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Tantalum(V) fluoride complexes of thio- and seleno-ether ligands and a comparison with the TaX_5 (X = Cl or Br) analogues

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ABSTRACT

Reaction of TaF_5 with SMe_2 and $RS(CH_2)_2SR$ (R = Me, Et or ^{i}Pr) in anhydrous CH_2Cl_2 solution produce colourless, extremely moisture sensitive crystals of $[TaF_4(SMe_2)_4][TaF_6]$ and $[TaF_4\{RS(CH_2)_2SR\}_2][TaF_6]$ respectively, which contain eight-coordinate cations and octahedral anions, whereas TaF_5 reacts with neat SR_2 (R = Me or Et) to form six-coordinate $[TaF_5(SR_2)]$. Very unstable $[TaF_5(SeMe_2)]$ and $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ were isolated with the selenoether ligands and also contain six-coordinate tantalum species. Selected complexes of $TaCl_5$ and $TaBr_5$ have been prepared for comparison. The complexes have been characterised by IR, UV/visible and ^1H and $^{19}F\{^1H\}$ NMR spectroscopies, and X-ray crystal structures are reported for $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$, $[(TaCl_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ and $[TaCl_5(SeMe_2)]$.

1. Introduction

The chemistry of hard, early transition metal halides and oxide-halides in the group oxidation state, with soft, neutral donor ligands such as phosphines, arsines, thio- or seleno-ethers is often very different to that found with hard O- or N-donor ligands [1]. We have reported soft donor complexes with TiX_4 (X = Cl, Br, sometimes I) [2,3], ZrX_4 and HfX_4 [4,5], WO_2X_2 and MoO_2X_2 (X = Cl, Br) [6,7], and $VOCl_3$ and VO_2Cl [8,9]. The hard/soft mis-match is greatest with the (very little studied) metal fluorides, and in these systems, including VOF_3 [10], VO_2F [9], TiF_4 [11] and WF_6 [12], fluorination of the donor heteroatom and/or of the hydrocarbon substituents may also occur, in addition to simple adduct formation. Detailed studies of the reactions of thio-, seleno- and telluro-ether ligands with NbF_5 and some comparable data for NbX_5 (X = Cl or Br) analogues have been described [13]. In the NbF_5 systems we also obtained the unexpected protonated thioether (sulfonium) cations $[LH][NbF_6]$ (L = *o*-$C_6H_4(CH_2SMe)_2$, [9]aneS_3); structurally characterised sulfonium ions are very rare and they are stabilized here by the large, very weakly coordinating hexafluoroanion [14].

Here we report our studies of TaF_5-chalcogenoether reactions. The only previous data on the TaF_5-thioether systems is of $[TaF_5(SR_2)]$ (R = Me or Et) and $[TaF_5(tht)_2]$ (tht = tetrahydrothiophen), identified only by a combination of microanalysis and vapour pressure data [15]. Chalcogenoether complexes of the heavier TaX_5 (X = Cl, Br) have long been known [1,6–21], but spectroscopic data are incomplete and we have re-examined a small number of examples to provide comparable data to the fluorides. Detailed studies of the reactions of TaX_5 (X = F, Cl or Br) with a variety of oxygen donor ligands including acyclic and cyclic ethers, have been described recently, the reactions including simple adduct formation, C–O bond cleavage and polymerisation of the ligands [22–27].

2. Results and discussion

2.1. $[TaF_5(ER_2)]$ and $[TaF_4(ER_2)_4][TaF_6]$ (ER_2 = SMe_2, SEt_2, $SeMe_2$)

The TaF_5 complexes are extremely moisture sensitive both in the solid state and in solution, and decomposition is instantaneous on exposure to moist air. The solid $[TaF_5(SR_2)]$ complexes decompose slowly at ambient temperatures, but can be stored for some weeks in a freezer. In this work all measurements were made on freshly prepared materials. $[TaF_5(SR_2)]$ (R = Me or Et) were made (Scheme 1) by distilling a large excess of SR_2 onto finely powdered TaF_5 at 77 K, and allowing the mixture to warm slowly to room temperature. On melting of the SR_2, the TaF_5 dissolved to give a clear, colourless solution, from which subsequent removal of the excess thioether *in vacuo*, gave $[TaF_5(SR_2)]$ as a white powder (R = Me), or a colourless oil which solidified in an ice bath (R = Et). The report [15] of the latter as a red oil is in error, although decomposed samples appear pink. The reaction of TaF_5 with $SeMe_2$ in anhydrous CH_2Cl_2 solution, gave a yellow solid, identified spectroscopically as $[TaF_5(SeMe_2)]$, which could be kept in a freezer for a few days, but decomposed at room temperature in a few hours, turning brown and then black.

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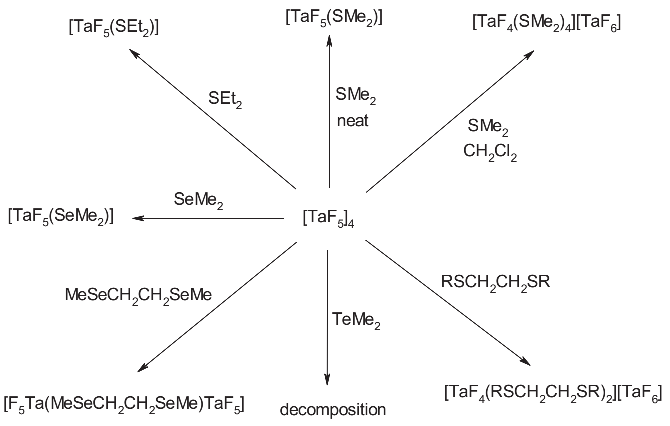

Scheme 1. Reactions of $[TaF_5]_4$ (TaF_5 is tetranuclear in the solid state, with single F bridges, for simplicity it is formulated as a monomer in the text).

The IR spectra of these $[TaF_5(ER_2)]$ complexes show several overlapping, broad Ta–F stretching modes ~600 cm^{-1} (theory $C_{4v} = 2a_1 + e$). The solid state (diffuse reflectance) UV/visible spectra show two broad features at ~27,000 and ~42,000 cm^{-1} (E = S) and ~25,500 and ~40,000 cm^{-1} (E = Se). The lower energy feature in each is clearly the ligand to metal charge transfer transition, $S/Se(\pi) \rightarrow Ta(t_{2g})$,[1] but there are various potential charge transfer assignments for the higher energy band, including $S/Se(\pi) \rightarrow Ta(e_g)$, $S/Se(\sigma) \rightarrow Ta(t_{2g})$ and $F(\pi) \rightarrow Ta(t_{2g})$. The $F(\pi) \rightarrow Ta(t_{2g})$ transitions are expected to be in the far-UV region [28] and may be discounted. A $S/Se(\pi) \rightarrow Ta(e_g)$ assignment leads to a ligand field splitting of ~15,000 cm^{-1}, which is too small for a 5 d element [29], and thus we assign the second feature to $S/Se(\sigma) \rightarrow Ta(t_{2g})$. Variable temperature ^{1}H and $^{19}F\{^1H\}$ NMR measurements were undertaken to explore the solution speciation; again great care is needed to exclude moisture which readily causes hydrolysis to $[TaF_6]^-$, $\delta^{19}F = +39.5$. In contrast to our previous study of the niobium systems [13], where ^{93}Nb NMR spectroscopy was very useful, the very large quadrupole moment, $Q \sim 3 \times 10^{-28}$ m^2 of ^{181}Ta ($I = 7/2$, 99.9%) [30] and the resulting fast relaxation, makes the ^{181}Ta resonances unobservably broad, and also eliminates observation of any spin–spin couplings. We note that $^2J_{FF}$ involving the terminal fluorines in $[Ta_2F_{11}]^-$ are ~30 Hz and only resolved at low temperatures [31], and their absence in the present spectra from compounds which are likely to have a greater electric field gradient is not unexpected. The ^{1}H NMR spectra in CD_2Cl_2 solution (Section 4) are singlets (R = Me) at room temperature and drift to higher frequency on cooling the solutions to 195 K, as dissociative exchange decreases. The $^{19}F\{^1H\}$ NMR spectra show single, very broad features at 295 K in the region $\delta = +85$ to +75, but on cooling these resonances move to lower frequency, and at 185 K two sharp singlets with integrals 1:4, are observed, consistent with square pyramidal TaF_5 units. The $[TaF_5(SeMe_2)]$ does not exhibit a ^{77}Se resonance at 295 K, but on cooling to 195 K a sharp resonance is seen at $\delta = 158$, which compares with that [13] in $[NbF_5(SeMe_2)]$ of $\delta = 247$, showing the usual trends in coordination chemical shifts between 4 d and 5 d analogues [2–5].

In contrast to the formation of $[TaF_5(SMe_2)]$ using SMe_2 as both reagent and solvent, a mixture of TaF_5 and SMe_2 in 1:≥3 molar ratio in anhydrous CH_2Cl_2, deposited very small colourless crystals of $[TaF_4(SMe_2)_4][TaF_6]$ upon refrigerating for several days. The crystals become opaque and soften at ambient temperatures with loss of SMe_2. After pumping *in vacuo* at ambient temperatures for some hours the composition approximates to $Ta_2F_{10}(SMe_2)$ (found: C, 3.7; H, 1.1. Calc. for $C_2H_6F_{10}STa_2$ C, 3.9; H, 1.0%). X-ray crystallographic data were collected from small, weakly diffracting crystals, which showed them to be isomorphous with $[NbF_4(SMe_2)_4][NbF_6]$ [13] (formula: $C_8H_{24}F_{10}S_4Ta_2$, RMM = 800.41, tetragonal cell: $a = b = 12.269(3)$ Å, $c = 13.913(4)$ Å, vol = 2094.3(8) Å^3, space group = P4/ncc (130), $Z = 4$, $T = 100$ K, $R_1 = 0.097$]. The model showed the expected $[TaF_6]^-$ anions and $[TaF_4(SMe_2)_4]^+$ cations, with some disorder evident in the latter which prevented satisfactory refinement, although the identity of the complex is not in doubt.

The IR spectrum of $[TaF_4(SMe_2)_4][TaF_6]$ shows a very strong feature at 606 cm^{-1} and strong sharper band at 576 cm^{-1} assigned respectively to the Ta–F vibrations in the eight-coordinate cation and six-coordinate anion respectively [32]. In solution in anhydrous CD_2Cl_2 the $^{19}F\{^1H\}$ NMR spectrum at 295 K is a broad singlet $\delta \sim +71$, but on cooling below 240 K, the resonance shifts to low frequency and then splits, and at 185 K shows two sharp singlets at 59.8 [4F] and 39.1 [6F], assigned to cation and anion respectively. The changes in the ^{19}F NMR spectrum are reversible on warming.

We also recorded $^{19}F\{^1H\}$ NMR spectra from mixtures of TaF_5 and ER_2 in CD_2Cl_2 with TaF_5:ER_2 mol. ratios from 3:1 to 1:5. All showed very broad single resonances at ambient temperatures, consistent with a mixture of rapidly exchanging species, but at 195 K those with the high TaF_5 content showed $[TaF_5(ER_2)]$ and $[Ta_2F_{11}]^-$ ($\delta = +115$, +71, and −81) [31] as major components, whilst for those containing excess SMe_2, $[TaF_4(SMe_2)_4][TaF_6]$ was the only significant tantalum species. The $^{19}F\{^1H\}$ NMR spectra of a mixture of TaF_5 and a large excess of SEt_2 in CD_2Cl_2 at 185 K showed two sharp resonances at $\delta = +68.8$ and +39.0 assigned to $[TaF_4(SEt_2)_4]^+$ and $[TaF_6]^-$ respectively, which broadened and merged into one peak above ~220 K; however this species only seems to exist in solution at low temperatures, as $[TaF_5(SEt_2)]$ (above) was isolated on removing the solvent. Similarly, at 195 K a CD_2Cl_2 solution of $[TaF_5(SeMe_2)]$ containing excess $SeMe_2$ shows $^{19}F\{^1H\}$ resonances at $\delta = +54.0$, +38.6 attributed to $[TaF_4(SeMe_2)_4][TaF_6]$ and ^{77}Se resonances at +156 and +6 due to the cation and "free" $SeMe_2$ respectively (the ^{77}Se chemical shift of $SeMe_2$ is solvent and temperature sensitive [33]). The resonances coalesce at ~200 K, and the solution decomposes very rapidly at room temperature, turning dark green. The deep colour suggests a lower oxidation state of Ta, and the $^{19}F\{^1H\}$ NMR spectrum of the decomposed solution shows $[TaF_6]^-$, $[Ta_2F_{11}]^-$, Me_2SeF_2 [34] and other unidentified species. In the corresponding NbF_5/ER_2 systems [13] we did not observe 1:2 complexes with SEt_2 or $SeMe_2$.

2.2. $[TaF_4\{RS(CH_2)_2SR\}_2][TaF_6]$ (R = Me, Et, ^{i}Pr)

The reaction of TaF_5 with the dithioethers $RS(CH_2)_2SR$ (R = Me, Et, ^{i}Pr) in a 1:2 mol. ratio in rigorously anhydrous CH_2Cl_2, results in precipitation of $[TaF_4\{RS(CH_2)_2SR\}_2][TaF_6]$ as white powders, which can be kept in sealed tubes in the freezer for some days, but decompose slowly at ambient temperature. From the filtrate or by refrigeration of more dilute solutions of $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$, colourless, extremely moisture sensitive crystals were obtained. Both $[TaF_4\{RS(CH_2)_2SR\}_2][TaF_6]$ (R = Et or ^{i}Pr) are more soluble than the dithiahexane complex and on refrigeration of CH_2Cl_2 solutions give extremely small crystals which redissolve very easily on warming and proved too weakly diffracting to obtain X-ray structural data. The X-ray structure of $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$ shows (Fig. 1 and Table 1) eight-coordinate (distorted dodecahedral) cations and octahedral anions. The cations contain interpenetrating flattened TaF_4 and elongated TaS_4 tetrahedra. The unit cell contains two different cations, both contain the dithioethers in the *DL* form, but Ta1 has the stereochemistry as S1–S4 as *SSRR*, while in Ta2 it is *SSSS*, most

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[1] Although the symmetry is C_{4v} rather than O_h, resolved splittings of the bands were not observed, hence the t_{2g}/e_g labels are retained.

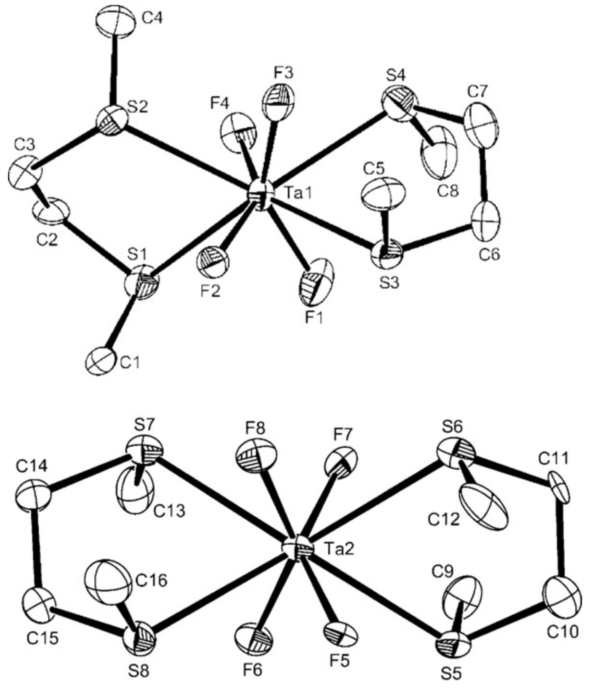


Fig. 1. The structures of the Ta1 and Ta2 centred cations in $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$ with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity.

clearly seen in the views presented in Fig. 2. The Ta–F and Ta–S bond lengths are essentially identical to those in the corresponding niobium complex [13], with S–Ta–S angles of ~75° within the chelate rings.

The ^1H NMR spectra of all three complexes show the resonances of the dithioethers, shifted to high frequency from the values in the parent ligands as expected, but even at 190 K there was no evidence of splitting due to the invertomers, suggesting pyramidal inversion and/or reversible dissociation is still fast on the NMR time-scale. The $^{19}F\{^1H\}$ NMR spectra from anhydrous CD_2Cl_2 solutions exhibit a single broad feature from each complex at 295 K, but on cooling these split and sharpen, and below ~240 K show a sharp resonance at $\delta = +39$ [6F] due to $[TaF_6]^-$ and a second sharp resonance at higher frequency [4F] with chemical shifts varying with the dithioether, attributed to the dodecahedral cations, $[TaF_4\{RS(CH_2)_2SR\}_2]^+$. The spectral features are reversible with temperature, although on allowing the solutions to stand at ambient temperatures for a few hours, new resonances develop, suggesting some fluorination of the dithioether and of the solvent. The IR and UV/visible spectra of the dithioether complexes are consistent with the formulations and are readily assigned by analogy with those of $[TaF_4(SMe_2)_4][TaF_6]$ discussed above.

Table 1
Selected bond lengths (Å) and angles (°) for $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$.

Ta1–F1	1.875(9	Ta1–F2	1.894(7)
Ta1–F3	1.881(9)	Ta1–F4	1.910(8)
Ta2–F7	1.893(8)	Ta2–F5	1.909(8)
Ta2–F6	1.916(7)	Ta2–F8	1.911(6)
Ta1–S1	2.712(4)	Ta1–S2	2.686(3)
Ta1–S3	2.713(4)	Ta1–S4	2.720(4
Ta2–S5	2.721(3)	Ta2–S6	2.715(3)
Ta2–S7	2.713(4)	Ta2–S8	2.698(3)
Ta3–F	1.829(11)–1.894(9)	Ta4–F	1.865(9)–1.902(7)
F1–Ta1–F3	143.1(4)	F2–Ta1–F4	145.1(3)
S2–Ta1–S1	74.50(10)	S3–Ta1–S4	75.22(11)
F7–Ta2–F5	143.9(3)	F8–Ta2–F6	144.2(3)
S8–Ta2–S7	75.30(10)	S6–Ta2–S5	75.16(10)

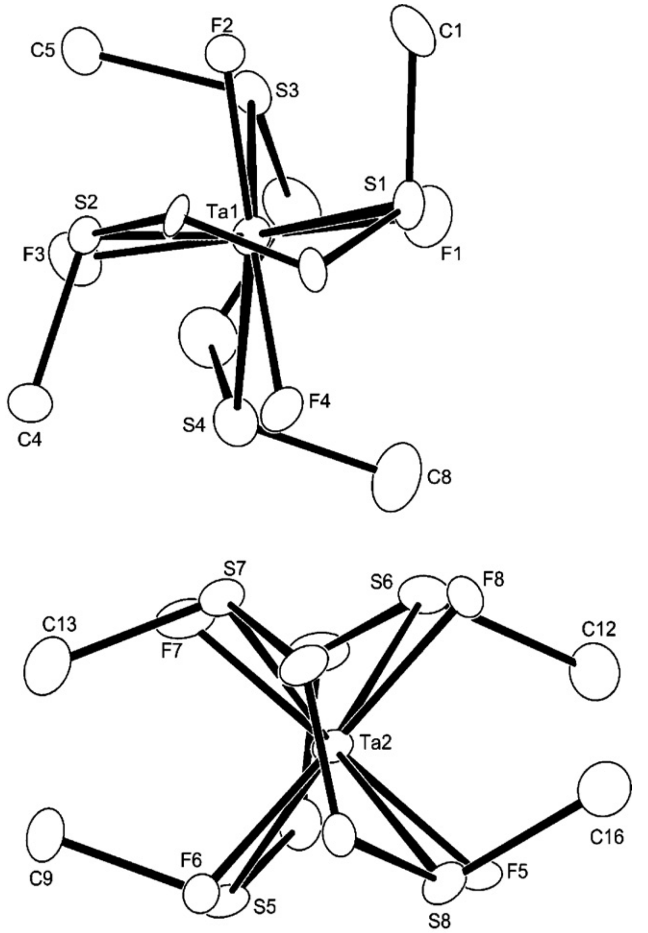


Fig. 2. The Ta1 and Ta2 centred cations in $[TaF_4\{MeS(CH_2)_2SMe\}_2][TaF_6]$, viewed down the pseudo S_4 axis of the approximately D_{2d} F_4S_4Ta eight-coordinate unit. Boundary ellipsoids are drawn at the 30% probability level, H atoms are omitted for clarity and the methylene C atoms are unlabelled.

2.3. $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$

The reaction of TaF_5 and $MeSe(CH_2)_2SeMe$ in anhydrous CH_2Cl_2 in a 2:1 mol. ratio, followed by rapid workup, gave $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ as an unstable pale orange-yellow solid. This was formulated as a ligand bridged dimer (*cf.* $[(TaCl_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ below). The IR and UV/visible spectra resemble those of $[TaF_5(SeMe_2)]$ as would be expected. However, in solution even at 190 K, there is still only a single broad $^{19}F\{^1H\}$ NMR resonance, rather than the expected two singlets due to a static TaF_5 square pyramid, indicating dynamic processes are still present. The complex exhibits a ^{77}Se NMR resonance at 185 K, $\delta = 202$, but the signal is lost on warming. There was no evidence for a dodecahedral cation $[TaF_4\{MeSe(CH_2)_2SeMe)_2]^+$, contrasting with the dithioether systems. Indeed addition of $MeSe(CH_2)_2SeMe$ to a CH_2Cl_2 solution of $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ at ambient temperatures produced very rapid darkening to brown and then black products, consistent with oxidative fluorination of the diselenoether. Treatment of a suspension of TaF_5 in CH_2Cl_2 with the telluroether ligands $TeMe_2$ or $o\text{-}C_6H_4(TeMe)_2$ immediately produced brown-black tars which were not studied further.

2.4. $[TaX_5(ER_2)]$ (X = Cl or Br, E = S or Se)

These (known) complexes [16–21] were re-prepared (Scheme 2) to obtain spectroscopic data for comparison with

Table 2
Selected bond lengths (Å) and angles (°) for $[TaCl_5(Me_2Se)]$.

Ta–Cl1	2.2881(13)	Ta1–Cl3	2.3149(12)
Ta1–Cl2	2.3160(9)	Ta1–Cl4	2.3274(14)
Ta1–Se1	2.7992(8)		
Cl1–Ta1–Cl3	95.46(5)	Cl1–Ta1–Cl2	96.70(2)
Cl3–Ta1–Cl2	90.34(4)	Cl1–Ta1–Cl4	96.22(5)
Cl2–Ta1–Cl4	88.30(4)	Cl3–Ta1–Se1	84.07(3)
Cl2–Ta1–Se1	83.31(2)	Cl4–Ta1–Se1	84.25(4)

Table 3
Selected bond lengths (Å) and angles (°) for $[(TaCl_5)_2\{MeSe(CH_2)_2SeMe\}]$.

Ta1–Cl5	2.2750(9)	Ta1–Cl4	2.3165(8)
Ta1–Cl1	2.3210(9)	Ta1–Cl3	2.3277(9)
Ta1–Cl2	2.3339(8)	Ta1–Se1	2.8030(5)
Cl5–Ta1–Cl4	97.72(3)	Cl5–Ta1–Cl1	95.96(3)
Cl4–Ta1–Cl1	89.37(3)	Cl5–Ta1–Cl3	97.66(3)
Cl4–Ta1–Cl3	88.61(3)	Cl5–Ta1–Cl2	96.36(3)
Cl1–Ta1–Cl2	89.79(3)	Cl3–Ta1–Cl2	88.90(3)
Cl4–Ta1–Se1	85.94(2)	Cl1–Ta1–Se1	81.34(3)
Cl3–Ta1–Se1	85.08(2)	Cl2–Ta1–Se1	80.02(2)

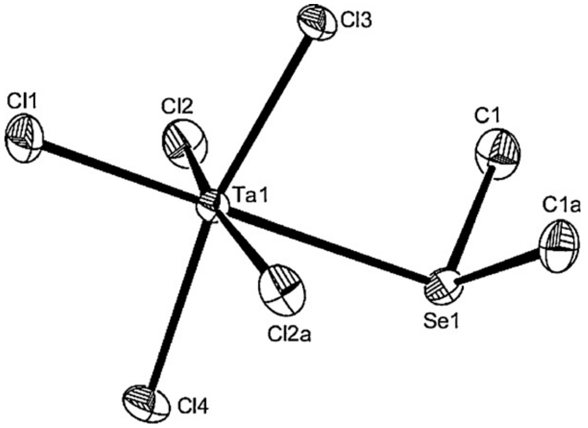


Fig. 3. The structure of $[TaCl_5(SeMe_2)]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level. Symmetry operation a = −*x*, *y*, *z*.

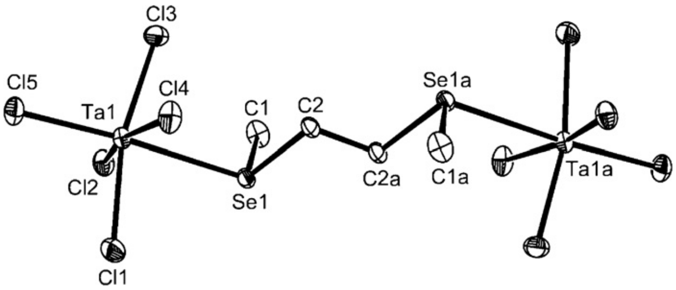
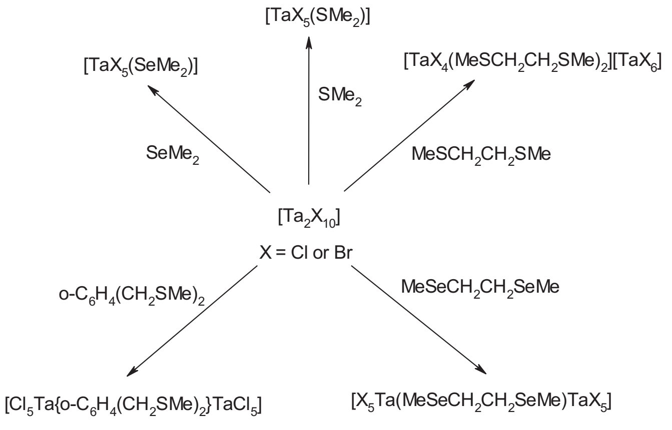


Fig. 4. The structure of $[(TaCl_5)_2\{MeSe(CH_2)_2SeMe\}]$ showing the atom labelling scheme. Ellipsoids are drawn at the 50% probability level. Symmetry operation: a = 1 − *x*, 2 − *y*, 2 − *z*.

those of the fluoride complexes. They are yellow or orange moisture sensitive solids, although considerably less sensitive than the fluorides, and indefinitely stable under anhydrous conditions. The ^{1}H NMR spectra are consistent with previous reports [35,36] and in contrast to the fluorides, there is no evidence for complexes with a coordination number greater than six at tantalum. The solid state UV/visible spectra show intense $X(\pi) \rightarrow Ta(t_{2g})$ [15,29] and weaker $E(\pi) \rightarrow Ta(t_{2g})$, the latter at rather lower energy than in the fluoride analogues as expected, since strong $F(\pi) \rightarrow Ta(t_{2g})$ donation raises the energy of the metal t_{2g} set. Yellow crystals of $[TaCl_5(SeMe_2)]$ were obtained and the structure (Fig. 3 and Table 2) shows the expected pseudo-octahedral geometry with ⟨Cl–Ta–Cl rather wider than ⟨Se–Ta–Cl. The crystals are isomorphous with $[NbCl_5(SeMe_2)]$ [13] and comparisons of corresponding bond lengths show slightly shorter Ta–Cl and Ta–Se compared to the niobium analogues, indicative of the slightly smaller covalent radius of the 5 d element. This conflicts with the data discussed above for the $[MF_4\{MeS(CH_2)_2SMe\}_2][MF_6]$, where essentially identical bond lengths were found for the two complexes.

2.5. $[TaX_4\{MeS(CH_2)_2SMe\}_2][TaX_6]$ (X = Cl or Br), $[(TaX_5)_2(\mu\text{-}MeSe(CH_2)_2SeMe)]$ and $[(TaX_5)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2SMe)_2\}]$

In marked contrast to the fluoride complexes described above, bidentate dithioether ligands mostly form ligand bridged $[(TaX_5)_2\{\mu\text{-}RS(CH_2)_2SR\}]$ or $[(TaX_5)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2SMe)_2\}]$ complexes with six-coordinate metal centres, and representative examples are described in the Section 4 with their spectroscopic data. 2,5-Diselenahexane forms only $[(TaX_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$, similar to the $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ described above, although the complexes with the heavier halogens are considerably more stable. The complexes are very moisture sensitive in solution and the structures of two examples of typical hydrolysis products $[Cl_5Ta(\mu\text{-}O)TaCl_3\{^iPrS(CH_2)_2S^iPr\}]$ and $[Cl_4Ta(\mu\text{-}O)(\mu\text{-}Me_2Se_2)TaCl_4]$ have been described elsewhere [37]. The structures of the ligand-bridged complexes are exemplified by that of $[(TaX_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$ (Fig. 4 and Table 3), which is isomorphous with the niobium analogue [13] and for which bond length comparisons show similar trends to those discussed in Section 2.4.



Scheme 2. Some reactions of $[TaX_5]_2$ (X = Cl or Br) (the pentahalides are dinuclear in the solid state $X_4Ta(\mu\text{-}X)_2TaX_4$, but are formulated at TaX_5 for simplicity in the text).

$MeS(CH_2)_2SMe$ reacted with TaX_5 in anhydrous CH_2Cl_2 solution, irrespective of the reactant ratio, to precipitate compounds of a 1:1 stoichiometry. These are very poorly soluble in chlorocarbons and decomposed by strong donor solvents. The far IR spectra, which show strong bands at 316 cm^{-1} (Cl) and 213 cm^{-1} (Br) corresponding to the t_{1u} modes of the respective $[TaX_6]^-$ [38], confirm the compositions as $[TaX_4\{MeS(CH_2)_2SMe\}_2][TaX_6]$. These are the only examples we have observed with dithioethers of eight-coordinate tantalum cations containing the heavier halogen co-ligands.

3. Conclusion

The results described above show that the thioether complexes of TaF_5 are distinctly different to those formed by TaX_5 (X = Cl, Br), the former showing a marked preference to form eight-coordinate cations, whilst the latter usually bind only a single S-donor to give six-coordination. Only for 2,5-dithiahexane were eight-coordinate cations observed for the heavier halides. The stability of the complexes is also very different in the two series. The TaX_5 (X = Cl, Br) adducts can be kept for many months in sealed tubes and hydrolyse with moisture to form initially oxide–halide complexes retaining the coordinated sulfur ligand [37], whereas the fluorides initially hydrolyse with displacement of the soft thioether by water and generation of $[TaF_6]^-$, and decompose quite rapidly even in sealed tubes at ambient temperatures by fluorination of the ligand (and attack on the glass). The stability trends are continued with the selenium ligands in that the adducts with TaX_5 (X = Cl, Br) are stable under dry conditions, whereas the fluorides are very unstable and degrade in hours at room temperature and very rapidly decompose in solution in the presence of excess selenoether. Although TaF_5 is clearly a very strong hard Lewis acid, and forms stable adducts with hard donors [1], with soft donors the results are consistent with much weaker donor–acceptor bonds, leading to complexes which are partially dissociated in non-coordinating solvents (even slightly in the solids) at room temperature, and fluorination of the ligand, probably accompanying metal centre reduction, is a facile decomposition route. The TaX_5 (X = Cl or Br) bond to the soft donors more strongly, resulting in more robust complexes.

The multinuclear NMR data also suggest the TaF_5 adducts are more dissociated in solution and that the dynamic ligand exchange processes slow at lower temperatures than in the NbF_5 analogues. Although both series of pentafluoride adducts are very moisture sensitive, the TaF_5 complexes are the more sensitive of the two. Whilst the qualitative differences noted are relatively small, they are consistent with TaF_5 as a somewhat harder Lewis acid than NbF_5, which would be most evident in the chemistry with soft donor ligands. Despite these small differences there is a very close parallel in behaviour between corresponding NbX_5 and TaX_5 adducts as would be expected.

4. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded from CD_2Cl_2 solutions using a Bruker AV300 spectrometer. $^{19}F\{^1H\}$ and $^{77}Se\{^1H\}$ NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external $CFCl_3$ and neat $SeMe_2$ respectively. UV/visible spectra were recorded from solid samples diluted with $BaSO_4$ using the diffuse reflectance attachment of a Perkin-Elmer Lambda 19 spectrometer. Microanalyses on new complexes were undertaken by Medac Ltd., except for some of the fluoride complexes, which decomposed at room temperature in a few hours (see Section 2), which precluded (outsourced) microanalytical data. Preparations were undertaken using standard Schlenk and glove box techniques under a N_2 atmosphere. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (hexane and diethyl ether). Anhydrous TaX_5 were obtained from Aldrich or Apollo and used as received. The ligands SR_2 (R = Me or Et) and $SeMe_2$ were obtained from Aldrich or Strem and dried over 4A molecular sieves. $TeMe_2$, $MeS(CH_2)_2SMe$, $EtS(CH_2)_2SEt$, $^iPrS(CH_2)_2S^iPr$, $MeSe(CH_2)_2SeMe$, o-$C_6H_4(CH_2SMe)_2$ and o-$C_6H_4(TeMe)_2$ were made by literature methods [39–43] and dried over molecular sieves.

4.1. [$TaF_5(SMe_2)$]

Finely powdered TaF_5 (0.28 g, 1.0 mmol) was placed in a Schlenk cooled in liquid nitrogen, and neat SMe_2 (~10 mL) distilled onto it *in vacuo*. The mixture was allowed to thaw and then stirred vigorously. The solid dissolved completely after about 10 min at ambient temperatures to give a colourless solution, which deposited white solid on further stirring. After 30 min the excess ligand was removed *in vacuo* and the white powder isolated and dried *in vacuo* at 40 °C. Yield: 0.36 g, 95%. Anal. calc. for $C_2H_6F_5STa$ (338.0): C, 7.1; H, 1.8. Found: C, 6.6; H, 2.1%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.25$ (s); 193 K: 2.55 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 79.0 (br, s); 190 K: 71.0 (s, [F]), 59.6 (s, [4F]). IR (Nujol/cm^{-1}): 630 (s), 614 (s), 593 (s). UV/vis (d.r.)/cm^{-1}: 27,000 and 41,700.

4.2. [$TaF_5(SEt_2)$]

Prepared similarly to the SMe_2 complex [15] and was obtained as a colourless oil after removing the excess SEt_2 *in vacuo* at 30 °C. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 1.48$ (t, [3H], CH_3), 3.15 (q, [2H], $^3J_{HH} = 8$ Hz, CH_2); 195 K: 1.53 (t), 3.32 (q). $^{19}F\{^1H\}$ NMR (CD_2Cl_2 295 K): 82.8 (br); 190 K: 80.1 (s, [F]), 70.6 (s, [4F]). IR (Nujol/cm^{-1}): 665 (sh), 630 (s), 576 (sh). UV/vis (d.r.)/cm^{-1}: 26,700 and 42,000.

4.3. [$TaF_5(SeMe_2)$]

Powdered TaF_5 (0.28 g, 1.0 mmol) was suspended in CH_2Cl_2 (10 mL) and $SeMe_2$ (0.18 g, 1 mmol) added with stirring, when the solid dissolved to give a pale yellow solution. After 10 min the solvent was removed *in vacuo* and the pale yellow powder washed with n-hexane (5 mL), filtered off and dried *in vacuo*. Yield: 0.40 g, 87%. All measurements were made on freshly prepared samples. In solution the complex darkens after ~2 h and deposits a black precipitate; the decomposition is very rapid with extra $SeMe_2$ present. The solid also darkens at room temperature overnight. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.25$ (s); 185 K: 2.40 (s). $^{19}F\{^1H\}$ NMR (CD_2Cl_2 295 K): 84.6 (br, s); 185 K: 71.0 (s, [F]), 61.0 (s, [4F]). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 295 K): no resonance; 185 K: 158.3 (s). IR (Nujol/cm^{-1}): $\upsilon = 630$ (sh), 612 (vs), 576 (vs). UV/vis (d.r.)/cm^{-1}: 25,500 and 40,000.

4.4. [$TaF_4(SMe_2)_4$][TaF_6]

Powdered TaF_5 (0.56 g, 2.0 mmol) was suspended in CH_2Cl_2 (20 mL) and SMe_2 (0.38 g, 6 mmol) added with stirring, when the solid dissolved to give a colourless solution. After 1 h the solution was filtered to remove small amounts of suspended material, and, the filtrate was concentrated to ~10 mL and refrigerated (−18° C) for 24 h. The colourless microcrystalline solid was collected by filtration and dried briefly in a stream of dry N_2 (pumping leads to loss of SMe_2). Refrigeration of the filtrate for 5 d. produced more colourless crystals. The crystals can be kept in a sealed tube in freezer for some days, but at room temperature rapidly become opaque and soften, losing SMe_2. The instability at ambient temperatures precludes obtaining satisfactory microanalyses. Yield: 0.45 g, 54%. ^1H NMR (CD_2Cl_2, 295 K): $\delta = 2.2$ (s); 185 K: 2.50 (s). $^{19}F\{^1H\}$ (CD_2Cl_2, 295 K): 71.6 (br, s); 220 K: 63.1 (s, [4F]), 42.0 (s, [6F]); 185 K: 59.8 (s [4F]), 39.1 (s, [6F]). IR (Nujol/cm^{-1}): $\upsilon = 606$ (s), 576 (s). UV/vis (d.r.)/cm^{-1}: 26,300 and 42,000.

4.5. [$TaF_4\{MeS(CH_2)_2SMe\}_2$][$TaF_6$]

Powdered TaF_5 (0.56 g, 2.0 mmol) was suspended in CH_2Cl_2 (20 mL) and $MeS(CH_2)_2SMe$ (0.24 g, 2 mmol) added with stirring, when the solid dissolved to give a colourless solution. After 1 h the solution was filtered to remove small amounts of undissolved solid and the filtrate was concentrated to ~10 mL, and refrigerated (−18° C) for 3–4 d. The colourless microcrystalline solid which deposited was collected by filtration and dried *in vacuo*. Yield: 0.40 g, 50%. Crystals used for the structure determination grew directly from a dilute solution in CH_2Cl_2 stored for 2 d. at −18 °C. Anal. calc. for $C_8H_{20}F_{10}S_4Ta_2$ (796.3): C, 12.1; H, 2.5. Found: C, 11.5;

H, 2.7%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.26 (s, [6H], Me), 3.00 (s, [4H], CH_2); 190 K: 2.14 (s, [6H]), 2.98 (s, [4H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 58.2 (br, s, [4F]), 41.3 (br, s, [6F]); 240 K: 56.3 (s, [4F]), 39.7 (s, [6F]). IR (Nujol/cm^{-1}): υ = 613 (s), 580 (br,s). UV/vis (d.r.)/cm^{-1}: 27,500 and 41,000.

4.6. $[TaF_4\{EtS(CH_2)_2SEt\}_2][TaF_6]$

Prepared analogously to complex 4.5 above. Yield: 55%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.39 (br, [6H], CH_3), 3.06 (br, [4H], CH_2), 3.42 (s, [4H], CH_2); 190 K: 1.37 (t, [6H]), 2.98 (q, [4H]), 3.34 (s, [4H]). $^{19}F\{^1H\}$ (CD_2Cl_2, 295 K): 60.4 (br, s, [4F]), 41.5 (br, s, [6F]); 220 K: 57.8 (s, [4F]), 39.0 (s, [6F]). IR (Nujol/cm^{-1}): υ = 610 (s), 577 (s,br). UV/vis (d.r.)/cm^{-1}: 27,800 and 41,000.

4.7. $[TaF_4\{^iPrS(CH_2)_2S^iPr\}_2][TaF_6]$

Prepared similarly to complex 4.5 above. It separates as a colourless microcrystalline solid from CH_2Cl_2 solution at −18 °C, but at room temperature transforms into a colourless wax, indicating a melting point near ambient. Yield: 45%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 1.30 (d, [12H], CH_3), 3.05 (s, [4H], CH_2), 3.51 (m, [2H], CH); 190 K: 1.36 (s, [12H]), 3.05 (s, [4H]), 3.60 (m, [2H]). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 79.0 (br, s); 220 K: 76.0 (s [4F]), 39.0 (s, [6F]). IR (Nujol/cm^{-1}): υ = 615 (s), 585 (vs, br). UV/vis (d.r.)/cm^{-1}: 27,000 and 41,300.

4.8. $[(TaF_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$

Powdered TaF_5 (0.56 g, 2.0 mmol) was suspended in CH_2Cl_2 (20 mL) and $MeSe(CH_2)_2SeMe$ (0.22 g, 1 mmol) added with stirring, when the solid dissolved to give a yellow solution. After 20 min the solvent was concentrated *in vacuo* to ~5 mL and dry n-hexane (10 mL) added to the stirred solution. The pale orange-yellow powder formed was filtered off and dried *in vacuo*. Yield: 0.40 g, 48%. In solution in CH_2Cl_2 at room temperature it darkens after ~2 h and deposits a black precipitate. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.53 (s, [6H], Me), 3.60 (s, [4H], CH_2). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 295 K): 83.0 (br, s); 185 K: 70.0 (vbr). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2/CD_2Cl_2, 295 K): no resonance; 185 K: 202.0 (s). IR (Nujol/cm^{-1}): υ = 638 (s, br), 580 (sh). UV/vis (d.r.)/cm^{-1}: 26,500 and 41,500.

4.9. $[TaCl_5(SMe_2)]$

$TaCl_5$ (0.36 g, 1.0 mmol) was suspended in anhydrous CH_2Cl_2 (10 mL). The suspension was stirred and under a flow of dinitrogen, SMe_2 (0.06 g, 1.0 mmol) was slowly added. The solid rapidly dissolved to produce a bright yellow solution and the reaction mixture was stirred for 30 min. The solvent was concentrated ~3 mL *in vacuo* and anhydrous hexane (5 mL) was added. A cream solid formed which was filtered off and dried *in vacuo*. Yield: 0.15 g, 36%. Anal. calc. for $C_2H_6Cl_5STa$ (420.2): C, 5.7; H, 1.4. Found: C, 5.9; H, 1.7%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.80 (s). IR (Nujol/cm^{-1}): υ = 394 (m), 368 (m), 349 (s). UV/vis (d.r.)/cm^{-1}: 25,640, 34,480, and 45,500.

4.10. $[TaCl_5(SeMe_2)]$

$TaCl_5$ (0.36 g, 1.0 mmol) was suspended in anhydrous CH_2Cl_2 (10 mL). The suspension was stirred and $SeMe_2$ (0.2 g, 1.0 mmol) was slowly added when the reaction mixture turned a deep straw yellow colour. After stirring for 30 min the solvent was concentrated to ~3 mL *in vacuo* and n-hexane (10 ml) was added. A yellow solid formed which was filtered off and dried *in vacuo*. The yellow filtrate was refrigerated for 1 week, producing a yellow solid and small yellow crystals. The supernatant liquid was removed using a syringe and the bright yellow solid was dried *in vacuo*. Overall yield: 0.23 g, 55%. Anal. calc. for $C_2H_6Cl_5SeTa$ (467.2): C, 5.2; H, 1.3. Found: C, 4.7; H, 1.7%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.76 (s). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2, 295 K): δ = 97.8 (s). IR (Nujol/cm^{-1}): υ = 390 (sh), 367 (m), 350 (s). UV/vis (d.r.)/cm^{-1}: 23,800, 35,200, and 43,700.

4.11. $[TaCl_4\{MeS(CH_2)_2SMe\}_2][TaCl_6]$

$TaCl_5$ (0.36 g, 1 mmol) was suspended in anhydrous CH_2Cl_2 (30 mL) and $MeS(CH_2)_2SMe$ (0.12 g, 1 mmol) added dropwise. Initially the $TaCl_5$ dissolved to give a pale yellow solution, but on stirring this rapidly precipitated a cream solid. After 30 min the solid was filtered off and dried *in vacuo*. Yield: 0.34 g, 71%. Anal. calc. for $C_8H_{20}Cl_{10}S_4Ta_2$ (960.5): C, 10.0; H, 2.1. Found: C, 10.9; H, 2.3%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.2 (s, [6H], Me), 2.8 (s, [4H], CH_2). IR (Nujol/cm^{-1}): υ = 325 (s), 316 (vs), 298 (s). UV/vis (d.r.)/cm^{-1}: 25,100, 33,000, and 43,900.

4.12. $[(TaCl_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}]$

$TaCl_5$ (0.36 g, 1 mmol) was suspended in anhydrous CH_2Cl_2 (30 mL) and $MeSe(CH_2)_2SeMe$ (0.13 g, 0.5 mmol) added dropwise. Initially the $TaCl_5$ dissolved to give a pale yellow solution, but on stirring for 1 h precipitated a yellow solid. After 1.5 h the solid was filtered off, and dried *in vacuo*. Yield 0.36 g, 73.5%. Anal. calc. for $C_4H_{10}Cl_{10}Se_2Ta_2$ (932.4): C, 5.2; H, 1.1. Found: C, 4.9; H, 1.4%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.8 (s, [6H], Me), 3.6 (s, [4H], CH_2). $^{77}Se\{^1H\}$ NMR: δ = 174.0. IR (Nujol/cm^{-1}): υ = 386 (m), 365 (sh), 332 (s). UV/vis (d.r.)/cm^{-1}: 23,800, 33,000, and 43,900. Yellow crystals were obtained by refrigerating the filtrate for several days.

4.13. $[(TaCl_5)_2\{\mu\text{-}o\text{-}C_6H_4(CH_2SMe)_2\}]$

o-$C_6H_4(CH_2SMe)_2$ (0.20 g, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (10 mL) and powdered $TaCl_5$ (0.36 g, 1.0 mmol) was added. The reaction mixture turned a bright yellow colour, was stirred for 2 h, concentrated to ~3 mL, and dry hexane (5 mL) was added. The solution was refrigerated for 3 d, when a yellow powder and some very small yellow crystals separated. Yield 0.11 g, 24%. Anal. calc. for $C_{10}H_{14}Cl_{10}S_2Ta_2$ (914.8): C, 13.1; H, 1.5. Found: C, 13.6; H, 1.9%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.6 (s, [6H], Me), 4.5 (s, [4H], CH_2), 7.3–7.7 (m, [4H], aromatic CH). IR (Nujol/cm^{-1}): υ = 349 (sh), 317 (s), 312 (sh). UV/vis (d.r.)/cm^{-1}: 26,800, 33,900, and 43,500.

4.14. $[TaBr_5(SMe_2)]$

$TaBr_5$ (0.27 g, 0.50 mmol) was suspended in anhydrous CH_2Cl_2 (15 mL) and under a flow of dinitrogen, SMe_2 (0.06 g, 1.0 mmol) was slowly added. The solid dissolved to form a bright orange-yellow solution and the reaction mixture was stirred for 30 min. The solvent was concentrated to ~3 mL *in vacuo* and anhydrous hexane (5 mL) was added dropwise with vigorous stirring. A yellow solid formed which was filtered off and dried *in vacuo*. Yield 0.24 g, 80%. Anal. calc. for $C_2H_6Br_5STa$ (642.6): C, 3.8; H, 1.0. Found: C, 4.2; H, 1.2%. ^{1}H NMR (CD_2Cl_2, 295 K): δ = 2.86 (s). IR (Nujol/cm^{-1}): υ = 254 (m), 238 (s), 228 (s). UV/vis (d.r.)/cm^{-1}: 22,000, 25,600, 31,000 (sh), and 43,500.

4.15. $[TaBr_5(SeMe_2)]$

Prepared similarly to the corresponding chloro-complex and isolated as a deep orange powder. Yield: 85%. Anal. calc. for $C_2H_6Br_5SeTa$ (689.5): C, 3.5; H, 0.9. Found: C, 3.3; H, 1.1%. ^{1}H NMR

Table 4
Crystal data and structure refinement details.[a]

Compound	$[TaF_4(MeS(CH_2)_2SMe)_2]$ $[TaF_6]$	$[TaCl_5(SeMe_2)]$	$[(TaCl_5)_2\{MeSe(CH_2)_2SeMe\}]$
Formula	$C_8H_{20}F_{10}S_4Ta_2$	$C_2H_6Cl_5SeTa$	$C_4H_{10}Cl_{10}Se_2Ta_2$
M	796.38	467.23	932.44
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group (no.)	Cc (9)	$Cmc2_1$ (36)	$P2_1/n$ (14)
a (Å)	14.065(4)	8.019(2)	6.9288(10)
b (Å)	26.278(7)	11.931(3)	13.0514(15)
c (Å)	10.717(4)	10.806(2)	11.1527(10)
α (°)	90	90	90
β (°)	101.32(4)	90	98.823(10)
γ (°)	90	90	90
U ($Å^3$)	3883.7(19)	1033.8(4)	996.6(2)
Z	8	4	2
μ (Mo-K_α) (mm^{-1})	11.772	15.371	15.944
$F(000)$	2944	840	836
Total number of reflections	18,965	4208	12,369
R_{int}	0.066	0.023	0.034
Unique reflections	7111	1047	2270
No. of parameters, restraints	441, 2	50, 1	83, 0
R_1, wR_2 $[I > 2\sigma(I)]$[b]	0.041, 0.094	0.013, 0.028	0.018, 0.039
R_1, wR_2 (all data)	0.048, 0.097	0.013, 0.029	0.020, 0.040

[a] Wavelength (Mo-K_α) = 0.71073 Å; θ(max) = 27.5°.

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

(CD_2Cl_2, 295 K): δ = 2.86 (s). $^{77}Se\{^1H\}$ NMR (CH_2Cl_2, 295 K): δ = 83.8 (s). IR (Nujol/cm^{-1}): υ = 237 (m), 226 (s). UV/vis (d.r.)/cm^{-1}: 21,500, 25,000, 33,000, and 41,600.

4.16. [$TaBr_4\{MeS(CH_2)_2SMe\}_2$][$TaBr_6$]

Prepared similarly to the chloro-complex and isolated as an orange-yellow powder. Yield 83%. Anal. calc. for $C_8H_{20}Br_{10}S_4Ta_2$ (1405.4): C, 6.8; H, 1.4. Found: C, 6.2; H, 1.4%. ^1H NMR (CD_2Cl_2, 295 K): δ = 2.25 (s, [6H], Me), 2.75 (s, [4H], CH_2). IR (Nujol/cm^{-1}): υ = 227 (sh), 213 (vs), 202 (s). UV/vis (d.r.)/cm^{-1}: 23,100, 26,650, 33,000, and 43,100.

4.17. [$(TaBr_5)_2\{\mu\text{-}MeSe(CH_2)_2SeMe\}$]

Prepared using the same method as the chloro-complex and isolated as a pale orange solid. Yield 85%. Anal. calc. for $C_4H_{10}Br_{10}Se_2Ta_2$ (1377.0): C, 3.5; H, 0.7. Found: C, 3.5; H, 1.0%. ^1H NMR (CD_2Cl_2, 295 K): δ = 2.7 (s, [6H], Me), 3.5 (s, [4H], CH_2). $^{77}Se\{^1H\}$ NMR: too poorly soluble. IR (Nujol/cm^{-1}) υ = 223 (sh), 210 (s), 205 (s). UV/vis (d.r.)/cm^{-1}: 21,800, 25,000 (sh), 31,500, and 41,700.

4.18. X-ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 4. Crystals were obtained as described above. Data collection for the $TaCl_5$ complexes used a Nonius Kappa CCD diffractometer fitted with monochromated (confocal mirrors) and Mo-K_α X-radiation (λ = 0.71073 Å). Crystals were held at 120 K in a nitrogen gas stream. Data collection for the TaF_5 complexes used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics (100 μm focus). Crystals were held at 100 K. Structure solution and refinement were generally routine [44,45].

5. Supplementary materials

CCDC reference numbers 858925–858927 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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