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FULL PAPER

Synthesis, properties and crystal structures of 6-, 7- and 8-coordinate Zr(IV) and Hf(IV) complexes involving thioether and selenoether ligands

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A series of 6-, 7- and 8-coordinate complexes of the form $[MCl_4(L–L)]$ (M = Zr, Hf; L–L = $MeE(CH_2)_2EMe$), $[ZrCl_4([9]aneS_3)]$ and $[MCl_4\{MeE(CH_2)_2EMe\}_2]$ (E = S or Se) has been obtained in moderate to high yield by reaction of $[MCl_4(Me_2S)_2]$ with one (or three for the 1 : 2 M : L–L species) molar equivalents of L–L in rigorously anhydrous CH_2Cl_2. The poorly soluble products have been characterised by far IR spectroscopy, diffuse reflectance UV-Vis spectroscopy and microanalyses. ^1H NMR data are reported for certain systems, although in the majority of cases the very poor solubility prevented useful NMR experiments. The crystal structures of six representative examples, the distorted octahedral $[ZrCl_4(Me_2S)_2]$ and $[HfCl_4\{MeSe(CH_2)_2SeMe\}]$, the metallocyclic $[(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2]$, the flattened dodecahedral $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$ and $[HfCl_4\{MeS(CH_2)_2SMe\}_2]$ and the 7-coordinate $[ZrCl_4([9]aneS_3)]$ are also described. The crystal structure of $[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$, formed during reaction of $[ZrCl_4(Me_2S)_2]$ with $MeSe(CH_2)_2SeMe$ in CH_2Cl_2 is also presented.

Introduction

While a wide range of middle and late transition metal complexes with thio- and seleno-ether ligands has been reported over the last two decades or so,[1–5] examples involving high oxidation state, hard early transition metal ions are very much more limited and correspondingly their properties have been little explored. There is inherent interest in the nature of the chalcogenoether ⟶ M interactions in these hard metal/soft ligand combinations and in the properties which they impart. Neutral compounds of this type involving these Group 16 donor ligands may also be potential candidates for single source CVD precursors to early transition metal chalcogenides. These are technologically important materials with uses in a range of electronic devices.[6–9] Winter and co-workers have established that the simple thio- and seleno-ether complexes, *e.g.* $[TiCl_4(SeEt_2)_2]$ do give $TiSe_2$ (or TiS_2 for thioethers) under vapour deposition conditions.[10,11] We have reported the synthesis, solution behaviour and structural properties of a series of Ti(IV) complexes of general formula $[TiX_4(L–L)]$, L–L = dithio- or diseleno-ether ligand.[12] These compounds adopt distorted octahedral coordination geometries and we saw no evidence for higher coordination numbers at Ti(IV) either using these ligands or using tripodal $MeC(CH_2EMe)_3$, E = S or Se.[13] In view of these observations we have initiated an investigation of the chemistry of $ZrCl_4$ and $HfCl_4$ with thioether and selenoether ligands. Very few complexes of these elements involving thioether coordination are known, to the best of our knowledge the only exceptions are $[MCl_4(SMe_2)_2]$, $[MCl_4(tht)_2]$ (tht = tetrahydrothiophene), $[MCl_4(SeMe_2)_2]$[14–16] and an early report on $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$[17] (all obtained by reaction of polymeric MCl_4 with excess ligand). Structural data have not been reported for any of these.

We report here the preparation and characterisation of a series of complexes of the form $[MCl_4(L–L)]$ (M = Zr; L–L = $MeS(CH_2)_2SMe$, $MeS(CH_2)_3SMe$, $MeSe(CH_2)_2SeMe$; M = Hf; L–L = $MeS(CH_2)_2SMe$, $MeSe(CH_2)_2SeMe$), $[MCl_4\{MeE(CH_2)_2EMe\}_2]$ (E = S or Se) and $[ZrCl_4([9]aneS_3)]$. The crystal structures of six representative examples, $[ZrCl_4(Me_2S)_2]$, $[(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2]$, $[HfCl_4\{MeSe(CH_2)_2SeMe\}]$, $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$, $[HfCl_4\{MeS(CH_2)_2SMe\}_2]$ and $[ZrCl_4([9]aneS_3)]$ are also described.

Results and discussion

Neither $ZrCl_4$ nor $[ZrCl_4(thf)_2]$ proved to be very satisfactory precursors for the preparation of di- or tri-thioether complexes of Zr(IV). Such reactions typically resulted in low yields or partially substituted species, even in the presence of excess chalcogenoether and with long reaction times, reflecting the strong affinity of Zr(IV) for hard O-donor or chloro ligands. In an early attempt to obtain a Zr(IV) complex of the bidentate $PhSe(CH_2)_2SePh$, $[ZrCl_4(thf)_2]$ was treated with the selenoether in anhydrous CH_2Cl_2, resulting in an immediate colour change to orange. Precipitation with hexane removed residual $[ZrCl_4(thf)_2]$ and concentration of the orange filtrate afforded a yellow solid. This solid was readily soluble in $CDCl_3$ and the ^1H NMR spectrum showed resonances associated with the aromatic phenyl groups (7.1–7.6 ppm), but importantly, no resonances corresponding to the methylene protons. Similarly the $^{13}C\{^1H\}$ NMR spectrum revealed resonances only in the range 127–130 ppm, associated with the phenyl groups. The identity of the yellow solid was established from these and the $^{77}Se\{^1H\}$ NMR spectrum which showed a singlet at 460 ppm, consistent with the product being PhSeSePh. Thus, reaction of the Zr(IV) precursor with the diselenoether results in significant decomposition, possibly through elimination of $CH_2{=}CH_2$. This behaviour is similar to that seen for the $TiCl_4/PhSe(CH_2)_2SePh$ system.[12]

However, under appropriate conditions, the discrete (and relatively soluble) $[MCl_4(SMe_2)_2]$ do provide good entries into this chemistry. Treatment of a solution of $[ZrCl_4(SMe_2)_2]$ with one molar equivalent of L–L (L–L = $MeE(CH_2)_2EMe$, $MeS(CH_2)_3SMe$ or $[9]aneS_3$) or three molar equivalents of $MeE(CH_2)_2EMe$ in rigorously anhydrous CH_2Cl_2 solution and with gentle vacuum (to remove volatile SMe_2) affords white solids of stoichiometry $[ZrCl_4(L–L)]$ or $[ZrCl_4\{MeE(CH_2)_2EMe\}_2]$ in moderate to high yields. The isolated complexes are hydrolytically unstable and therefore were stored in an

N_2-purged glove-box. Similarly, reaction of $[HfCl_4(Me_2S)_2]$ with one or three molar equivalents of $MeE(CH_2)_2EMe$ in anhydrous CH_2Cl_2 gives $[HfCl_4\{MeE(CH_2)_2EMe\}]$ and $[HfCl_4\{MeE(CH_2)_2EMe\}_2]$ respectively, although for hafnium considerably longer reaction times were necessary.

The far IR spectra of the 1 : 1 [MCl_4(L–L)] systems in this work all show broad M–Cl stretching vibrations, with ν(Zr–Cl) occurring at *ca.* 360 cm^{-1} and ν(Hf–Cl) at *ca.* 330 cm^{-1}. While the broadness of the bands prevented conclusive assignment of the geometry as *cis* (four bands) or *trans* (one band), the short interdonor chain lengths in the ligands used here dictates only *cis* coordination when chelating. The M–Cl stretching vibrations in *cis*-$[MCl_4(SMe_2)_2]$ occur in similar regions of the spectrum.[14]

For the 8-coordinate [MCl_4(L–L)$_2$], for which we assume a flattened dodecahedral geometry akin to that seen for $[TiX_4\{o\text{-}C_6H_4(EMe_2)_2\}_2]$ (E = P or As)[18] and see below for $[MCl_4\{MeS(CH_2)_2SMe\}_2]$, two ν(M–Cl) are expected (D_{2d}, theory b_2 + e) (literature 305 cm^{-1} for $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$).[17] These occur at *ca.* 300 (M = Zr) and *ca.* 280 cm^{-1} (M = Hf), *i.e.* considerably lower frequency than for the 1 : 1 compounds, consistent with the increased coordination numbers. For the macrocyclic complex, $[ZrCl_4([9]aneS_3)]$, ν(Zr–Cl) appears as a strong, broad absorption at 332 cm^{-1}, intermediate between the values for the 6- and 8-coordinate species.

The Zr(IV) and Hf(IV) complexes are d^0 species and hence the lowest energy UV/Vis transitions are expected to be of the ligand ⟶ metal charge transfer (LMCT) type. We have reported[12] the LMCT spectra of Ti(IV) dithio- and diseleno-ethers which proved useful in identifying the donor set present, whilst in related work[18] the spectra of [$TiCl_4$(L–L)$_x$] (x = 1, 2; L–L = $o\text{-}C_6H_4(PMe_2)_2$ or $o\text{-}C_6H_4(AsMe_2)_2$) showed identifiable differences bewteen 6- and 8-coordinate metal centres. The Zr and Hf complexes are white or pale cream which means that the LMCT bands lie in the UV region and hence may be less informative, however we have carried out similar studies. The very poor solubility of the complexes in non-coordinating solvents and their hydrolytic instability limited UV/Vis spectroscopic studies to the solid state. Diffuse reflectance spectra were recorded for powdered samples diluted with dried $BaSO_4$. $ZrCl_4$ and $HfCl_4$, which are chloride bridged polymers[19] with 6-coordinated metal centres, exhibited the lowest energy Cl ⟶ M charge transfer bands at 39,000 and 41,300 cm^{-1} respectively. All the 6-coordinate complexes in the present study exhibited strong broad features in the range 37,000–39,000 (Zr) or 39,000–41,000 cm^{-1} (Hf) which are thus readily assigned as $\pi(Cl) \longrightarrow t_{2g}(M)$.† Using the optical electronegativity model[20] and these data lead to χ_{opt} values for Zr(IV) of *ca.* 1.7 and for Hf(IV) of *ca.* 1.6, and using χ_{opt} $S(Se)R_2$ of 2.8 leads to predictions of the energies of π(S(Se)) ⟶ Zr(Hf) of 33,000 and 36,000 cm^{-1}. Weak broad features in these regions are thus assigned as $\pi(S/Se) \longrightarrow t_{2g}(M)$. The diffuse reflectance spectra of the 8-coordinate [MCl_4(L–L)$_2$] (L–L = $MeS(CH_2)_2SMe$, $MeSe(CH_2)_2SeMe$) are different in profile to the 1 : 1 complexes, although as expected the energies are similar. For the approximately D_{2d} donor arrangement we observe an intense feature assigned as $\pi(Cl) \longrightarrow M(b_1)$ and a well-defined shoulder on the low energy side attributed to the $\pi(S/Se) \longrightarrow M(b_1)$ transition. The greater relative intensity of the π(S/Se) ⟶ M transition in the 8-coordinate species compared with the 6-coordinate, is reasonable given the greater number of S/Se donors present.

The compounds are generally extremely poorly soluble in non-coodinating solvents such as chlorocarbons (they readily dissolve in coordinating solvents such as MeCN or Me_2CO, with liberation of L–L). Thus, in most cases, even after long accumulation times, ^1H NMR spectroscopic studies (CD_2Cl_2) revealed only traces of free ligand. However, $[ZrCl_4\{MeS(CH_2)_2SMe\}]$ and $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$ were sufficiently soluble to allow ^1H NMR spectroscopic measurements. The ^1H NMR data for $[MCl_4(Me_2S)_2]$ and $[MCl_4(Me_2Se)_2]$ have been reported already and our data are in good agreement.[14,16]

At 300 K the ^1H NMR spectrum of $[ZrCl_4\{MeS(CH_2)_2SMe\}]$ shows two singlets (3.02, 2.35 ppm). $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$ reveals singlets at 3.01 and 2.41 ppm. Cooling the solutions in 20 °C intervals results in broadening and splitting of the resonances. At 213 K, both sysytems show 'free' ligand (2.65, 2.06 ppm) and complex overlapping multiplets at 3.34, 3.01 and 2.38 ppm associated with coordinated thioether. We tentatively propose that these data indicate that the 1 : 1 and 1 : 2 Zr : $MeS(CH_2)_2SMe$ compounds exist as mixtures of similar species in solution, probably containing $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$, $[ZrCl_4\{MeS(CH_2)_2SMe\}]$, free $MeS(CH_2)_2SMe$ and, for mass balance, another Zr-containing species, probably $ZrCl_4$.

X-Ray crystallography

In view of the absence of any crystallographic data on zirconium or hafnium complexes with thio- or seleno-ether coordination, and the limited structural information available from the spectroscopic studies above, we undertook X-ray crystallographic analyses on several of the examples prepared in this work. The range of systems for which we obtained crystals include representative examples of 6-, 7- and 8-coordination and include thio-and seleno-ether ligands and both zirconium and hafnium centres.

Crystals of $[ZrCl_4(Me_2S)_2]$, $[(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2]$, $[HfCl_4\{MeSe(CH_2)_2SeMe\}]$, $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$ and $[HfCl_4\{MeS(CH_2)_2SMe\}_2]$ were obtained by slow evaporation from very dilute solutions of the complex in CH_2Cl_2. This method was not successful for $[ZrCl_4([9]aneS_3)]$ due to its even lower solubility. Extremely small (weakly diffracting) crystals of $[ZrCl_4([9]aneS_3)]$ were however obtained by allowing solutions of $[ZrCl_4(Me_2S)_2]$ and $[9]aneS_3$ in CH_2Cl_2 to slowly diffuse together.

The structure of the precursor $[ZrCl_4(Me_2S)_2]$ was determined to provide bond length and angle distributions on the parent complex and to permit comparisons with the new complexes. The structure shows (Fig. 1, Table 1) the expected distorted octahedral geometry with mutually *cis* Me_2S ligands. The Zr–S bond distances (2.754(3), 2.788(2) Å) are considerably longer than the Zr–Cl distances (2.361(2)–2.425(2) Å) despite the similarities in the covalent radii of chlorine and sulfur. The

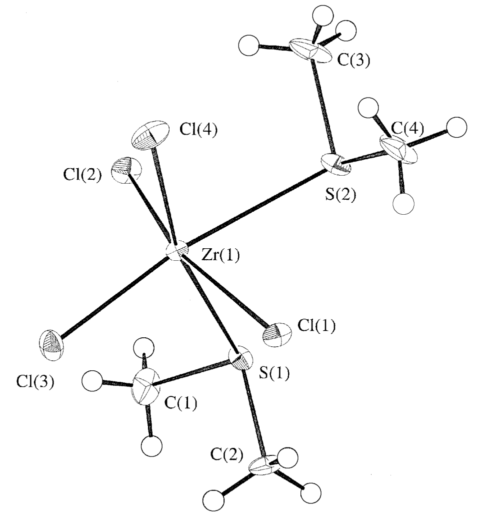

Fig. 1 View of the structure of $[ZrCl_4(Me_2S)_2]$ with numbering scheme adopted. Ellipsoids are shown at the 40% probability level.

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† Although the actual symmetry is C_{2v} rather than O_h, no resolved splittings were evident and hence the O_h (t_{2g}) notation is retained. We were similarly unable to resolve splitting in the spectra of the titanium analogues.[12]

Table 1 Selected bond lengths (Å) and angles (°) for [$ZrCl_4(Me_2S)_2$]

Zr(1)–S(1)	2.754(3)	Zr(1)–Cl(2)	2.425(2)
Zr(1)–S(2)	2.788(2)	Zr(1)–Cl(3)	2.361(2)
Zr(1)–Cl(1)	2.386(2)	Zr(1)–Cl(4)	2.386(3)
Cl(1)–Zr(1)–Cl(2)	157.14(8)	Cl(2)–Zr(1)–S(1)	79.30(8)
Cl(1)–Zr(1)–Cl(3)	97.09(8)	Cl(2)–Zr(1)–S(2)	80.94(7)
Cl(1)–Zr(1)–Cl(4)	96.83(8)	Cl(3)–Zr(1)–Cl(4)	104.72(10)
Cl(1)–Zr(1)–S(1)	83.29(8)	Cl(3)–Zr(1)–S(1)	88.75(8)
Cl(1)–Zr(1)–S(2)	81.32(8)	Cl(3)–Zr(1)–S(2)	167.87(9)
Cl(2)–Zr(1)–Cl(3)	97.23(8)	S(1)–Zr(1)–S(2)	79.12(7)
Cl(2)–Zr(1)–Cl(4)	96.65(8)		

bond angles at Zr show significant distortions from an ideal octahedron. For example, the axial Cl–Zr–Cl angle is 157.14(8)°, with the Cl's leaning over the Me_2S ligands. The *cis* Cl–Zr–Cl angles are all greater than 96°. Correspondingly, the S–Zr–S angle is very acute (79.12(7)°) given that there is no strain imposed by chelation in this species. These trends may arise from the spatial requirements of the chlorines due to repulsion between their lone pairs. Similar trends in bond lengths and angles occur in the [TiX_4(L–L)] (L–L = dithio- or diseleno-ether ligands)[12] and in a series of distorted octahedral Sn(IV) derivatives, [SnX_4(L–L)] (X = Cl, Br or I; L–L = dithio-, diseleno- or ditelluro-ether),[21–23] as well as in *cis*-[$SnBr_4(Me_2S)_2$] where there is no chelate ring.[24]

The structure of the dinuclear [$(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2$] shows (Fig. 2, Table 2) each Zr(IV) centre coordinated to four terminal Cl ligands and to two S-donor atoms from two different bridging dithioether ligands, giving an unusual 12-membered metallocyclic species with a distorted octahedral coordination environment at Zr(IV). The S atoms occupy mutually *cis* coordination sites with Zr–S bond distances of 2.761(2)–2.792(2) Å. Despite S and Cl having similar radii, these bond distances are *ca.* 0.4 Å longer than *d*(Zr–Cl), indicating weak Zr–S interactions. Again, *d*(Zr–Cl) *trans* Cl are significantly longer (by *ca.* 0.02–0.03 Å) than *d*(Zr–Cl) *trans* S, and the Cl(1)–Zr(1)–Cl(3) and Cl(5)–Zr(2)–Cl(7) bond angles are 156.05(7) and 153.18(6)° respectively (these Cl's are tilted to lie over the neutral S donor atoms), confirming a significant distortion from a regular octahedral arrangement. The reason for the formation of a binuclear molecule for the [$(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2$] may be the trimethylene interdonor linkage in the dithioether. Upon chelation this would give a 6-membered chelate ring, whereas the dimethylene unit (in the corresponding $MeS(CH_2)_2SMe$) would give the more stable 5-membered chelate ring. Thus, the driving force for chelation may be small in the former and the formation of the binuclear compound may be driven by its lower solubility. The corresponding Ti(IV) species, [$TiCl_4\{MeS(CH_2)_3SMe\}$] is mononuclear with the dithioether chelating, *d*(Ti–Cl) = 2.235(2), 2.285(2), *d*(Ti–S) = 2.644(2) Å, with similar patterns in the Ti–Cl and Ti–S bond lengths and bond angles.[12]

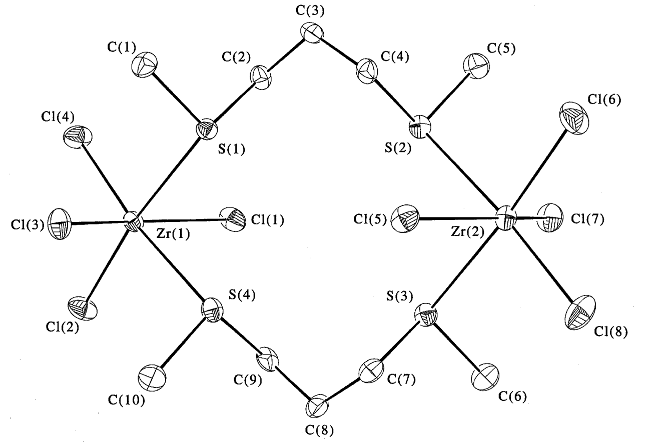

Fig. 2 View of the structure of [$(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2$] with atom numbering scheme. 40% probability ellipsoids are shown and H atoms are omitted for clarity.

Table 2 Selected bond lengths (Å) and angles (°) for [$(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2$]

Zr(1)–Cl(1)	2.385(2)	Zr(2)–Cl(5)	2.395(2)
Zr(1)–Cl(2)	2.370(2)	Zr(2)–Cl(6)	2.372(2)
Zr(1)–Cl(3)	2.404(2)	Zr(2)–Cl(7)	2.408(2)
Zr(1)–Cl(4)	2.370(2)	Zr(2)–Cl(8)	2.370(2)
Zr(1)–S(1)	2.783(2)	Zr(2)–S(2)	2.792(2)
Zr(1)–S(4)	2.777(2)	Zr(2)–S(3)	2.761(2)
Cl(1)–Zr(1)–Cl(2)	97.85(6)	Cl(5)–Zr(2)–Cl(6)	98.65(6)
Cl(1)–Zr(1)–Cl(3)	156.05(7)	Cl(5)–Zr(2)–Cl(7)	153.18(6)
Cl(1)–Zr(1)–Cl(4)	98.37(6)	Cl(5)–Zr(2)–Cl(8)	98.47(6)
Cl(1)–Zr(1)–S(1)	82.18(5)	Cl(5)–Zr(2)–S(2)	83.05(5)
Cl(1)–Zr(1)–S(4)	81.89(6)	Cl(5)–Zr(2)–S(3)	83.44(5)
Cl(2)–Zr(1)–Cl(3)	97.21(6)	Cl(6)–Zr(2)–Cl(7)	98.03(6)
Cl(2)–Zr(1)–Cl(4)	99.49(6)	Cl(6)–Zr(2)–Cl(8)	98.87(7)
Cl(2)–Zr(1)–S(1)	170.21(6)	Cl(6)–Zr(2)–S(2)	87.28(6)
Cl(2)–Zr(1)–S(4)	90.78(6)	Cl(6)–Zr(2)–S(3)	171.99(6)
Cl(3)–Zr(1)–Cl(4)	97.37(6)	Cl(7)–Zr(2)–Cl(8)	99.53(6)
Cl(3)–Zr(1)–S(1)	79.84(5)	Cl(7)–Zr(2)–S(2)	76.93(5)
Cl(3)–Zr(1)–S(4)	79.40(5)	Cl(7)–Zr(2)–S(3)	77.36(5)
Cl(4)–Zr(1)–S(1)	90.17(5)	Cl(8)–Zr(2)–S(2)	173.33(6)
Cl(4)–Zr(1)–S(4)	169.57(6)	Cl(8)–Zr(2)–S(3)	88.42(6)
S(1)–Zr(1)–S(4)	79.52(5)	S(2)–Zr(2)–S(3)	85.29(5)

The crystal structure of the related 1 : 1 species [$HfCl_4\{MeSe(CH_2)_2SeMe\}$] shows (Fig. 3, Table 3) a discrete mononuclear complex with the diselenoether chelating in the DL form and hence occupying two *cis* coordination sites. The bond angles at Hf show similar trends to those in the 6-coordinate Zr(IV) species above. The Hf–Se bond distances of 2.844(2) and 2.848(2) Å are slightly longer than in the Zr(IV) thioethers, reflecting the larger radius of Se over S. The structure of this molecule is also similar to that of the Ti(IV) thioether, [$TiCl_4\{MeS(CH_2)_2SMe\}$] (Ti–S = 2.6106(9), 2.6010(8) Å).

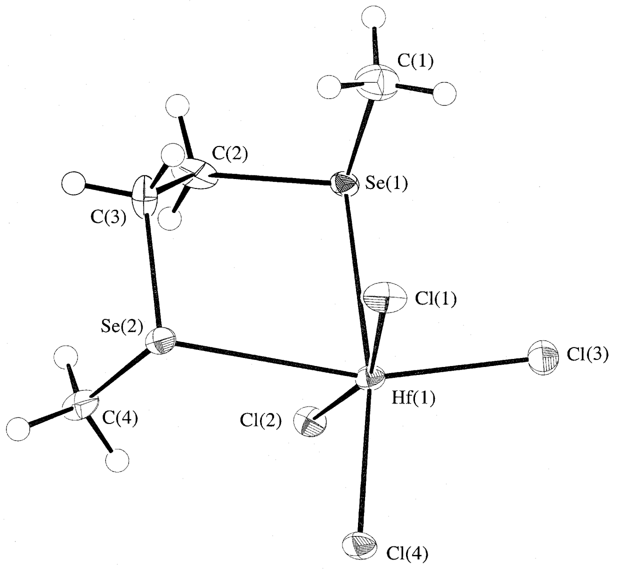

Fig. 3 View of the structure of [$HfCl_4\{MeSe(CH_2)_2SeMe\}$] with numbering scheme adopted. Ellipsoids are shown at the 40% probability level.

The 2 : 1 ligand : metal species [$MCl_4\{MeS(CH_2)_2SMe\}_2$] (M = Zr, Fig. 4, Table 4; M = Hf, Fig. 5, Table 5. Note that the crystal quality for the Hf complex was rather poor, hence the final structure determination is less reliable than for the Zr analogue.) show coordination through four Cl's and two chelating dithioether ligands, giving a flattened dodecahedral environment at M(IV). Both species show crystallographic

Table 3 Selected bond lengths (Å) and angles (°) for [$HfCl_4${MeSe-$(CH_2)_2$SeMe}]

Hf(1)–Se(1)	2.844(2)	Hf(1)–Cl(2)	2.397(5)
Hf(1)–Se(2)	2.848(2)	Hf(1)–Cl(3)	2.348(6)
Hf(1)–Cl(1)	2.396(6)	Hf(1)–Cl(4)	2.364(6)
Se(1)–Hf(1)–Se(2)	79.86(7)	Se(2)–Hf(1)–Cl(4)	91.6(2)
Se(1)–Hf(1)–Cl(1)	88.8(2)	Cl(1)–Hf(1)–Cl(2)	161.6(2)
Se(1)–Hf(1)–Cl(2)	78.4(2)	Cl(1)–Hf(1)–Cl(3)	95.3(2)
Se(1)–Hf(1)–Cl(3)	84.8(2)	Cl(1)–Hf(1)–Cl(4)	96.0(2)
Se(1)–Hf(1)–Cl(4)	169.2(2)	Cl(2)–Hf(1)–Cl(3)	96.7(2)
Se(2)–Hf(1)–Cl(1)	78.7(2)	Cl(2)–Hf(1)–Cl(4)	94.6(2)
Se(2)–Hf(1)–Cl(2)	86.0(2)	Cl(3)–Hf(1)–Cl(4)	104.3(2)
Se(2)–Hf(1)–Cl(3)	163.6(2)		

Table 4 Selected bond lengths (Å) and angles (°) for [$ZrCl_4${MeS-$(CH_2)_2$SMe}$_2$]

Zr(1)–Cl(1)	2.486(2)	Zr(1)–S(1)	2.853(2)
Zr(1)–Cl(2)	2.485(2)	Zr(1)–S(2)	2.828(2)
S(1)–Zr(1)–S(1)′	71.28(9)	Cl(1)–Zr(1)–S(1)′	73.83(7)
S(1)–Zr(1)–S(2)	133.03(7)	Cl(1)–Zr(1)–S(2)	142.92(7)
S(1)–Zr(1)–S(2)′	129.31(6)	Cl(1)–Zr(1)–S(2)′	71.81(6)
S(2)–Zr(1)–S(2)′	71.89(9)	Cl(2)–Zr(1)–Cl(2)′	145.31(10)
Cl(1)–Zr(1)–Cl(1)′	145.09(10)	Cl(2)–Zr(1)–S(1)	71.75(6)
Cl(1)–Zr(1)–Cl(2)	95.68(7)	Cl(2)–Zr(1)–S(1)′	142.91(7)
Cl(1)–Zr(1)–Cl(2)′	94.58(7)	Cl(2)–Zr(1)–S(2)	80.08(7)
Cl(1)–Zr(1)–S(1)	77.94(7)	Cl(2)–Zr(1)–S(2)′	71.92(7)

Table 5 Selected bond lengths (Å) and angles (°) for [$HfCl_4${MeS-$(CH_2)_2$SMe}$_2$]

Hf(1)–Cl(1)	2.470(6)	Hf(1)–S(1)	2.819(7)
Hf(1)–Cl(2)	2.473(6)	Hf(1)–S(2)	2.846(7)
Cl(1)–Hf(1)–Cl(1′)	145.8(3)	Cl(2)–Hf(1)–S(1)	143.3(2)
Cl(1)–Hf(1)–Cl(2)	94.0(2)	Cl(2)–Hf(1)–S(1′)	71.8(2)
Cl(1)–Hf(1)–Cl(2′)	96.2(2)	Cl(2)–Hf(1)–S(2)	73.5(2)
Cl(1)–Hf(1)–S(1)	71.7(2)	Cl(2)–Hf(1)–S(2′)	77.9(2)
Cl(1)–Hf(1)–S(1′)	80.8(2)	Cl(2′)–Hf(1)–S(1)	71.8(2)
Cl(1)–Hf(1)–S(2)	71.5(2)	Cl(2′)–Hf(1)–S(1′)	73.5(2)
Cl(1)–Hf(1)–S(2′)	142.7(2)	Cl(2′)–Hf(1)–S(2)	77.9(2)
Cl(1′)–Hf(1)–Cl(2)	96.2(2)	Cl(2′)–Hf(1)–S(2′)	71.8(2)
Cl(1′)–Hf(1)–Cl(2′)	94.0(2)	S(1)–Hf(1)–S(1′)	72.7(2)
Cl(1′)–Hf(1)–S(1)	80.8(2)	S(1)–Hf(1)–S(2)	128.6(2)
Cl(1′)–Hf(1)–S(1′)	71.7(2)	S(1)–Hf(1)–S(2′)	133.4(2)
Cl(1′)–Hf(1)–S(2)	142.7(2)	S(1′)–Hf(1)–S(2)	133.4(2)
Cl(1′)–Hf(1)–S(2′)	71.5(2)	S(1′)–Hf(1)–S(2′)	128.6(2)
Cl(2)–Hf(1)–Cl(2′)	144.6(3)	S(2)–Hf(1)–S(2′)	71.2(2)

2-fold symmetry. The coordinated dithioether ligands adopt the DL arrangement, with the Me substituents on a single dithioether lying on different sides of the ZrS_2 plane. The Zr–Cl distances of 2.486(2) and 2.485(2) Å are significantly longer (by *ca.* 0.1 Å) than in the 6-coordinate species described above. The Zr–S distances (2.853(2), 2.828(2) Å) are also *ca.* 0.1 Å longer. These differences are consistent with the increase in coordination number and the associated increase in steric crowding at the metal.

Given that both 6- and 8-coordination at Zr(IV) are achieved using certain bidentate thio- and seleno-ethers, the [9]aneS_3 complex was prepared to establish whether the ligand architecture would lead to unusual 7-coordination. The structure of [$ZrCl_4$([9]aneS_3)] (Fig. 6, Table 6) does indeed confirm this, showing the Zr(IV) centre coordinated to four terminal Cl's and to all three S atoms of the [9]aneS_3 ligand, giving a distorted seven-coordinate 4,3 geometry. The Zr–Cl bond distances lie in the range 2.398(10)–2.454(12) Å, while the Zr–S distances are substantially longer, in the range 2.706(13)–2.775(10) Å. The crystal obtained was very small and weakly diffracting, hence leading to higher than normal residuals and precluding detailed discussion or comparison of the geometric parameters. However, the average Zr–Cl bond distance (2.42 Å) is longer than

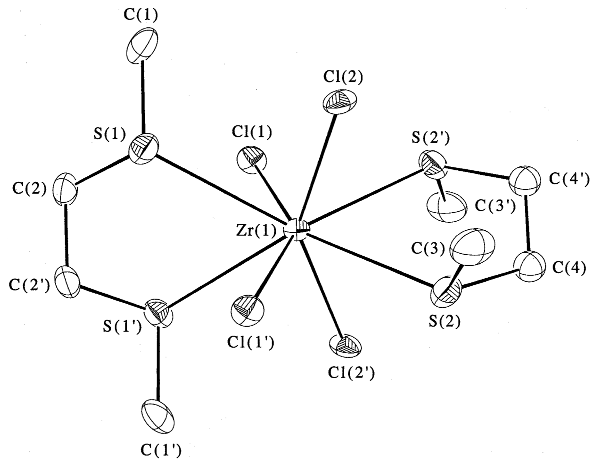

Fig. 4 View of the structure of [$ZrCl_4${MeS$(CH_2)_2$SMe}$_2$] with numbering scheme adopted. Ellipsoids are shown at the 40% probability level and H atoms are omitted for clarity.

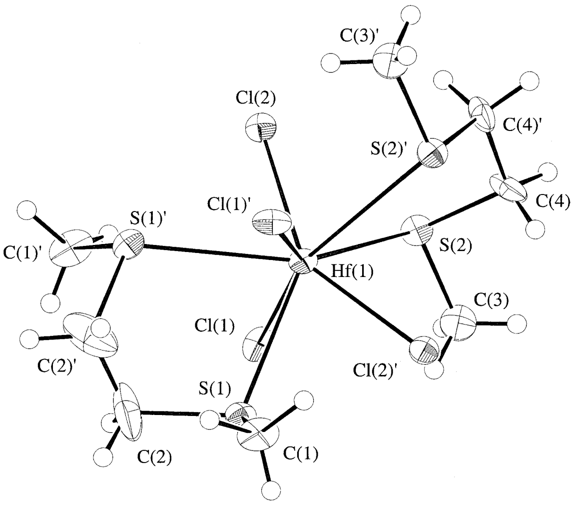

Fig. 5 View of the structure of [$HfCl_4${MeS$(CH_2)_2$SMe}$_2$] with numbering scheme adopted. Ellipsoids are shown at the 40% probability level.

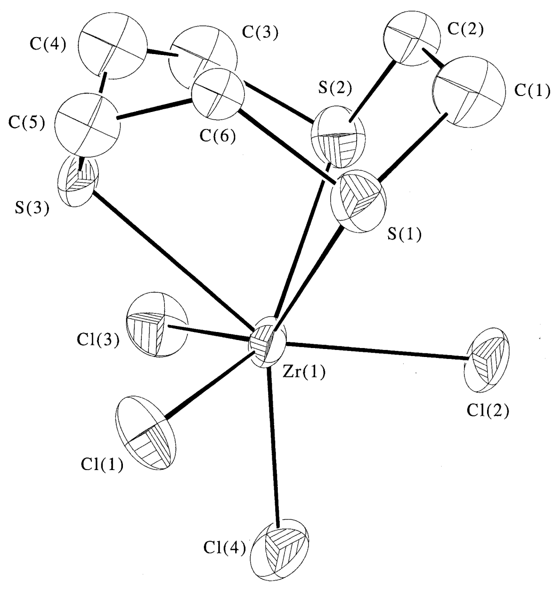

Fig. 6 View of the structure of [$ZrCl_4$([9]aneS_3)] with atom numbering scheme. 40% probability ellipsoids are drawn and H atoms are omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for $[ZrCl_4([9]aneS_3)]$

Zr(1)–Cl(1)	2.438(11)	Zr(1)–S(1)	2.775(10)
Zr(1)–Cl(2)	2.398(10)	Zr(1)–S(2)	2.706(13)
Zr(1)–Cl(3)	2.422(10)	Zr(1)–S(3)	2.754(11)
Zr(1)–Cl(4)	2.454(12)		
S(1)–Zr(1)–S(2)	73.9(4)	S(3)–Zr(1)–Cl(1)	73.8(4)
S(1)–Zr(1)–S(3)	74.6(3)	S(3)–Zr(1)–Cl(2)	142.0(4)
S(1)–Zr(1)–Cl(1)	75.3(4)	S(3)–Zr(1)–Cl(3)	74.3(3)
S(1)–Zr(1)–Cl(2)	75.1(3)	S(3)–Zr(1)–Cl(4)	136.0(4)
S(1)–Zr(1)–Cl(3)	142.5(4)	Cl(1)–Zr(1)–Cl(2)	119.2(4)
S(1)–Zr(1)–Cl(4)	133.5(4)	Cl(1)–Zr(1)–Cl(3)	114.9(4)
S(2)–Zr(1)–S(3)	73.4(4)	Cl(1)–Zr(1)–Cl(4)	81.8(4)
S(2)–Zr(1)–Cl(1)	139.7(4)	Cl(2)–Zr(1)–Cl(3)	121.0(4)
S(2)–Zr(1)–Cl(2)	76.5(4)	Cl(2)–Zr(1)–Cl(4)	82.0(4)
S(2)–Zr(1)–Cl(3)	77.5(4)	Cl(3)–Zr(1)–Cl(4)	84.0(4)
S(2)–Zr(1)–Cl(4)	138.4(4)		

Table 7 Selected bond length and angles for $[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$

Zr(1)–Cl(2)	2.358(3)	Zr(1)–Cl(6)	2.435(3)
Zr(1)–Cl(3)	2.577(3)	Cl(1)–C(3)	1.737(11)
Zr(1)–Cl(3)′	2.650(3)	S(1)–C(1)	1.791(11)
Zr(1)–Cl(4)	2.416(3)	S(1)–C(2)	1.763(10)
Zr(1)–Cl(5)	2.389(3)	S(1)–C(3)	1.775(11)
Cl(2)–Zr(1)–Cl(3)	94.30(10)	Cl(3)′–Zr(1)–Cl(5)	86.91(9)
Cl(2)–Zr(1)–Cl(3)′	172.77(10)	Cl(3)′–Zr(1)–Cl(6)	86.92(8)
Cl(2)–Zr(1)–Cl(4)	93.22(9)	Cl(4)–Zr(1)–Cl(5)	92.06(9)
Cl(2)–Zr(1)–Cl(5)	100.31(10)	Cl(4)–Zr(1)–Cl(6)	171.62(9)
Cl(2)–Zr(1)–Cl(6)	92.89(9)	Cl(5)–Zr(1)–Cl(6)	92.49(9)
Cl(3)–Zr(1)–Cl(3)′	78.47(9)	Zr(1)–Cl(3)–Zr(1)′	101.53(9)
Cl(3)–Zr(1)–Cl(4)	87.03(9)	C(1)–S(1)–Cl(2)	100.7(5)
Cl(3)–Zr(1)–Cl(5)	165.39(9)	C(1)–S(1)–C(3)	103.1(5)
Cl(3)–Zr(1)–Cl(6)	86.80(8)	C(2)–S(1)–C(3)	104.0(5)
Cl(30′–Zr(1)–Cl(4)	86.30(8)		

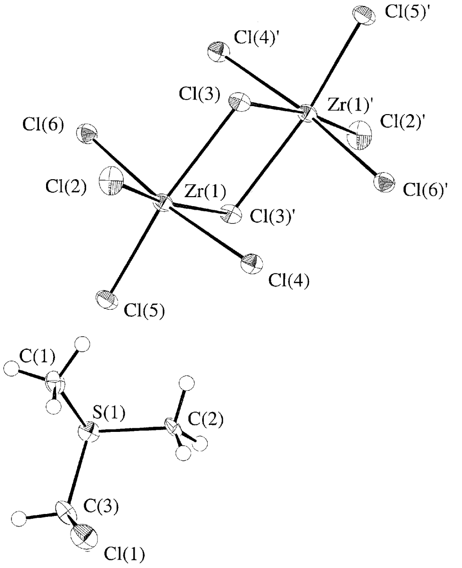

Fig. 7 View of the structures of the $[Me_2SCH_2Cl]^+$ cation and $[Zr_2Cl_{10}]^{2-}$ anion in $[MeSCH_2Cl]_2[Zr_2Cl_{10}]$ with numbering scheme adopted. Ellipsoids are shown at the 40% probability level.

that in $[(ZrCl_4)_2\{\mu\text{-}MeS(CH_2)_3SMe\}_2]$ (2.39 Å), probably reflecting the increased steric crowding at the metal in the 7-coordinate species.

During an attempt to grow crystals of $[ZrCl_4\{MeSe(CH_2)_2SeMe\}]$, solutions of $[ZrCl_4(Me_2S)_2]$ and $MeSe(CH_2)_2SeMe$ in CH_2Cl_2 were allow to diffuse together slowly. After several days, a few small colourless crystals appeared. The structure shows (Fig. 7, Table 7) that these have the composition $[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$, involving a pseudo-pyramidal sulfonium cation and a μ-dichloro Zr_2Cl_{10} dianion. The formation of a sulfonium cation does have a precedent in zirconium chemistry. Thus, reaction of $ZrCl_4$ with 1-*tert*-butyl-4,4-dimethyl-2-methylthio-3-trimethylsilyl-1,3,2,4-diazaphosphasiletidine in CH_2Cl_2 results in addition of methylene chloride forming the cationic 2-chloromethylthio derivative and $[Zr_2Cl_{10}]^{2-}$. The structure of this salt has been determined crystallographically.[25] The geometric parameters in $[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$ are also similar to those for the dizirconium anion in other salts, *e.g.* $[H^+1,3,5\text{-}(OMe)_3C_6H_3]_2[Zr_2Cl_{10}]$[26] and $[4\text{-}{}^tBuC_6H_4CH_2P(Ph)_2NHSiMe_3]_2[Zr_2Cl_{10}]$.[27]

Conclusions

These results demonstrate that Zr(IV) and Hf(IV) thio- and seleno-ether complexes with different coordination numbers may be obtained in high yield using the remarkably versatile synthetic method described. The specific ligand architecture is probably the major factor in controlling the coordination number. The first crystallographic studies on complexes in this family have been conducted. These have revealed the structural consequences of altering the coordination number at M(IV), revealing a correlation between the M–Cl stretching frequencies and the M–Cl bond lengths. They also allow comparisons between thio- and seleno-ether derivatives and zirconium and hafnium systems and have also established a *trans* influence of Cl > S on the hard M(IV) ions.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using a Perkin-Elmer 1710 spectrometer over the range 220–4000 cm^{-1}. ^1H NMR spectra were recorded in CD_2Cl_2 using a Bruker DPX400 spectrometer. UV-Vis spectra were recorded by diffuse reflectance using $BaSO_4$ as dilutant on a Perkin-Elmer Lambda19 spectrometer. Microanalyses were obtained from the University of Strathclyde Microanalytical Laboratory. $[ZrCl_4(Me_2S)_2]$, $[HfCl_4(Me_2S)_2]$ and the dithioether and diselenoether ligands were prepared by the literature methods,[28–31] while $[9]aneS_3$ was purchased from Aldrich. Standard Schlenk techniques and rigorously anhydrous solvents were used for all preparations and manipulations.

Synthesis

$[ZrCl_4\{MeS(CH_2)_2SMe\}]$. To a stirring solution of $[ZrCl_4(Me_2S)_2]$ (200 mg, 0.56 mmol) in dry, degassed CH_2Cl_2 (40 cm^3) was added 1.1 molar equivalents $MeS(CH_2)_2SMe$ (76 mg, 0.62 mmol) in CH_2Cl_2 (10 cm^3) at room temperature. The solution was reduced by half *in vacuo*, stirred for 24 hours and concentrated further to afford a white solid that was filtered off, washed with CH_2Cl_2 and dried *in vacuo*. Yield 0.12 g, 61%. Required for $[C_4H_{10}Cl_4S_2Zr]$: C, 13.5; H, 2.8%. Found: C, 13.5; H, 2.9%. IR (Nujol): ν(Zr–Cl) 363 br s cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 32.0 br, 39.4.

$[ZrCl_4\{MeS(CH_2)_3SMe\}]$. Prepared using the same method as above, with $MeS(CH_2)_3SMe$ (84 mg, 0.62 mmol), to afford a white solid. Yield 0.14 g, 68%. Required for $[C_5H_{12}Cl_4S_2Zr]$: C, 16.3; H, 3.3%. Found: C, 15.9; H, 3.3%. IR (Nujol): ν(Zr–Cl) 363 br s cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 31.2 br, 39.0.

$[ZrCl_4\{MeSe(CH_2)_2SeMe\}]$. Prepared using the same method as above, with $MeSe(CH_2)_2SeMe$ (134 mg, 0.62 mmol), to afford a white solid. Yield 0.15 g, 58%. Required for $[C_4H_{10}Cl_4Se_2Zr]$: C, 10.7; H, 2.2%. Found: C, 11.0; H, 2.5%. IR (Nujol): ν(Zr–Cl) 364 br s cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 30.1 br, 37.7.

$[ZrCl_4\{MeSe(CH_2)_3SeMe\}]$. Prepared using the same method as above, with $MeS(CH_2)_3SMe$ (143 mg, 0.62 mmol), to afford a white solid. Yield 0.12 g, 46%. Required for $[C_5H_{12}Cl_4Se_2Zr]$: C, 13.0; H, 2.6%. Found: C, 12.7; H, 2.8%. IR (Nujol):

Table 8 Crystallographic data

	$[ZrCl_4(Me_2S)_2]$	$[(ZrCl_4)_2\{MeS(CH_2)_3SMe\}_2]$	$[HfCl_4\{MeSe(CH_2)_2SeMe\}]$	$[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$	$[HfCl_4\{MeS(CH_2)_2SMe\}_2]$	$[ZrCl_4([9]aneS_3)]$	$[Me_2SCH_2Cl]_2[Zr_2Cl_{10}]$
Formula	$C_4H_{12}Cl_4S_2Zr$	$C_{10}H_{24}Cl_8S_4Zr_2$	$C_4H_{10}Cl_4HfSe_2$	$C_8H_{20}Cl_4S_4Zr$	$C_8H_{20}Cl_4HfS_4$	$C_6H_{12}Cl_4S_3Zr$	$C_6H_{16}Cl_{12}S_2Zr_2$
M	357.29	738.60	536.34	477.52	564.79	413.37	760.20
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group	Cc	$Pbca$	$P2_1$	$P4_12_12$	$P4_32_12$	$P2_1/c$	$P2_1/n$
a/Å	6.4219(2)	15.8646(2)	7.4864(2)	9.9696(3)	9.9760(2)	11.5442(10)	9.2646(3)
b/Å	25.7274(8)	15.4382(2)	11.5652(4)	9.9696	9.9760	8.4604(7)	14.5290(5)
c/Å	8.3971(3)	21.6118(4)	8.1257(2)	17.5265(4)	17.4881(4)	13.9222(13)	9.3074(4)
β/°	106.9505(11)	90	116.501(2)	90	90	98.270(4)	91.9700(11)
U/Å^3	1327.09(7)	5293.18(12)	629.61(3)	1742.02(7)	1740.43(6)	1345.6(2)	1252.09(7)
Z	4	8	2	4	4	4	2
μ(Mo-Kα)/cm^{-1}	18.97	19.06	148.47	17.01	70.54	20.36	22.69
Unique obs. Reflns.	1376	5961	1359	1111	1112	3973	2659
Obs. reflections with $[I > 3\sigma(I)]$	1308	3205	1281	867	898	725	1349
R	0.043	0.042	0.056	0.041	0.080	0.098	0.053
Rw	0.063	0.049	0.068	0.053	0.109	0.116	0.061

ν(Zr–Cl) 366 br s cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 31.0 br, 37.0.

$[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$. Prepared using the same method as above, with $[ZrCl_4(Me_2S)_2]$ (100 mg, 0.28 mmol) and $MeS(CH_2)_2SMe$ (103 mg, 0.84 mmol), to afford a white solid. Yield 0.10 g, 72%. Required for $[C_8H_{20}Cl_4S_4Zr]$: C, 20.1; H, 4.2%. Found: C, 20.4; H, 4.0%. IR (Nujol): ν(Zr–Cl): 307, 301 cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 33.0 sh, 37.2.

$[ZrCl_4\{MeSe(CH_2)_2SeMe\}_2]$. Prepared using the same method as above, with $MeSe(CH_2)_2SeMe$ (181 mg, 0.84 mmol), to afford a white solid. Yield 0.13 g, 68%. Required for $[C_8H_{20}Cl_4Se_4Zr]$: C, 14.5; H, 3.0%. Found: C, 14.8; H, 2.8%. IR (Nujol) ν(Zr–Cl): 305, 299 cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 32.0 sh, 36.6.

$[ZrCl_4([9]aneS_3)]$. As above, but using $[9]aneS_3$. White solid. Yield 0.19 g, 82%. Required for $[C_6H_{12}Cl_4S_3Zr]$: C, 17.4; H, 2.9%. Found: C, 17.1; H, 3.3%. IR (Nujol): ν(Zr–Cl) 332 br s cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 32.0 sh, 37.2.

$[HfCl_4\{MeS(CH_2)_2SMe\}]$. As for $[ZrCl_4\{MeS(CH_2)_2SMe\}]$, but using $[HfCl_4(Me_2S)_2]$ (250 mg, 0.56 mmol) and $MeS(CH_2)_2SMe$ (76 mg, 0.62 mmol). The reaction was stirred for 48 hours. White solid. Yield 0.14 g, 55%. Required for $[C_4H_{10}Cl_4HfS_2]$: C, 10.9; H, 2.3%. Found: C, 11.1; H, 2.5%. IR (Nujol) ν(Hf–Cl): 329 br cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 35.0 br, 40.8.

$[HfCl_4\{MeSe(CH_2)_2SeMe\}]$. As above, but using $MeSe(CH_2)_2SeMe$ (134 mg, 0.62 mmol). White solid. Yield 0.14 g, 47%. Required for $[C_4H_{10}Cl_4HfSe_2]$: C, 9.0; H, 1.9%. Found: C, 9.2; H, 2.0%. IR (Nujol): ν(Hf–Cl) 329 br cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 34.5 br, 39.0.

$[HfCl_4\{MeS(CH_2)_2SMe\}_2]$. As above, but using $[HfCl_4(Me_2S)_2]$ (125 mg, 0.28 mmol) and $MeS(CH_2)_2SMe$ (103 mg, 0.84 mmol). White solid. Yield 0.09 g, 58%. Required for $[C_8H_{20}Cl_4HfS_4]$: C, 17.0; H, 3.6%. Found: C, 16.7; H, 3.4%. IR (Nujol): ν(Hf–Cl) 283, 279 cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 35.0 sh, 38.5.

$[HfCl_4\{MeSe(CH_2)_2SeMe\}_2]$. As above, but using $MeSe(CH_2)_2SeMe$ (181 mg, 0.84 mmol). White solid. Yield 0.11 g, 52%. Required for $[C_8H_{20}Cl_4HfSe_4]$: C, 12.8; H, 2.7%. Found: C, 12.6; H, 2.5%. IR (Nujol): ν(Hf–Cl) 280, 273 cm^{-1}. UV/Vis spectrum ($\nu_{max} \times 10^3$ cm^{-1}): 34.0 sh, 38.0.

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 8. Data collection used an Enraf-Nonius Kappa CCD diffractometer (T = 150 K) with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å). Structure solution and refinement were generally straightforward.[32–34] The data for $[MCl_4\{MeS(CH_2)_2SMe\}_2]$ showed systematic absences consistent with the enantiomorphic tetragonal space groups $P4_12_12$ (no. 92) and $P4_32_12$ (no. 96). For the Hf species the Flack parameter[35] clearly supported assignment of the space group as $P4_32_12$. However, for the Zr complex we were unable to establish the correct enantiomorph as the Flack parameter could not be determined. In this case the structure was refined in space group $P4_12_12$. Also, $[ZrCl_4\{MeS(CH_2)_2SMe\}_2]$ showed some disorder in the CH_2CH_2 unit linking the S atoms in one of the dithioethers. This was modelled satisfactorily using split occupancies for some C atoms giving a major (67%) and a minor (33%) component. Although this would suggest disorder of the methyl carbons on this ligand too, these could not be split convincingly and therefore the disorder was modelled by allowing higher than usual anisotropic thermal parameters for the methyl carbons. Selected bond lengths and angles are presented in Tables 1–7.

CCDC reference numbers 164532–164534 and 179859–179862.

See http://www.rsc.org/suppdata/dt/b2/b201080c/ for crystallographic data in CIF or other electronic format.

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