was treated with SOCl$_2$ (15 ml, 205.4 mmol) at room temperature. Warming the colorless suspension at 343 K for 15 min afforded a solution which was then cooled to 278 K giving colorless crystals of [HfCl$_4$(SOCl$_2$)]$_2$ (64% yield, including a further crop from the mother liquor cooled at 243 K) with satisfactory analytical data (Hf, Cl), after drying *in vacuo*. IR (KBr, Nujol), cm^{-1}: 1122s, ν(S=O); 503 m, ν_{as}(S–Cl); 479m, ν_{S}(S–Cl). Crystal data: M, 878.5; P4 Siemens; crystal size, $0.3 \times 0.3 \times 0.09$ mm; $T = 293(2)$ K; monoclinic, $P2_1/c$; $a = 6.6876(5)$, $b = 21.581(4)$, $c = 7.2813(4)$ Å; $\beta = 114.654(5)°$; $V = 955.1(2)$ Å^3; $Z = 2$; D_{calc} 3.055 g cm^{-3}; $\mu = 12.746$ mm^{-1}; reflections: 3549 (collected), 2797 (unique); $R_1 = 0.043$. The structure was solved by using direct methods and refined anisotropically by means of SHELXTL-Plus.[8] CCDC reference number: 186/1503. See http// www.rsc.org/suppdata/dt/1999/2275 for crystallographic files in .cif format.

‡ The crystal data[5] of [ZrCl$_4$(SOCl$_2$)]$_2$ have been recalculated in the space group $P2_1/c$ for a better comparison with the titanium and the hafnium analogs.

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