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# Mono- and dinuclear complexes of sulfones with the tetrachlorides of group 4

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The reactions of dialkyl sulfones [$R_2SO_2$: R = Me (**a**), Et (**b**), Ph (**c**), $R_2$ = –$(CH_2)_4$– (**d**)] with the metal tetrachlorides of Group 4 [$MCl_4$: M = Ti (**1**), Zr(**2**), Hf (**3**)] give different products mainly depending on the sulfone/M molar ratio. Compounds of formula [$M_2Cl_8(R_2SO_2)_2$] [M = Ti, $R_2$ = –$(CH_2)_4$– (**1d**); M = Zr, R = Et (**2b**), R = Ph (**2c**)] and [$MCl_4(R_2SO_2)_2$] (sulfone/M = 2) [M = Ti, R = Me (**1aa**); M = Zr, R = Me (**2aa**), R = Ph (**2cc**), $R_2$ = –$(CH_2)_4$– (**2dd**); M = Hf, R = Me (**3aa**), $R_2$ = –$(CH_2)_4$– (**3dd**)] have been obtained. By X-ray diffraction methods the dinuclear titanium and zirconium adducts, [$Ti_2Cl_8$(μ-sulfolane-*O,O′*)$_2$] (**1d**) and [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O,O′*)$_2$] (**2c**) have been established to contain bridging sulfone and hexacoordinated metal centres, while the mononuclear zirconium complex [$ZrCl_4(Me_2SO_2)_2$] (**2aa**) has *cis*-monodentate sulfones in a slightly distorted octahedral geometry. The reaction between $TiCl_4$ and sulfolane (tetrahydrothiophene 1,1-dioxide) in $SOCl_2$ affords the 1 : 1 adduct independent of the sulfone/Ti molar ratio. Ligand-exchange and inter-conversion between mononuclear and dinuclear species have been observed by NMR, while the spectral features of the $SO_2$ moiety have been assigned by IR- and Raman spectroscopies.

## Introduction

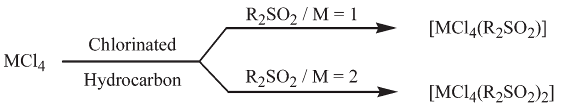
Some of us recently reported[1] that thionyl chloride forms unstable, oxygen-bonded 1 : 1 complexes with $TiCl_4$ of formula [$Ti_2Cl_8(SOCl_2)_2$], three crystal modifications being isolated in the temperature range between 220 and 234 K. In the same paper $ZrCl_4$ and $HfCl_4$ were reported to form adducts of the same stoichiometry stable at room temperature. On increasing the donor number of the Lewis base, *i.e.*, on going from $SOCl_2$ to $SeOCl_2$ ($DN_{SOCl_2} = 0.4$; $DN_{SeOCl_2} = 12.2$),[2] zirconium tetrachloride was found to give 1 : 1 or 2 : 1 adducts of formula [$ZrCl_4(SeOCl_2)_n$], $n = 1$ or 2, depending on the stoichiometry of the reagents.[3]

Some coordination compounds of alkyl sulfones have been prepared, in agreement with their weak donor properties, the DN value of tetrahydrothiophene 1,1-dioxide (sulfolane) being 14.8,[4] according to Gutmann. Known examples are the adducts of LiCl,[5] $SnCl_4$,[5b,6] $MgCl_2$,[5c] $HgX_2$,[5c] $TlCl_3$,[5c] $BF_3$[7] with sulfolane or of transition metal compounds with dimethyl sulfone, [$Rh_2(CF_3COO)_4(Me_2SO_2)_2$],[8] diethyl sulfone, [$Co_2Cl_4$(μ-$Et_2SO_2$-*O,O′*)$_2$],[9] or sulfolane such as [$MCl_2(C_4H_8SO_2)$], M = Mn,[5c] Co,[5c,10] Cu,[5c,11] Zn,[5c] Cd,[5c] and [$Co(C_4H_8SO_2)_3](ClO_4)_2$.[10] A few of these compounds have been structurally characterized.[5,8,9]

These observations prompted us to investigate the reactions of Group 4 metal tetrachlorides $MCl_4$ (M = Ti, Zr, Hf) with sulfones and here we report the spectroscopic and structural characterisation of both mononuclear and dinuclear derivatives.

## Results and discussion

The tetrachlorides of Group 4, $MCl_4$, M = Ti, Zr, Hf, react exothermally with sulfones $R_2SO_2$ [R = Me, Et, Ph; $R_2$ = –$CH_2)_4$–] forming different products, predominantly, but not exclusively (*vide infra*), depending on the sulfone/$MCl_4$ molar ratio, see Scheme 1.



Sulfone / M = 1: M = Ti, $R_2$ = $(CH_2)_4$ ; M = Zr, R = Et, Ph.

Sulfone / M = 2: M =Ti, R = Me; M = Zr, R = Me, Ph, $R_2$ = –$(CH_2)_4$– ; M = Hf, R = Me, $R_2$ = –$(CH_2)_4$–

**Scheme 1** Preparation of Ti, Zr and Hf sulfone complexes.

All compounds with a sulfone/$MCl_4$ molar ratio of 2 have a solubility in chlorinated solvents which depends on the nature of both the metal (Hf < Zr ≪ Ti) and the sulfone [Me < Ph < Et ≈ –$(CH_2)_4$–]. The different solubility of the complexes allowed the isolation of the solid products (see Experimental section) to be carried out. The products are readily hydrolized by moisture with release of the sulfone. In the case of titanium(IV), the dinuclear [$Ti_2Cl_8$(μ-sulfolane-*O,O′*)$_2$] (**1d**) has been obtained in $SOCl_2$ as solvent even in the presence of a large excess of sulfolane, suggesting that the bis-adduct of titanium is not stable under our experimental conditions.

### X-Ray crystallography

The sulfolane adduct [$Ti_2Cl_8$(μ-sulfolane-*O,O′*)$_2$] (**1d**) is a centrosymmetric dimer containing bridging sulfolano ligands, see Fig. 1 and Table 1. The two titanium atoms in the dinuclear unit (Ti···Ti distance 5.33 Å) form a $Ti_2O_4S_2$ eight-membered ring. The titanium atom has a distorted octahedral geometry as generally found in *cis*-adducts of formula $TiCl_4$(oxygenated ligand)$_2$.[12] The Cl(3)–Ti–Cl(4) angle is 165.81°, and compares well with the range 161.08(4)–172.1° observed in *cis*-octahedral derivatives of titanium(IV) containing oxygen donors such as [$TiCl_4(MeCO)_2O$][12a] and [$TiCl_4L_2$], L = $Et_2O$,[12f] THF[12g]. The mean Ti–$Cl_{eq}$ (eq = equatorial) bond distance of 2.219 Å (av.) is slightly shorter than the Ti–$Cl_{ax}$ (ax = axial) bond distance of 2.289 Å (av.). The O–Ti–$Cl_{ax}$ bond angle is 84.87° (av.).

The sulfolane ligand is characterized by S–O distances (1.463 Å, av.) slightly longer than those observed in the plastic phase of sulfolane[13] (1.45 Å), and by an O–S–O angle of 116.1° similar to that observed in [LiCl(sulfolane)][5a] [S–O, 1.447(2) Å; O–S–O, 114.8(1)°], whose structure consists of a three-dimensional infinite network containing four-coordinate lithium atoms, with Cl and O,O′-sulfolano bridges.

The structure of [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O,O′*)$_2$] (**2c**) has also been solved: to the best of our knowledge, it represents the first

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† Deceased on December 26th, 2003.

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**Table 1** Selected bond distances (Å) and angles (°) for [$Ti_2Cl_8$(μ-sulfolane-O,O′)$_2$] (**1d**)

| | | | |
|---|---|---|---|
| Ti–O(1′) | 2.146(2) | Ti–O(2) | 2.180(2) |
| Ti–Cl(1) | 2.2125(8) | Ti–Cl(2) | 2.2261(8) |
| Ti–Cl(3) | 2.2471(8) | Ti–Cl(4) | 2.3304(8) |
| S–O(1) | 1.462(2) | S–O(2) | 1.465(2) |
| O(1′)–Ti–O(2) | 80.00(6) | Cl(2)–Ti–Cl(3) | 95.06(3) |
| O(1′)–Ti–Cl(1) | 91.44(5) | O(1′)–Ti–Cl(4) | 85.85(5) |
| O(2)–Ti–Cl(1) | 171.37(5) | O(2)–Ti–Cl(4) | 85.24(5) |
| O(1′)–Ti–Cl(2) | 169.46(5) | Cl(1)–Ti–Cl(4) | 93.08(3) |
| O(2)–Ti–Cl(2) | 89.48(5) | Cl(2)–Ti–Cl(4) | 93.96(3) |
| Cl(1)–Ti–Cl(2) | 99.09(4) | Cl(3)–Ti–Cl(4) | 165.81(3) |
| O(1′)–Ti–Cl(3) | 83.29(5) | O(1)–S–O(2) | 116.1(1) |
| O(2)–Ti–Cl(3) | 83.90(5) | S–O(1)–Ti′ | 143.0(1) |
| Cl(1)–Ti–Cl(3) | 96.28(3) | S–O(2)–Ti | 140.7(1) |

**Table 2** Selected bond distances (Å) and angles (°) for [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$]·$C_2H_2Cl_4$ (**2c**·$C_2H_2Cl_4$) (primed atoms related to unprimed equivalents by the symmetry operation −*x*, −*y*, −*z* + 1)

| | | | |
|---|---|---|---|
| Zr–O(1) | 2.257(3) | Zr–O(2) | 2.264(3) |
| Zr–Cl(1) | 2.422(1) | Zr–Cl(3) | 2.407(1) |
| Zr–Cl(2) | 2.356(1) | Zr–Cl(4) | 2.359(1) |
| S–O(1) | 1.456(3) | S–O(2′) | 1.463(3) |
| O(1)–Zr–O(2) | 82.8(1) | Cl(4)–Zr–Cl(3) | 96.00(6) |
| O(1)–Zr–Cl(2) | 171.84(9) | O(1)–Zr–Cl(1) | 82.28(9) |
| O(2)–Zr–Cl(2) | 89.18(9) | O(2)–Zr–Cl(1) | 83.26(8) |
| O(1)–Zr–Cl(4) | 90.34(9) | Cl(2)–Zr–Cl(1) | 95.51(6) |
| O(2)–Zr–Cl(4) | 173.11(9) | Cl(4)–Zr–Cl(1) | 95.91(6) |
| Cl(2)–Zr–Cl(4) | 97.71(6) | Cl(3)–Zr–Cl(1) | 160.71(5) |
| O(1)–Zr–Cl(3) | 82.53(9) | O(1)–S–O(2′) | 115.8(2) |
| O(2)–Zr–Cl(3) | 83.09(9) | S–O(1)–Zr | 147.6(2) |
| Cl(2)–Zr–Cl(3) | 97.86(6) | S′–O(2)–Zr | 144.5(2) |

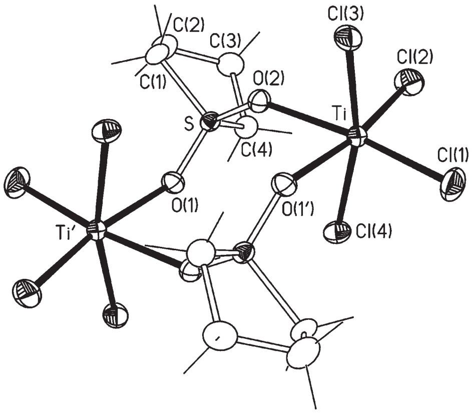

**Fig. 1** View of the molecular structure of [$Ti_2Cl_8$(μ-sulfolane-*O*,*O*′)$_2$] (**1d**). Thermal ellipsoids are at 30% probability (primed atoms related to unprimed equivalents by the symmetry operation −*x* + 1, −*y*, −*z*).

structurally characterized compound containing coordinated diphenyl sulfone. It is centrosymmetric with a Zr···Zr distance of 5.498 Å and bridging diphenylsulfone groups, see Fig. 2 and Table 2. The two hexacoordinated zirconium atoms in the dimer form a $Zr_2O_4S_2$ eight-membered ring.

The mean Zr–$Cl_{eq}$ bond distance of 2.357 Å (av.) is slightly shorter than the mean Zr–$Cl_{ax}$ bond distance of 2.415 Å. Deviations the O–Zr–Cl angles from the ideal octahedral geometry of the same type as those found in the titanium derivative **1d** are observed in **2c**. Bond distances are similar to those observed in the O-ligated adducts of $ZrCl_4$:[14] the diphenyl sulfone ligand has S–O distances (1.459 Å, av.) and an O–S–O bond angle of 115.76°, comparable to those observed in uncoordinated diphenyl sulfone[15] (1.436 Å and 119.21°).

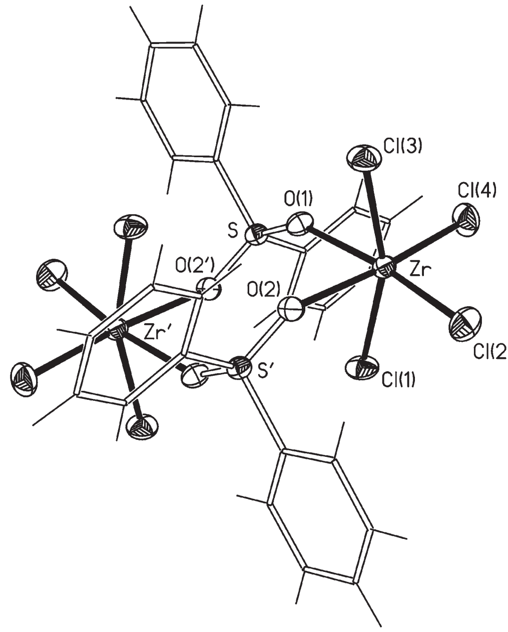

**Fig. 2** View of the molecular structure of [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] in [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$]·$C_2H_2Cl_4$ (**2c**·$C_2H_2Cl_4$). Thermal ellipsoids of Zr, Cl, S and O atoms are at 30% probability, those of C atoms have been omitted for clarity.

The structures of [$Ti_2Cl_8$(μ-sulfolane-*O*,*O*′)$_2$] (**1d**) and [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] (**2c**) are reminiscent of those of the zirconium(IV) and cobalt(II) derivatives [$Zr_2Cl_8$[μ-$Ph_3$AsN)(Tolyl)$SO_2$-*O*,*O*′)$_2$][16] [$Co_2Cl_4$(μ-$Et_2SO_2$-*O*,*O*′)$_2$], respectively, the latter being a by-product of the reaction of [CoCl($PEt_3$)$_3$] with disodium ethane-1,2-thiolato.[9] The two metal atoms are linked by the oxygen atoms of two substituted sulfone ligands forming a $M_2O_4S_2$ eight-membered ring. The S–O distances, 1.448 and 1.51 Å, av., and the O–S–O angle, 109.9 and 117.1°, for the zirconium and cobalt derivatives, respectively, are comparable to those observed in our compounds.

It is interesting to observe that at variance with the structurally characterized dinuclear adducts of Group 4 tetrachlorides which generally have bridging chlorides,[1,17,18] the dinuclear compounds reported in this paper contain sulfone bridges. Probably the bite of the terminal sulfolane or diphenyl sulfone ligand would be too small, making the monodentate arrangement on a single metal centre highly unfavourable.

The bis-adduct [$ZrCl_4$($Me_2SO_2$)$_2$] (**2aa**) crystallizes in the space group $P2_12_12_1$ with four molecules in the unit cell. The coordination at zirconium is slightly distorted octahedral, see Fig. 3 and Table 3, with the dimethyl sulfone ligands in *cis*-position [(O(1)–Zr–O(2) 84.5(3)°]. The Zr–Cl distances (2.393 Å, av.), as well as the Zr–O distances (2.174 Å, av.) are similar to those observed in **2c** and comparable to other O-adducts of $ZrCl_4$.[14] The structural parameters of the dimethyl sulfone ligand [S–O 1.430 Å, av.; O–S–O 115.0(4) °] are similar to those found in the rhodium(II) complex [$Rh_2$($CF_3$COO)$_4$($Me_2SO_2$)$_2$] [S–O 1.453 Å, av.; O–S–O 115.48(6) °],[8] and comparable to those reported for uncoordinated $Me_2SO_2$ [S–O 1.448 Å, av.; O–S–O 117.2(6) °].[19]

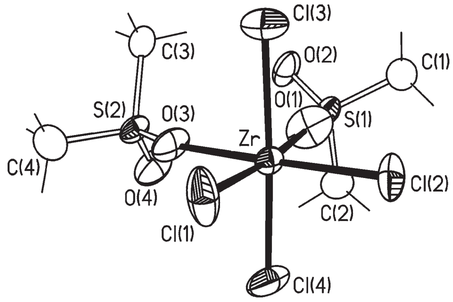

**Fig. 3** The molecular structure of [$ZrCl_4$($Me_2SO_2$)$_2$] (**2aa**). Thermal ellipsoids are at 30% probability.

It is noteworthy that the compounds described in the present paper, either the cyclic dinuclear compounds or the mononuclear one, show a comparable deformation of the coordination sphere of the metal, so that the chlorine atoms are leaning towards the oxygen ligands. As a matter of fact, the $Cl_{ax}$–M–$Cl_{ax}$ angles are smaller than

**Table 3** Selected bond distances (Å) and angles (°) for [$ZrCl_4(Me_2SO_2)_2$] (**2aa**)

| | | | |
|---|---|---|---|
| Zr–O(1) | 2.173(6) | Zr–O(3) | 2.175(6) |
| Zr–Cl(1) | 2.367(3) | Zr–Cl(2) | 2.378(2) |
| Zr–Cl(4) | 2.405(3) | Zr–Cl(3) | 2.422(3) |
| S(1)–O(1) | 1.425(6) | S(2)–O(3) | 1.464(5) |
| S(1)–O(2) | 1.431(6) | S(2)–O(4) | 1.399(7) |
| O(1)–Zr–O(3) | 84.5(3) | O(1)–Zr–Cl(3) | 85.2(2) |
| O(1)–Zr–Cl(1) | 172.8(2) | O(3)–Zr–Cl(3) | 86.2(2) |
| O(3)–Zr–Cl(1) | 88.6(2) | Cl(1)–Zr–Cl(3) | 92.4(1) |
| O(1)–Zr–Cl(2) | 90.3(2) | Cl(2)–Zr–Cl(3) | 94.1(1) |
| O(3)–Zr–Cl(2) | 174.7(2) | Cl(4)–Zr–Cl(3) | 169.0(1) |
| Cl(1)–Zr–Cl(2) | 96.7(1) | S(1)–O(1)–Zr | 174.8(6) |
| O(1)–Zr–Cl(4) | 85.8(2) | S(2)–O(3)–Zr | 151.9(5) |
| O(3)–Zr–Cl(4) | 86.6(2) | O(1)–S(1)–O(2) | 115.0(4) |
| Cl(1)–Zr–Cl(4) | 95.8(2) | O(3)–S(2)–O(4) | 115.8(4) |
| Cl(2)–Zr–Cl(4) | 92.3(1) | | |

180° [165.81(3), 160.71(5), and 169.0(1)° for **1d**, **2c**·$C_2H_2Cl_4$ and **2aa**, respectively] and, correspondingly, the $Cl_{eq}$–M–$Cl_{eq}$ angles are larger than 90° [99.09(4), 97.71(6) and 96.7(1)° for **1d**, **2c**·$C_2H_2Cl_4$ and **2aa**, respectively]. This trend is present also in the sulfur and selenium adducts of $ZrCl_4$ and it has been attributed to the repulsion between the lone pairs of the chlorine atoms.[20]

## $^1$H NMR spectroscopy

The $^1$H NMR spectra of the [$MCl_4(Me_2SO_2)_2$] complexes [M = Zr (**2aa**), Hf (**3aa**)] in $CD_2Cl_2$ at room temperature show a single broad peak at 3.39 ppm (Zr) and two equally broad peaks at 3.43 and 2.95 ppm (Hf). On the other hand, the titanium complex **1aa** shows only one single narrow peak at 3.25 ppm. By lowering the temperature down to −80 °C (−90 °C for the titanium derivative), two sharp singlets are observed for all three complexes, namely the signal at higher fields (2.95 ppm), due to the uncomplexed ligand, and the signal at lower field attributed to the metal-coordinated dimethyl sulfone (3.38 ppm for titanium, 3.41 ppm for zirconium and 3.43 ppm for hafnium). This has been confirmed by addition of an excess of the ligand to the solution, see Fig. 4, the intensity of the peaks at −90 °C being consistent with the expected concentrations of [$MCl_4(Me_2SO_2)_2$] and $Me_2SO_2$. The broad spectra reported in Fig. 4 are clearly due to a ligand-exchange process.

The coalescence temperature depends on the nature of the metal: it is below −70 °C for titanium, around 0 °C for zirconium and just above 25 °C in the case of hafnium, so that the relative rates of exchange are in the following order: $k_{Ti} \gg k_{Zr} > k_{Hf}$. This behaviour is consistent with the trend observed in the water exchange process within transition d elements belonging to the same Group.[21]

A more complicated situation has been found for the dinuclear complexes [$M_2Cl_8(\mu\text{-}R_2SO_2\text{-}O,O')_2$], particularly in the case of R = Et. The $^1$H NMR spectrum in $CD_2Cl_2$ of [$Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2$] (**2b**) shows two broad signals at 3.63 ($CH_2$) and 1.60 ppm ($CH_3$) at room temperature. By lowering the temperature down to −80 °C, two different ethyl resonances are observed at 3.90 ($CH_2$) and 1.62 ($CH_3$) and at 3.45 ($CH_2$) and 1.45 ($CH_3$) ppm.

In order to study the behaviour of **2b** in solution, two samples were prepared, one containing a large excess of additional $Et_2SO_2$ (sulfone/**2b** molar ratio = 4), the other one with a sulfone/**2b** molar ratio of about 0.5. The variable-temperature spectra are reported in Fig. 5. In the former case (Fig. 5(A)), two sets of well-separated resonances were observed at −80 °C, attributed to uncomplexed [2.93 ppm ($CH_2$), 1.24 ppm ($CH_3$)] and to coordinated $Et_2SO_2$ [3.45 ppm ($CH_2$), 1.43 ppm ($CH_3$)] of the mononuclear derivative [$ZrCl_4(Et_2SO_2)_2$] (**2bb**), probably formed in solution in the presence of the large excess of $Et_2SO_2$.

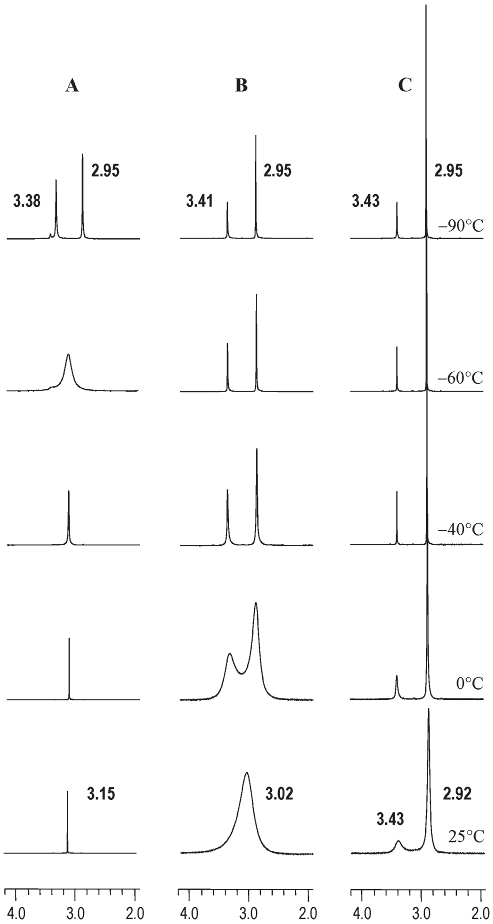

**Fig. 4** $^1$H NMR spectra in $CD_2Cl_2$: (A) $TiCl_4(Me_2SO_2)_2$ (**1aa**) + $Me_2SO_2$, (B) $ZrCl_4(Me_2SO_2)_2$ (**2aa**) + $Me_2SO_2$, (C) $HfCl_4(Me_2SO_2)_2$ (**3aa**) + $Me_2SO_2$.

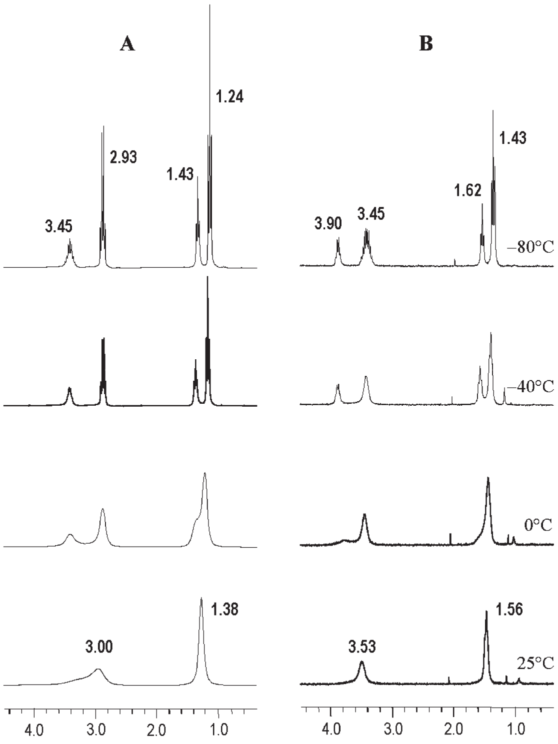

**Fig. 5** $^1$H NMR spectra in $CD_2Cl_2$: (A) $Et_2SO_2$ + $Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2$ (**2b**) ($Et_2SO_2$/**2b** molar ratio = 4), (B) $Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2$ (**2b**) ($Et_2SO_2$/**2b** molar ratio = 0.5).

In the second experiment (Fig. 5(B)) the two broad peaks at 3.53 and 1.56 ppm at room temperature give two couples of well resolved resonances at −80 °C, which match the situation observed for **2b**, in the same solvent at the same temperature without addition of diethyl sulfone. This suggests that the solutions of [$Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2$] (**2b**) in dichloromethane contain both the dinuclear 1 : 1 derivative **2b** [resonances (−80 °C) at 3.90 ppm ($CH_2$) and 1.62 ppm ($CH_3$)] and the 2 : 1 complex [$ZrCl_4(Et_2SO_2)_2$] (**2bb**) [resonances (−80 °C) at 3.45 ppm ($CH_2$) and 1.43 ppm ($CH_3$)], the relative amounts of the two components depending on the $Et_2SO_2$/Zr molar ratio. In fact,

**Table 4** Asymmetric and symmetric OSO stretching absorptions of complexed and uncomplexed sulfones (FT-Raman values are reported in parenthesis)

| Compound | $\tilde{\nu}_{as}$(OSO)/cm$^{-1}$ | $\tilde{\nu}_{s}$(OSO)/cm$^{-1}$ | $\Delta\tilde{\nu}$/cm$^{-1}$ | Bonding mode |
|---|---|---|---|---|
| Sulfolane[a] | 1301s (1302vw) | 1148s (1142s) | 153 (160) | — |
| $[Ti_2Cl_8(\mu\text{-sulfolane-}O,O')_2]$[b] | 1220vs (–)[c] | 1090s (1096ms) | 130 (–) | Bidentate[d] |
| $[ZrCl_4(sulfolane)_2]$[b] | 1297–1280vs (1297w) | 1073–1056s (1079–1060m) | 224 (227) | Monodentate |
| $Me_2SO_2$[b] | 1301s (1269w) | 1137s (1121s) | 164 (148) | — |
| $[TiCl_4(Me_2SO_2)_2]$[b] | 1295–1266s (1278–1263m) | 1114–1093s (1110–1090s) | 177 (171) | Monodentate |
| $[ZrCl_4(Me_2SO_2)_2]$[b] | 1290–1267s (1284–1269w) | 1112–1082s (1100–1082m) | 182 (185) | Monodentate[d] |
| $[HfCl_4(Me_2SO_2)_2]$[b] | 1284–1271vs (1283–1271m) | 1111–1085s (1106–1082s) | 180 (183) | Monodentate |
| $[Et_2SO_2]$[b] | 1287s (1280w) | 1138–1125s (1122s) | 156 (158) | — |
| $[Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2]$[b] | 1207s (–)[c] | 1100s (1110s) | 107 (–) | Bidentate |
| $Ph_2SO_2$[b] | 1309s (1308vw) | 1154s (1153s) | 155 (155) | — |
| $[Zr_2Cl_8(\mu\text{-}Ph_2SO_2\text{-}O,O')_2]$[b] | 1227s (–)[c] | 1123s (1133s) | 104 (–) | Bidentate[d] |
| $[ZrCl_4(Ph_2SO_2)_2]$[b] | 1309–1297s (1310–1295m) | 1133–1111s (1131–1111s) | 181 (182) | Monodentate |

[a] Neat liquid, FT-IR and FT-Raman. [b] Nujol mull for FT-IR and neat substance by FT-Raman. [c] Too weak to be detected. [d] X-Ray structure is available.

when the $^1$H NMR spectrum of $[Zr_2Cl_8(\mu\text{-}Et_2SO_2\text{-}O,O')_2]$ (**2b**) is recorded in the presence of an excess of $ZrCl_4$, *i.e.* under conditions preventing the presence in solution of free sulfone through fortuitous hydrolysis, well resolved signals at 3.81 ($CH_2$) and 1.73 ppm ($CH_3$) are observed even at room temperature, the situation not changing on lowering the temperature down to −80 °C (3.82 and 1.67 ppm). The small difference observed in the chemical shifts [3.90 and 1.62 *vs.* 3.81 and 1.73 ppm is probably due to the presence of solid $ZrCl_4$.

In conclusion, the NMR spectra of Fig. 5(B) suggest the existence in solution of an equilibrium between mononuclear and dinuclear species.

Finally the different spectral patterns at −80 °C, see Fig. 5, of the methylene signals of the bonded diethyl sulfone (quartet for **2b** and overlapped quartets for **2bb**) deserve some additional comments. Only in the mononuclear derivative **2bb** the rotation around the Zr–O– and/or the S–C bond could be hindered so to generate some inequivalence in the chemical shifts of the four $CH_2$'s. This behaviour also depends on the nature of the sulfone ligand: in fact, no splitting is observed for the methyl signals of the bonded $Me_2SO_2$ in **2aa** even at −90 °C (see Fig. 4(B)).

## Infrared and Raman spectroscopy

Sulfone coordination to a metal centre results in spectroscopic modifications of the $SO_2$ vibrations with respect to the uncomplexed molecule, especially for the asymmetric [$\tilde{\nu}_{as}$(OSO)] and symmetric [$\tilde{\nu}_{s}$(OSO)] stretching modes, see Table 4. In agreement with the expected reduction of the sulfur–oxygen bond order on coordination, the OSO stretching modes are shifted to lower wavenumbers. Furthermore, similarly to carboxylato complexes,[22] the separation $\Delta\tilde{\nu}$ between the asymmetric [$\tilde{\nu}_{as}$(OSO)] and symmetric [$\tilde{\nu}_{s}$(OSO)] stretching vibrations is expected to be influenced by the type of coordination. In particular, bridging bidentate coordination should result in a less pronounced separation than in the free molecule, due to the S–O bond order decrease and to the consequent reduction of OSO vibrational coupling.[23] Moreover, in the case of chelation vibrational coupling is expected to be lower, thus producing a further decrease of $\Delta\tilde{\nu}$, because of the decreased O–S–O angle. *Vice versa*, a greater separation is expected for a monodentate sulfone, essentially reflecting the larger red-shift of the symmetric stretching mode [$\tilde{\nu}_{s}$(OSO)] (pseudo single-bond order of the coordinated S–O bond).

In order to further strengthen the $SO_2$ vibrational assignments, Raman spectroscopy has been used. For uncoordinated sulfones, both IR asymmetric and symmetric stretching vibrations are of high intensity while the Raman spectra show intense symmetric stretching vibrations, whereas the corresponding asymmetric mode is often not easily detected[24] (see Table 4). Due to the essentially localised character of the sulfone ligand vibrations, a similar difference in the intensity of the [$\tilde{\nu}$(OSO)] Raman vibrations is expected for symmetric bidentate coordination. In fact, the structurally characterised complexes containing bridging bidentate sulfones (**1d** and **2c**) exhibit strong [$\tilde{\nu}_{s}$(OSO)] Raman bands, while the asymmetric ones are too weak to be detected (Fig. 6(a) and (b)). On the other hand, an intensification of the [$\tilde{\nu}_{as}$(OSO)] mode is observed for the monodentate ligation in **2aa** (Fig. 6(c)), as a consequence of the $SO_2$ asymmetric configuration. These Raman features turned out to be particularly useful to locate the OSO stretching bands in these complexes. The wavenumber values of the asymmetric and symmetric stretchings and the related separations are summarised in Table 4: when solid-state splitting of the $\tilde{\nu}_{as}$(OSO) and/or $\tilde{\nu}_{s}$(OSO) vibrations was observed, the respective barycentre was used to determine the separation $\Delta\tilde{\nu}$.

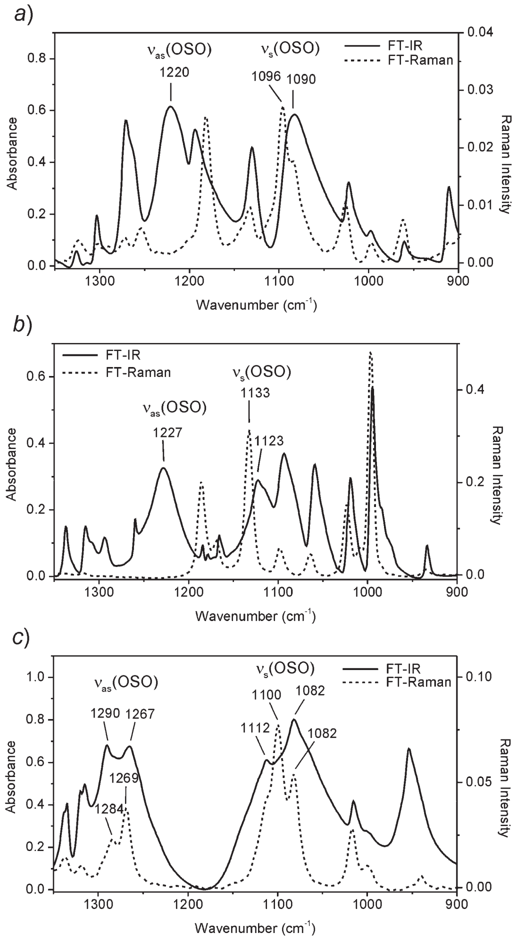

**Fig. 6** Vibrational spectra in the OSO stretching region of: (a) $[TiCl_4(\mu\text{-sulfolane-}O,O')]_2$ (**1d**), (b) $[ZrCl_4(\mu\text{-}Ph_2SO_2\text{-}O,O')]_2$ (**2c**), (c) $ZrCl_4(Me_2SO_2)_2$ (**2aa**).

As established by X-ray diffractometry, *vide infra*, the dinuclear complexes $[Ti_2Cl_8(\mu\text{-sulfolane-}O,O')_2]$ (**1d**) and $[Zr_2Cl_8(\mu\text{-}Ph_2SO_2\text{-}O,O')_2]$ (**2c**) contain bridging bidentate sulfones: the measured $\Delta\tilde{\nu}$ separations are significantly smaller than those observed in the uncomplexed species (see Table 4); on the other hand, the mononuclear compound $[ZrCl_4(Me_2SO_2)_2]$ (**2aa**) containing the monodentate sulfone displays a greater separation $\Delta\tilde{\nu}$ with respect to that found in the uncomplexed dimethyl sulfone. Accordingly, the bonding mode of sulfones in the other complexes was inferred from the measured separations on the basis of the $\Delta\tilde{\nu}$, as previously discussed. Thus, contrary to some earlier considerations,[25] the sulfone coordination mode can be inferred from vibrational spectroscopy. In conclusion, when $\Delta\tilde{\nu}$ is significantly greater than in the corresponding uncomplexed molecule, monodentate coordination is to expected; the opposite being the case for bidentate coordination.

## Conclusions

This paper describes preparations and structural characterisations of sulfone derivatives of the tetrachlorides of Group 4 metals. It has been shown that $TiCl_4$ reacts with sulfolane, in $SOCl_2$ as solvent, to give a 1 : 1 dinuclear compound containing sulfone bridges rather than chloride bridges, similar to the situation already established for the $TiCl_4/SOCl_2$ adduct of formula $[Ti_2Cl_8(SOCl_2)_2]$. This is due to the low stability of the 2 : 1 adducts in these experimental conditions, contrary to what is observed with more basic ligands containing oxygen or nitrogen as donor atoms.[26] On the other hand, in chlorinated hydrocarbons as solvents, both 1 : 1 and 2 : 1 adducts have been obtained, depending on the stoichiometry of the reagents for all three Group 4 metals. Combination of IR and Raman spectroscopies turned out to be a valid method for determining the coordination mode of the sulfone ligand confirming that the 1 : 1 adducts are dinuclear with bridging bidentate sulfones, while the 2 : 1 complexes are mononuclear with monodentate sulfone coordination.

## Experimental

All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified nitrogen. The reaction vessels were oven-dried prior to use. Solvents were dried by conventional methods. IR spectra were recorded at 2 cm$^{-1}$ resolution on a Nicolet Nexus FT-IR spectrophotometer; the analysis being carried out in the transmission mode, on Nujol mulls prepared under rigorous exclusion of moisture and oxygen. Raman spectra were recorded at 4 cm$^{-1}$ resolution on a Bruker FRA 106 FT-Raman module attached to a Bruker IFS88 FT-IR spectrophotometer, equipped with a Nd:YAG excitation laser (1064 nm) and a highly sensitive Ge detector. The solid samples were analysed in quartz tubes filled and sealed under a dry and oxygen-free atmosphere. $^1H$ NMR spectra were recorded with a Varian VXR 300 NMR spectrometer in $CD_2Cl_2$ (reference peak at 5.30 ppm) with a pulse width of 7 µs (40°) and a relaxation delay of 1.5 s.

$TiCl_4$ (Merck) was distilled at atmospheric pressure. $ZrCl_4$ (Fluka) and $HfCl_4$ (Cezus Chemie) were treated with boiling $SOCl_2$; the solutions were partially evaporated under reduced pressure, and heptane was added to precipitate the metal chloride. The suspension was filtered off and the solid was dried *in vacuo* at *ca*. 200 °C over several hours. Sulfolanes were distilled over $CaH_2$ prior to use, $Me_2SO_2$ (Aldrich), $Et_2SO_2$ (Aldrich) and $Ph_2SO_2$ (Aldrich) were used as received.

### Synthesis

**$[Ti_2Cl_8(\mu\text{-sulfolane-}O,O')_2]$ (1d).** A solution of $TiCl_4$ (3 ml, 27.4 mmol) in $SOCl_2$ (50 ml) was treated with sulfolane (13 ml, 136.5 mmol) at room temperature to give a yellow solution. After addition of hexane (50 ml), a light yellow microcrystalline product separated out. The solid was recovered by filtration, washed three times with hexane and dried *in vacuo* at room temperature affording 1.5 g (28% yield) of $[Ti_2Cl_8(\mu\text{-sulfolane-}O,O')_2]$ (**1d**). Found: Cl, 45.8; Ti, 15.3%. $C_4H_8Cl_4O_2STi$ requires: Cl, 45.8; Ti, 15.4%. $^1H$ NMR ($CDCl_3$–$SOCl_2$): 3.41 (m, 4H), 2.31 (m, 4H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3004wm, 1444m, 1401m, 1325w, 1303m, 1271s, 1265m (sh), 1220vs, 1193ms, 1130s, 1090s, 1082s, 1022m, 911m, 785wm, 730s, 660w, 552wm, 514w, 458s, 411vs, 379vs, 355m (sh), 302s, 215m. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3005w, 2999w, 2987wm, 2945w (sh), 2936m, 2871w, 1443w, 1399w, 1182m, 1133w, 1096ms, 1085wm, 1025w, 961w, 873m, 786w, 729w, 662ms, 564w, 516w, 445w, 404vs, 392m (sh), 372m, 356m, 301s, 269w, 195m, 176s, 154m.

**$[MCl_4(\text{sulfolane})_2]$, M = Zr (2dd), Hf (3dd).** Only the preparation of the zirconium adduct is described in detail, the hafnium compound being obtained in a similar way.

*(a) In dichloromethane*. The chloride $ZrCl_4$ (3.59 g, 15.39 mmol) was suspended in 100 ml of $CH_2Cl_2$ and a solution of 3 ml of sulfolane (31.48 mmol) in $CH_2Cl_2$ (20 ml) was then added dropwise at room temperature. At the end of the addition, a slightly turbid pale yellow solution was obtained, which was filtered to remove the insoluble material. The volume of the clear solution was reduced *in vacuo* to about 50 ml and 30 ml of hexane were then added. The colourless crystalline solid thus formed was filtered off, washed with two 10-ml portions of hexane and dried *in vacuo* at room temperature, obtaining 4.88 g (67% yield) of $[ZrCl_4(\text{sulfolane})_2]$ (**2dd**) Found: Cl, 28.6; Zr, 18.3%. $C_8H_{16}Cl_4O_4S_2Zr$ requires Cl, 29.9; Zr, 19.3%. IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3001w, 1449w (sh), 1408m, 1297vs, 1288s, 1271s, 1251s, 1205w, 1138s, 1104ms (sh), 1073s, 1056s, 1030w (sh), 999w, 909s, 777m, 734s, 673w, 569m, 518w, 442s. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3002w, 2983m, 2943s, 2882w, 1450m, 1408m, 1297w, 1253m, 1204w, 1138w, 1105m, 1079m, 1060m, 1032m, 966m, 874m, 787w, 735w, 674s, 569w, 519w, 440m, 395w, 383w, 347vs, 302w, 143s.

**$[HfCl_4(\text{sulfolane})_2]$ (3dd).** Colourless solid, 71% yield. Found: Cl, 23.9; Hf, 32.1%. $C_8H_{16}Cl_4HfO_4S_2$ requires Cl, 25.3; Hf, 31.8%.

*(b) In neat sulfolane*. The chloride $ZrCl_4$ (8.9 g, 38.19 mmol) was treated with sulfolane (30 ml) (exothermic reaction). The colourless suspension was filtered off and $CH_2Cl_2$ (30 ml), toluene (30 ml) and hexane (30 ml) were added to the filtrate.[27] After 15 days, the colourless microcrystalline solid was collected by filtration, washed three times with hexane and dried *in vacuo* affording 2.7 g (15% yield) of $[ZrCl_4(\text{sulfolane})_2]$ (**2dd**). Found: Cl, 28.9; Zr, 19.8%. $C_8H_{16}Cl_4O_4S_2Zr$ requires Cl, 29.9; Zr, 19.3%.

**$[HfCl_4(\text{sulfolane})_2]$ (3dd).** Colourless solid, 21% yield. Found: Cl, 24.8; Hf, 31.6%. $C_8H_{16}Cl_4HfO_4S_2$ requires Cl, 25.3; Hf, 31.8%.

**Synthesis of $[MCl_4(Me_2SO_2)_2]$, M = Ti (1aa), Zr (2aa), Hf (3aa)].** Only the preparation of the zirconium complex is described in detail, the corresponding titanium and hafnium compounds being obtained similarly. To a suspension of $ZrCl_4$ (3.69 g, 15.8 mmol) in 120 ml of dichloromethane, $Me_2SO_2$ (2.99 g, 31.8 mmol) dissolved in 40 ml of dichloromethane was added dropwise at room temperature. At the end of the addition, the mixture was stirred for additional 2 h, which led to the formation of the colourless microcrystalline product. This was recovered by filtration, washed with hexane and dried *in vacuo* at room temperature. An additional crop of product was recovered, in a similar way, by adding 30 ml of hexane to the mother-liquor, for a total yield of 5.98 g (89%) of $[ZrCl_4(Me_2SO_2)_2]$ (**2aa**). Found: Cl, 33.4; Zr, 21.4%. $C_4H_{12}Cl_4O_4S_2Zr$ requires Cl, 33.7; Zr, 21.6%. $^1H$ NMR ($CD_2Cl_2$): 3.39 (s, 12H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3030w, 3006m, 1422vw, 1397w, 1336m, 1317m, 1290s, 1267s, 1112m, 1082s, 1015w, 953s, 775ms, 702w, 490ms, 459ms, 397w, 353s, 335s, 318s, 301m (sh), 291m (sh). FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3030w, 3010mw, 2939w (sh), 2925ms, 1425w, 1390wm (sh), 1337vw, 1319vw, 1284w, 1269wm, 1100ms, 1082m, 1017w, 777ms, 705vs, 498m, 464m, 406w, 344vs, 323m (sh), 294ms, 145vs.

**$[TiCl_4(Me_2SO_2)_2]$ (1aa).** Yellow crystals, 78% yield. Found: Cl, 37.3; Ti, 12.1%. $C_4H_{12}Cl_4O_4S_2Ti$ requires Cl, 37.5; Ti, 12.7%. $^1H$ NMR ($CD_2Cl_2$): 3,25 (s, 12H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3030w, 3006m, 1424vw, 1398w, 1336m, 1317m, 1285ms (sh), 1266s, 1114s–1093s, 1014w, 950s, 773ms, 700w, 490ms, 473s, 409s, 393wm (sh), 364s, 333s, 294m. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3021m, 3005m, 2924s, 1430w,

**Table 5** Crystal data and details of the structure refinement for [$Ti_2Cl_8$(μ-sulfolane-*O*,*O*′)$_2$] (**1d**), [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] in [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$]·$C_2H_2Cl_4$ (**2c**·$C_2H_2Cl_4$) and [$ZrCl_4(Me_2SO_2)_2$] (**2aa**)

| Compound | **1d** | **2c**·$C_2H_2Cl_4$ | **2aa** |
|---|---|---|---|
| Empirical formula | $C_8H_{16}Cl_8O_4S_2Ti_2$ | $C_{26}H_{22}Cl_{12}O_4S_2Zr_2$ | $C_4H_{12}Cl_4O_4S_2Zr$ |
| Formula weight | 619.73 | 1070.40 | 421.28 |
| Temperature/K | 293(2) | 293(2) | 293(2) |
| Crystal system | Monoclinic | Triclinic | Orthorhombic |
| Space group | $P2_1/n$ (no. 14) | $P\bar{1}$ (no. 2) | $P2_12_12_1$ (no. 19) |
| $a$/Å | 10.987(2) | 9.466(1) | 7.074(1) |
| $b$/Å | 8.828(1) | 10.357(1) | 13.239(2) |
| $c$/Å | 11.659(1) | 11.654(2) | 16.400(4) |
| $\alpha$/° | — | 71.80(1) | — |
| $\beta$/° | 100.00(1) | 69.52(1) | — |
| $\gamma$/° | — | 82.48(1) | — |
| $V$/Å$^3$ | 1113.7(3) | 1016.5(2) | 1535.9(5) |
| $Z$ | 2 | 1 | 4 |
| $D_c$/Mg m$^{-3}$ | 1.848 | 1.745 | 1.822 |
| $\mu$/mm$^{-1}$ | 1.875 | 1.434 | 1.674 |
| Data/restr./param. | 3254/0/109 | 3541/6/207 | 1583/0/137 |
| $R(F_o)$ [$I > 2\sigma(I)$]$^a$ | 0.0335 | 0.0386 | 0.0346 |
| $R_w$ ($F_o^2$) [$I > 2\sigma(I)$]$^a$ | 0.0808 | 0.1014 | 0.0828 |
| Goodness-of-fit on $F^{2a}$ | 1.032 | 0.997 | 1.006 |

[a] $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (AQ)^2 + BQ]$ where $Q = [\max(F_o^2,0) + 2F_c^2]/3$; Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(N - P)]^{1/2}$, where $N$, $P$ are the numbers of observations and parameters, respectively.

1421w, 1405w (sh), 1395m, 1335vw, 1317w, 1278w, 1263m, 1110s, 1091ms, 1017w, 1101w, 948w, 775m, 704vs, 491ms, 480m, 412ms, 386s, 364vs, 329w, 297s, 174vs, 150m.

**[$HfCl_4(Me_2SO_2)_2$] (3aa).** Colourless crystals, 82% yield. Found: Cl, 26.9; Hf, 34.0%. $C_4H_{12}Cl_4HfO_4S_2$ requires Cl, 27.89; Hf, 35.11%. $^1$H NMR ($CD_2Cl_2$): 3.43 (s, 12H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3030w, 3004m, 1424w, 1400wm, 1338m, 1321m, 1284m (sh), 1271vs, 1111s, 1085s, 1013w, 952s, 777ms, 703w, 491ms, 471s, 401m, 343m, 326ms (sh), 312vs, 293s. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3030m, 3008m, 2926s, 1425w, 1414w, 1400w (sh), 1393m, 1338vw, 1320vw, 1283w (sh), 1271m, 1106s, 1082m, 1015w, 1101w, 947w, 778m, 707vs, 492s, 475m, 402m, 345vs, 328s, 306m (sh), 295s, 157s.

**[$ZrCl_4(Ph_2SO_2)_2$] (2cc).** To a suspension of $ZrCl_4$ (3.70 g, 15.9 mmol) in 100 ml of dichloromethane was added dropwise, at room temperature, a solution of 7.03 g of $Ph_2SO_2$ (32.2 mmol) in 50 ml of dichloromethane. At the end of the addition, a slightly turbid pale yellow solution was obtained, which was filtered to remove the insoluble material and 80 ml of hexane were then added to the filtrate. The colourless crystalline solid thus formed was filtered off, washed with two portions (20 ml each) of hexane and dried *in vacuo* at room temperature, thus obtaining 8.48 g (80% yield) of [$ZrCl_4(Ph_2SO_2)_2$] (**2cc**). Found: Cl, 20.8; Zr, 13.0%. $C_{24}H_{20}Cl_4O_4S_2Zr$ requires Cl, 21.2; Zr, 13.6%. $^1$H NMR ($C_2D_2Cl_4$): 8.01 (d, 8H), 7.66 (t, 4H), 7.54 (t, 8H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$:3087wm, 3061wm, 1581m, 1449vs, 1309s, 1297m, 1162wm, 1133s, 1111s, 1100m (sh), 1062s, 1050s, 1021m, 995m, 975w, 932w, 848w, 760m (sh), 755m, 729s, 699w, 685m, 678w (sh), 589m (sh), 581s, 563mw (sh), 557m, 495m, 462w, 428w, 348s, 337s, 325s, 293m, 206vw. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3163w, 3091w (sh), 3069s, 1582s, 1480w, 1446w, 1310m, 1295w (sh), 1186m, 1164m, 1131s, 1111m, 1099w, 1052m, 1024m, 997vs, 931vw, 702ms, 613m, 586w, 498w, 358m (sh), 341m, 327ms, 294m, 253ms, 213w, 171w, 147s, 116s.

**[$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] (2c).** Anhydrous $ZrCl_4$ (5.52 g, 23.7 mmol) was suspended in 120 ml of dichloromethane and $Ph_2SO_2$ (5.01 g, 22.9 mmol), dissolved in 40 ml of dichloromethane, was added dropwise to the suspension. At the end of the addition, the reaction mixture was further stirred at room temperature for 2 h and the solvent was then completely removed under reduced pressure. The resulting solid was transferred to an extractor equipped with a porous septum and a reflux condenser and extracted for 12 h using tetrachloroethane as solvent. At the end of the extraction, a small amount of insoluble material remained on the septum. The extract was treated with 50 ml of hexane and cooled at 0 °C. The colourless crystalline solid thus formed was filtered off, washed with two portions (20 ml each) of hexane and dried *in vacuo* at room temperature, obtaining 7.91 g (74% yield) of [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] (**2c**). Found: Cl, 29.8; Zr, 18.8%. $C_{12}H_{10}Cl_4O_2SZr$ requires Cl, 31.4; Zr, 20.2%. $^1$H NMR ($C_2D_2Cl_4$): 8.25–7.45 (unresolved multiplets). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 3084w, 3060w, 1575m, 1449s, 1395w, 1337m, 1293m, 1227s, 1166w, 1130w (sh), 1123s, 1093s, 1059s, 1019m, 995s, 934w, 790w, 753s, 740s, 700w, 677s, 611w, 586s, 554ms, 417w, 389m, 360vs, 344vs, 310w. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3156vw, 3084m, 3066s, 1579s, 1450w, 1318vw, 1186ms, 1169w, 1133s, 1098w, 1064w, 1023m, 996vs, 935vw, 757vw, 703m, 611m, 364vs, 341m, 317ms, 280m, 220m, 147s.

**[$Zr_2Cl_8$(μ-$Et_2SO_2$-*O*,*O*′)$_2$] (2b).** A suspension of $ZrCl_4$ (3.57 g, 15.3 mmol) in 100 ml of dichloromethane was added of 1.81 g (14.8 mmol) of $Et_2SO_2$ dissolved in 30 ml of dichloromethane. Following a procedure similar to that described for the preparation of (**2c**), were obtained 4.51 g (83% yield) of [$Zr_2Cl_8$(μ-$Et_2SO_2$-*O*,*O*′)$_2$] (**2b**) as a colourless crystalline solid. Found: Cl, 38.9; Zr, 25.3%. $C_4H_{10}Cl_4O_2SZr$ requires Cl, 39.9; Zr, 25.7%. $^1$H NMR ($CD_2Cl_2$): 3.63 (s br, 4H), 1.60 (s br, 6H). IR (Nujol) $\tilde{\nu}$/cm$^{-1}$: 2994w, 1454m, 1405w, 1382w, 1297m, 1279m, 1226w (sh), 1207s, 1100s, 1066w, 1048wm, 1036wm, 968w, 798m, 784w (sh), 735w, 502m, 477w, 419m, 371m (sh), 336m (sh), 340s, 302m. FT-Raman $\tilde{\nu}$/cm$^{-1}$: 3004w, 2964m, 2946w, 2925ms, 2880w, 2672w, 1455m, 1404w, 1386w, 1236w, 1174s, 1110s, 1078w, 1051m, 979w, 639s, 510w, 475w, 418m, 373vs, 348s, 294m, 177w, 148s.

## X-Ray diffraction studies

Single crystals suitable for the X-ray diffractometric studies were obtained by slowly cooling a $SOCl_2$ solution of [$Ti_2Cl_8$(μ-sulfolane-*O*,*O*′)$_2$] (**1d**), a boiling $C_2H_2Cl_4$ solution of [$Zr_2Cl_8$(μ-$Ph_2SO_2$-*O*,*O*′)$_2$] (**2c**), and by slow diffusion of hexane into a $CH_2Cl_2$ solution of [$ZrCl_4(Me_2SO_2)_2$] (**2aa**). The X-ray diffraction experiments were carried out at room temperature ($T$ = 293 K) by means of a Bruker P4 diffractometer equipped with a graphite-monochromated Mo-Kα radiation. The samples were sealed in glass capillaries under an atmosphere of dinitrogen. The intensity data collection was carried out with the $\omega/2\theta$ scan mode, collecting a redundant set of data. Three standard reflections were measured every 97 measurements to check sample decay. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of the $\psi$-scan method.[28] The structure solutions were obtained by means of the automatic direct methods contained in SHELXS97.[29] The refinements, based on full-matrix least squares on $F^2$, were done by means of the SHELXL97[29] programme. Some other utilities contained in the WINGX suite[30] were also used. The more relevant crystal parameters are listed in Table 5.

The systematic absences in the diffraction intensity data of **1d** univocally indicated the monoclinic $P2_1/n$ space group. The structure solution showed that the asymmetric unit was a [$TiCl_4$(μ-sulfolane-*O*,*O*′)] group, forming dinuclear molecules through the inversion centre. The final refinement cycle was done by using anisotropic thermal parameters for all the heavy atoms and allowing the hydrogen atoms to ‘ride’ on the connected carbon atoms. The resulting reliability factors are listed in Table 5. The solution of the structure of **2c**·$C_2H_2Cl_4$ was found in the triclinic centrosymmetric $P\bar{1}$ space group. The structure was found to consist of dinuclear molecules, obtained by the action of the inversion operator placed at 0 0 ½ on the {$ZrCl_4$(μ-$Ph_2SO_2$-*O*,*O*′)} asymmetric unit. The unit cell contains one molecule of $C_2H_2Cl_4$, placed on the inversion centre at ½ 0 0. The initial refinement cycles showed slightly excessive values for some anisotropic thermal parameters of the phenyl carbon atoms and definitely large values for the isotropic thermal parameters of the Cl and C atoms of $C_2H_2Cl_4$, the latter being characterised by a slightly unreliable geometry, probably due to disorder in the phenyl groups and especially in the position of $C_2H_2Cl_4$. Some geometric constraints were then introduced to force $C_2H_2Cl_4$ to keep a reasonable geometry. The final refinement cycle was carried on with anisotropic thermal parameters for all the heavy atoms and isotropic for the hydrogen and the carbon atoms of $C_2H_2Cl_4$, giving the reliability factors listed in Table 5.

The solution of the structure of **2aa** was found in the orthorhombic space group $P2_12_12_1$. The asymmetric unit corresponds to the molecule. The final refinement cycle was done by using anisotropic thermal parameters for all the heavy atoms and allowing the hydrogen atoms ‘ride’ on the connected carbon atoms. The resulting reliability factors are listed in Table 5.

CCDC reference numbers 236507–236509.

See http://www.rsc.org/suppdata/dt/b4/b405871b/ for crystallographic data in CIF or other electronic format.

### $^1H$ NMR experiments

**[$MCl_4(Me_2SO_2)_2$] in the presence of $Me_2SO_2$, M = Ti, Zr, Hf.** Only the preparation of solutions of the zirconium complex **2aa** is described in detail, the corresponding titanium and hafnium derivatives, **1aa** and **3aa** being handled similarly. To a suspension of 15.1 mg (0.036 mmol) of **2aa** in 1 ml of $CD_2Cl_2$, $Me_2SO_2$ (2.3 mg, 0.025 mmol) was added. The reaction mixture was stirred for 10 min at room temperature and then decanted. The clear colourless solution was transferred into a NMR tube and analysed at variable temperature (Fig. 4). Samples of **1aa** [11.1 mg, 0.029 mmol, 1 ml of $CD_2Cl_2$, 5.9 mg (0.063 mmol) of $Me_2SO_2$] and **3aa** (7.7 mg, 0.015 mmol, 1 ml of $CD_2Cl_2$; 4.5 mg, 0.048 mmol of $Me_2SO_2$), were examined under similar conditions.

**The 2b–$Et_2SO_2$ system.** Compound [$Zr_2Cl_8$(μ-$Et_2SO_2$-*O*,*O*′)$_2$] (0.055 g, 0.16 mmol was suspended in 1.2 ml of $CD_2Cl_2$ and 0.078 g (0.64 mmol) of $Et_2SO_2$ were added. After stirring for 5 min at room temperature, a clear colourless solution was obtained, which was transferred into a NMR tube and analysed at different temperatures (Fig. 5(A)).

Compound **2b** (0.087 g, 0.25 mmol) was suspended in 1.2 ml of $CD_2Cl_2$ and treated with 0.029 g (0.024 mmol) of $Et_2SO_2$. After stirring for 10 min at room temperature and then decanting, the clear colourless solution thus obtained was transferred into a NMR tube and analysed at variable temperature (Fig. 5(B)).

**The 2b–$ZrCl_4$ system.** A suspension of $ZrCl_4$ (0.046 g, 0.20 mmol) in $CD_2Cl_2$ (1 ml) was treated with 0.029 g (0.08 mmol) of [$Zr_2Cl_8$(μ-$Et_2SO_2$-*O*,*O*′)$_2$], (**2b**). After 15 min stirring at room temperature, the colourless solution was transferred into a NMR tube and analysed: $^1H$ NMR: 3.81 (q, 2H), 1.73 (t, 3H).

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