DALTON
COMMUNICATION

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

Fausto Calderazzo,[a] Michele D'Attoma,[a] Fabio Marchetti[b] and Guido Pampaloni *[a]

[a] *Università di Pisa, Dipartimento di Chimica e Chimica Industriale, Via Risorgimento 35, I-56126, Pisa, Italy. E-mail: pampa@dcci.unipi.it*
[b] *Università di Roma "La Sapienza", Dipartimento di Ingegneria Chimica, dei Materiali e delle Materie Prime e Metallurgia, Via del Castro Laurenziano 7, Box 15 Roma 62, I-00185 Roma, Italy*

Received 22nd May 2000, Accepted 21st June 2000

The reaction of $TiCl_4$ with $SeOCl_2$ affords the μ-oxo derivative $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)$ through a deoxygenation reaction of $SeOCl_2$ to $SeCl_4$ whereas $ZrCl_4$ gives 1 : 1 or 1 : 2 adducts of formula $ZrCl_4(SeOCl_2)_n$, $n = 1, 2$.

Recently some of us reported that thionyl chloride forms oxygen-bonded adducts with $TiCl_4$ of formula $[TiCl_4(SOCl_2)]_2$ (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 $SOCl_2$ ($DN_{SOCl_2} = 0.4$; $DN_{SeOCl_2} = 12.2$),[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 $TiCl_4{\cdot}2SeOCl_2$ 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 $SnCl_4{\cdot}2SeOCl_2$ (835 cm^{-1}, $\Delta = 120$ cm^{-1})[4] and $SbCl_5{\cdot}SeOCl_2$ (757 cm^{-1}, $\Delta = 198$ 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 $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O){\cdot}CH_2Cl_2$ 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 $TiCl_3(SeOCl_2)_2$ 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 Cl(2)–Ti···Ti′–Cl(2′) dihedral angle being 44.3°. The seleninyl ligand maintains the trigonal pyramidal geometry typical of the free molecule.[9] As observed in $SnCl_4{\cdot}2SeOCl_2$[10] and $SbCl_5{\cdot}SeOCl_2$,[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 different temperatures (even at −60 °C) and with different Se/Ti molar ratios, $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)$ 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 $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)$ was formed by a deoxygenation reaction of $SeOCl_2$ operated by $TiCl_4$ as in eqn. (1).

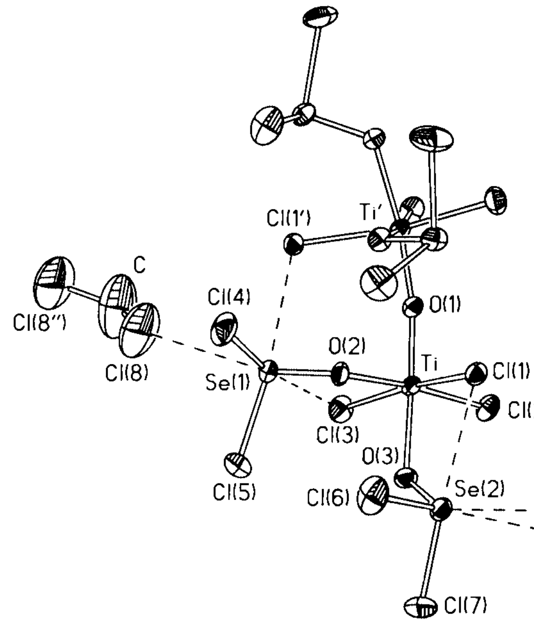

Fig. 1 View of the molecular structure of $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O){\cdot}CH_2Cl_2$, showing the weaker interactions of the selenium atoms with their neighbouring chlorine atoms. Ellipsoids are at 30% probability. Dichloromethane hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–Cl(1) 2.431, Ti–Cl(2) 2.252, Ti–O(1) 1.787, Se–O 1.644(4) (av.), Se–Cl 2.145(2) (av.), Se···Cl 2.938–3.465; Ti–O(1)–Ti′ 159.9(1).

$$2\,TiCl_4 + 5\,SeOCl_2 \longrightarrow [TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O) + SeCl_4 \quad (1)$$

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

$$ZrCl_4 + SeOCl_2 \longrightarrow ZrCl_4(SeOCl_2) \quad (2)$$

$$ZrCl_4 + 2\,SeOCl_2 \longrightarrow ZrCl_4(SeOCl_2)_2 \quad (3)$$

DOI: 10.1039/b004057f

adduct of $ZrCl_4$ with $SOCl_2$ has been found, again in agreement with the reported DN's ($DN_{SOCl_2} < DN_{SeOCl_2}$).

The derivatives of titanium(IV) and zirconium(IV), $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)$ and $ZrCl_4(SeOCl_2)_2$ promptly react with excess $SOCl_2$|| with formation of $TiCl_4$ and $[SeCl_3]_2[ZrCl_6]$,[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.

$$[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O) + 5\,SOCl_2 \longrightarrow 2\,TiCl_4 + 4\,SeCl_4 + 5\,SO_2 \quad (4)$$

$$ZrCl_4(SeOCl_2)_2 + 2\,SOCl_2 \longrightarrow [SeCl_3]_2[ZrCl_6] + 2\,SO_2 \quad (5)$$

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.

Acknowledgements

The authors wish to thank the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST, Roma), Programmi di Ricerca di Interesse nazionale (1998–1999), for financial support.

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 $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)\cdot CH_2Cl_2$ (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 $CH_2Cl_{16}O_5Se_4Ti_2$: Cl, 46.3; Ti, 8.9%. An additional crop of yellow crystals of $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)\cdot CH_2Cl_2$ (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 $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)$ (89% yield) as a microcrystalline yellow powder exceedingly sensitive to moisture. Found: Cl, 50.9; Ti, 9.9%. Calcd. for $Cl_{14}O_5Se_4Ti$: Cl, 50.2; Ti, 9.7%. IR (Nujol) $\nu(cm^{-1})$: 858 (m), 830 (s), 796 (s), 724 (m).

‡ Crystal data for $[TiCl_3(SeOCl_2)_2]_2(\mu\text{-}O)\cdot CH_2Cl_2$ (yellow): $CH_2Cl_{16}O_5Se_4Ti_2$, $M = 1072.9$, monoclinic, space group $P2/n$ (no. 13), $\mu(\text{Mo-K}\alpha) = 7.301\ mm^{-1}$, $a = 12.753(1)$, $b = 8.495(1)$, $c = 13.350(1)$ Å, $\beta = 65.58(2)°$, $V = 1439.4(2)$, $Z = 2$, $T = 293.2$ K, 3327 reflections collected, 2538 independent reflections [$R_{int} = 0.0213$], 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) $SeOCl_2/ZrCl_4$ molar ratio = 1 : 1. Preparation of $ZrCl_4(SeOCl_2)\cdot 0.5CH_2Cl_2$. 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 $ZrCl_2$ (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 $ZrCl_4(SeOCl_2)\cdot 0.5CH_2Cl_2$ 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 $C_{0.5}HCl_7OSeZr$ requires: Cl, 48.2; Zr, 20.7%. IR (Nujol) $\nu(cm^{-1})$: 1263 (w), 871 (s), 802 (m), 765 (m), 723 (m), 669 (w). (b) $SeOCl_2/ZrCl_4$ molar ratio = 2 : 1. Preparation of $ZrCl_4(SeOCl_2)_2$. 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 $ZrCl_4(SeOCl_2)_2\cdot 0.5CH_2Cl_2$ 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 $C_{0.5}HCl_9O_2Se_2Zr$: Cl, 46.7; Zr, 15.0%. IR (Nujol) $\nu(cm^{-1})$: 1262 (w), 858 (s, br), 722 (m, br).

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

1 F. Calderazzo, M. D'Attoma, F. Marchetti, G. Pampaloni and S. I. Troyanov, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2275.

2 V. Gutmann, A. Steininger and E. Wychera, *Monatsh. Chem.*, 1966, **97**, 461; V. Gutmann, *CHEMTECH*, 1977, 255; V. Gutmann, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum Press, New York, London, 1978.

3 R. Weber, *Pogg. Ann.*, 1865, **125**, 325, quoted in *Gmelins Handbuch der Anorganischen Chemie*, "*Selen*" *B*, Gmelin Verlag GmbH, Claustahl-Zellerfeld, 8th edn., 1949, p. 144.

4 J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, 1959, **81**, 2290.

5 C. R. Wise, *J. Am. Chem. Soc.*, 1923, **45**, 1233.

6 *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 77th edn., 1996–1997.

7 G. H. Westphal and F. Rosenberger, *J. Mol. Spectrosc.*, 1980, **83**, 355.

8 M. Burgard, J. P. Brunette and M. J. F. Leroy, *Inorg. Chem.*, 1976, **15**, 1225.

9 Electron diffraction structure of $SeOCl_2$: D. Gregory, I. Hargittai and M. Kolonits, *J. Mol. Struct.*, 1976, **31**, 261.

10 Y. Hermodsson, *Acta Crystallogr.*, 1960, **13**, 656.

11 Y. Hermodsson, *Acta Chem. Scand.*, 1967, **21**, 1313.

12 J. Beck, P. Biedenkopf, K. Müller-Buschbaum, J. Richter and K.-J. Schlitt, *Z. Anorg. Allg. Chem.*, 1996, **622**, 292.

13 *Gmelins Handbuch der Anorganischen Chemie*, "*Selen*" *B*, Gmelin Verlag GmbH, Claustahl-Zellerfeld, 8th edn., 1949, p. 141.