

Reactivity of SeOCl_2 with titanium and zirconium tetrachlorides. The unexpected formation of a μ -oxo-bridged titanium(IV) derivative

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The reaction of TiCl_4 with SeOCl_2 affords the μ -oxo derivative $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})$ through a deoxygenation reaction of SeOCl_2 to SeCl_4 whereas ZrCl_4 gives 1:1 or 1:2 adducts of formula $\text{ZrCl}_4(\text{SeOCl}_2)_n$, $n = 1, 2$.

Recently some of us reported that thionyl chloride forms oxygen-bonded adducts with TiCl_4 of formula $[\text{TiCl}_4(\text{SOCl}_2)]_2$ (three modifications were isolated between 220 and 234 K) which are unstable at room temperature.¹ On the other hand, ZrCl_4 and HfCl_4 give 1:1 adducts which are stable at room temperature or higher.

As the donor number (DN) of SeOCl_2 , as defined by Gutmann, was reported to be considerably higher than that of SOCl_2 ($\text{DN}_{\text{SOCl}_2} = 0.4$; $\text{DN}_{\text{SeOCl}_2} = 12.2$),² it was of interest to extend our studies to seleninyl chloride in an attempt to clarify the nature of an insufficiently described compound of formula $\text{TiCl}_4 \cdot 2\text{SeOCl}_2$ which has been reported to be yellow^{3,4} or colourless.⁵ Moreover, a weaker chalcogen-oxygen bond is expected for selenium with respect to sulfur,⁶ a parameter which could interfere with the behaviour of a simple acid-base adduct.

We have found that, by operating at room temperature, the addition of a dichloromethane solution of SeOCl_2 to a solution of TiCl_4 in the same solvent gives a pale yellow solid.[†] The observed IR absorptions of coordinated SeOCl_2 at 858 (m) and 830 (s) cm^{-1} (Nujol), with wavenumber shifts (97 and 125 cm^{-1}) with respect to uncoordinated SeOCl_2 (955 cm^{-1}),⁷ are similar to $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ (835 cm^{-1} , $\Delta = 120 \text{ cm}^{-1}$)⁴ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$ (757 cm^{-1} , $\Delta = 198 \text{ cm}^{-1}$).⁸ Single crystals were grown by slowly cooling (-30°C) a saturated dichloromethane solution, and an X-ray analysis showed[‡] the compound to be a dinuclear derivative of titanium(IV) of formula $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O}) \cdot \text{CH}_2\text{Cl}_2$ with an oxygen atom bridging two titanium centres, the slightly distorted octahedral geometry at titanium being completed by three Cl atoms and two oxygen atoms from the SeOCl_2 ligand, see Fig. 1. The two $[\text{TiCl}_3(\text{SeOCl}_2)_2]$ units connected by the bridging oxygen are related by a two-fold axis passing through O(1). An identical operation relates the two halves of the lattice dichloromethane. The two titanium coordination octahedra have staggered equatorial ligands, the $\text{Cl}(2)\text{--Ti}\cdots\text{Ti}'\text{--Cl}(2')$ dihedral angle being 44.3° . The seleninyl ligand maintains the trigonal pyramidal geometry typical of the free molecule.⁹ As observed in $\text{SnCl}_4 \cdot 2\text{SeOCl}_2$ ¹⁰ and $\text{SbCl}_5 \cdot \text{SeOCl}_2$,¹¹ additional inter- and intra-molecular interactions between the selenium and chlorine atoms are observed, selenium achieving 3 + 3 coordination as shown in Fig. 1. Although the bond distances between the selenium atoms and their three nearest neighbours range from 1.639 to 2.154 Å, three longer distances (dashed lines in Fig. 1) are observed between 2.938 and 3.465 Å, the greatest value representing the CH_2Cl_2 chlorine atoms-selenium separation. Although the reaction between TiCl_4 and SeOCl_2 has been repeated several times, at

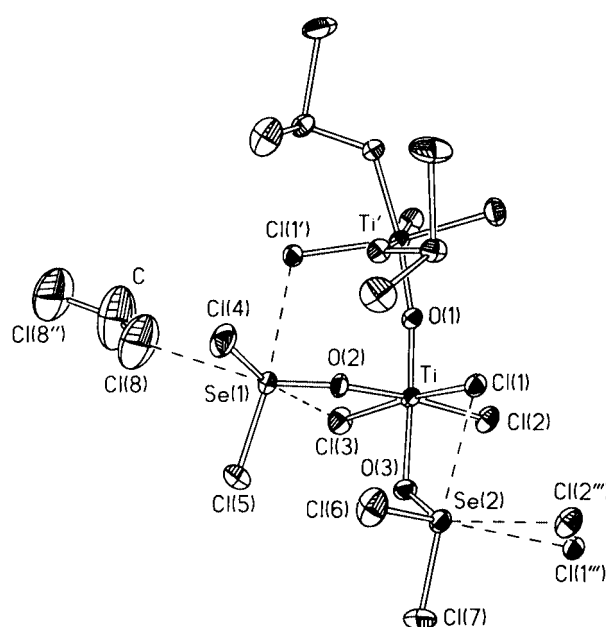
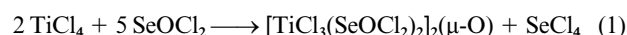
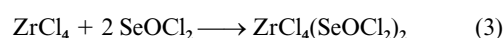
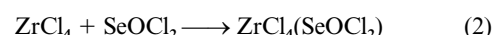


Fig. 1 View of the molecular structure of $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O}) \cdot \text{CH}_2\text{Cl}_2$, showing the weaker interactions of the selenium atoms with their neighbouring chlorine atoms. Ellipsoids are at 30% probability. Dichloromethane hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $\text{Ti--Cl}(1)$ 2.431, $\text{Ti--Cl}(2)$ 2.252, $\text{Ti--O}(1)$ 1.787, Se--O 1.644(4) (av.), Se--Cl 2.145(2) (av.), $\text{Se}\cdots\text{Cl}$ 2.938–3.465; $\text{Ti--O}(1)\cdots\text{Ti}'$ 159.9(1).

different temperatures (even at -60°C) and with different Se/Ti molar ratios, $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})$ was the only product observed.[§] The ^{77}Se NMR spectrum of the mother-liquor after removal of the dinuclear titanium derivative showed a peak at δ 395 assigned to SeCl_4 (by comparison with an authentic sample) thus suggesting that $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})$ was formed by a deoxygenation reaction of SeOCl_2 operated by TiCl_4 as in eqn. (1).

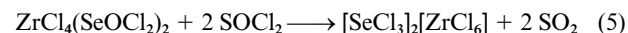


At variance with titanium tetrachloride, ZrCl_4 reacts with SeOCl_2 in dichloromethane without formation of SeCl_4 ; as a matter of fact, 1:1 or 1:2 adducts are obtained depending on the molar ratio of the reagents, see eqn. (2) and (3).[¶] No 1:2



adduct of ZrCl_4 with SOCl_2 has been found, again in agreement with the reported DN's ($\text{DN}_{\text{SOCl}_2} < \text{DN}_{\text{SeOCl}_2}$).

The derivatives of titanium(IV) and zirconium(IV), $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})$ and $\text{ZrCl}_4(\text{SeOCl}_2)_2$ promptly react with excess SOCl_2 with formation of TiCl_4 and $[\text{SeCl}_3]_2[\text{ZrCl}_6]$,¹² respectively, see eqn. (4) and (5), formation of SO_2 being the



driving force of the reaction. Noteworthy is the fact that TiCl_4 does not react with SeCl_4 under the same experimental conditions used for zirconium.

Thus, although SeOCl_2 behaves as a stronger base than SOCl_2 , the decreasing chalcogen-to-oxygen bond strength on going from sulfur to selenium plays an important role in determining the nature of the products.

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Notes and references

† A solution of SeOCl_2 (0.44 ml, 6.4 mmol) in CH_2Cl_2 (70 ml) was added dropwise at room temperature to a solution of TiCl_4 (0.7 ml, 6.4 mmol) in CH_2Cl_2 (25 ml). The pale yellow solution was stirred at room temperature and cooled at ca. 4 °C for 48 h producing a solid which was filtered off and dried *in vacuo* at room temperature giving $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})\cdot\text{CH}_2\text{Cl}_2$ (1.25 g) as a microcrystalline, moisture-sensitive pale-yellow solid. Found: Cl (inorganic, after treatment of the sample with a boiling aqueous solution of KOH), 46.3; Ti, 8.8%. Calcd. for $\text{CH}_2\text{Cl}_6\text{O}_5\text{Se}_4\text{Ti}_2$: Cl, 46.3; Ti, 8.9%. An additional crop of yellow crystals of $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})\cdot\text{CH}_2\text{Cl}_2$ (0.103 g, 98% total yield based on selenium), suitable for an X-ray diffraction study, formed on cooling the mother-liquor at ca. –30 °C for 24 h. The same reaction was repeated using a Se/Ti molar ratio of 2.5:1 and mixing a solution of the reactants at ca. –60 °C. The immediate formation of a yellow solid was observed which was filtered off and dried *in vacuo* at room temperature affording $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})$ (89% yield) as a microcrystalline yellow powder exceedingly sensitive to moisture. Found: Cl, 50.9; Ti, 9.9%. Calcd. for $\text{Cl}_{14}\text{O}_5\text{Se}_4\text{Ti}_2$: Cl, 50.2; Ti, 9.7%. IR (Nujol) $\nu(\text{cm}^{-1})$: 858 (m), 830 (s), 796 (s), 724 (m).

‡ Crystal data for $[\text{TiCl}_3(\text{SeOCl}_2)_2]_2(\mu\text{-O})\cdot\text{CH}_2\text{Cl}_2$ (yellow): $\text{CH}_2\text{Cl}_6\text{O}_5\text{Se}_4\text{Ti}_2$, $M = 1072.9$, monoclinic, space group $P2_1/n$ (no. 13), $\mu(\text{Mo-K}\alpha) = 7.301 \text{ mm}^{-1}$, $a = 12.753(1)$, $b = 8.495(1)$, $c = 13.350(1) \text{ \AA}$, $\beta = 65.58(2)^\circ$, $V = 1439.4(2)$, $Z = 2$, $T = 293.2 \text{ K}$, 3327 reflections

collected, 2538 independent reflections [$R_{\text{int}} = 0.0213$], 128 variables, $R_1 = 0.0409$, $wR_2 = 0.0823$. CCDC reference number 186/2044. See <http://www.rsc.org/suppdata/dt/b0/b004057f/> for crystallographic files in .cif format.

§ When a Se/Ti molar ratio of 1:1 was used, the solution contained the corresponding amount of unreacted TiCl_4 .

¶ (a) $\text{SeOCl}_2/\text{ZrCl}_4$ molar ratio = 1:1. Preparation of $\text{ZrCl}_4(\text{SeOCl}_2)_2\cdot 0.5\text{CH}_2\text{Cl}_2$. A solution of SeOCl_2 (0.37 ml, 5.4 mmol) in CH_2Cl_2 (70 ml) was added dropwise at room temperature to a suspension of ZrCl_4 (1.25 g, 5.4 mmol) in CH_2Cl_2 (100 ml). After 12 h stirring at room temperature, the colourless solid was filtered off and dried *in vacuo* at room temperature affording 1.195 g (50% yield) of $\text{ZrCl}_4(\text{SeOCl}_2)_2\cdot 0.5\text{CH}_2\text{Cl}_2$ as a colourless solid exceedingly sensitive to moisture. Found: Cl (inorganic, after treatment of the sample with a boiling aqueous solution of KOH), 48.0; Zr, 21.9%. Calcd. for $\text{C}_{0.5}\text{HCl}_7\text{OSeZr}$ requires: Cl, 48.2; Zr, 20.7%. IR (Nujol) $\nu(\text{cm}^{-1})$: 1263 (w), 871 (s), 802 (m), 765 (m), 723 (m), 669 (w). (b) $\text{SeOCl}_2/\text{ZrCl}_4$ molar ratio = 2:1. Preparation of $\text{ZrCl}_4(\text{SeOCl}_2)_2$. A solution of SeOCl_2 (0.69 ml, 10.1 mmol) in CH_2Cl_2 (70 ml) was added dropwise at room temperature to a suspension of ZrCl_4 (1.07 g, 4.6 mmol) in CH_2Cl_2 (100 ml). After 12 h stirring at room temperature, the volume of the orange solution was reduced to 20 ml and the colourless solid was filtered off and dried *in vacuo* at room temperature affording 1.275 g (46% yield) of $\text{ZrCl}_4(\text{SeOCl}_2)_2\cdot 0.5\text{CH}_2\text{Cl}_2$ as a colourless solid exceedingly sensitive to moisture. Found: Cl (inorganic, after treatment of the sample with a boiling aqueous solution of KOH), 46.8; Zr, 15.1%. Calcd. for $\text{C}_{0.5}\text{HCl}_6\text{O}_5\text{Se}_2\text{Zr}$: Cl, 46.7; Zr, 15.0%. IR (Nujol) $\nu(\text{cm}^{-1})$: 1262 (w), 858 (s, br), 722 (m, br).

|| SeOCl_2 reacts at room temperature with SOCl_2 forming SeCl_4 and SO_2 .¹³

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