Comparison of homoleptic d^1 and d^2 transition-metal tellurolates: syntheses and crystal structures of [M{TeSi(SiMe$_3$)$_3$}$_4$] (M = V, Mo)

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The homoleptic tellurolates [M{TeSi(SiMe$_3$)$_3$}$_4$] (M = V, Mo) are synthesized and X-ray crystallographic investigations and preliminary reactivity studies presented.

Owing to their inherent simplicity and fundamental importance, homoleptic transition-metal complexes continue to attract considerable attention. For example, recently determined crystal structures[1] of WMe$_6$[2] and ReMe$_6$[3] support the idea that in the absence of π effects, ML$_6$ species may adopt non-octahedral geometries in contrast to the prediction of ligand-field theory. We have reported d^0 homoleptic, silyl selenolates and tellurolates[4] of the Group 4 elements of the type [M{ESi-(SiMe$_3$)$_3$}$_4$] (M = Ti, Zr, Hf; E = Se, Te) and investigated the Lewis-base induced elimination of Te[Si(SiMe$_3$)$_3$]$_2$ to yield terminal, doubly bonded Te^{2-} and bridging Se^{2-} ligands.[5,6] Here we describe the preparation and solid-state structures of related vanadium(IV) and molybdenum(IV) analogues which provides a rare opportunity to compare a series of d^0, d^1 and d^2 homoleptic derivatives. Tellurolate complexes of Groups 5 and 6 are rare.[4] [W(SeR)$_4$] and [M(SeR)$_3$] (M = Nb, Ta; R = Ph, naphthyl) were reported by Andra in 1970,[7] although nothing is known regarding their structures or reaction chemistry.

We carried out the reactions† which successfully yielded homoleptic tellurolates of Mo^{IV} and V^{IV} [eqns. (1) and (2)]

$$[\mathrm{Mo(C_6H_4Me\text{-}2)_4}] + 4\mathrm{HTeSi(SiMe_3)_3} \longrightarrow [\mathrm{Mo\{TeSi(SiMe_3)_3\}_4}] \quad (1)$$

dark purple; 71%

$$[\mathrm{V\{N(SiMe_3)_2\}_2\{TeSi(SiMe_3)_3\}}] + 2\mathrm{HTeSi(SiMe_3)_3} \longrightarrow [\mathrm{V\{TeSi(SiMe_3)_3\}_4}] \quad (2)$$

black; 20%

While the synthesis of the Mo species is quite straightforward, the formation of [V{TeSi(SiMe$_3$)$_3$}$_4$] is clearly more complex. There appear to be similarities between this transformation and reactions of RO$^-$ or RS$^-$ with V^{II}[8] and V^{III}[9] which can only be explained by disproportionation at vanadium. In the case of reaction (2), the yield is the same under a dinitrogen or argon atmosphere and no lower-valent, vanadium-containing species could be cleanly isolated from the reaction mixture.

Both tellurolate complexes are very soluble in hydrocarbon solvents and are best crystallized from hexamethyldisiloxane (HMDSO). The d^1 vanadium complex showed a broad signal at δ 0.7 ($\Delta\nu_{1/2}$ *ca.* 70 Hz) in the ^{1}H NMR spectrum and a signal at *m*/*z* 1553 in the EIMS for the molecular ion. While the compound was typically isolated along with small, variable amounts of Te$_2$[Si(SiMe$_3$)$_3$]$_2$, recrystallized samples that were apparently pure (*i.e.* no diamagnetic impurities by ^{1}H NMR spectroscopy) still showed a magnetic moment that was lower than the predicted value (μ_{eff} = 1.56 μ_B, Evans' method[10,11]) and analysed low for carbon (combustion analysis). The d^2 molybdenum compound is diamagnetic and displayed sharp singlets in ^{1}H and ^{13}C{^{1}H} NMR spectra. The IR spectra were essentially identical to those observed for [M{TeSi(SiMe$_3$)$_3$}$_4$] (M = Ti, Zr, Hf)[6] showing strong bands at *ca.* 1242 and 836 cm^{-1} due to the Si(SiMe$_3$)$_3$ groups.

As representative of the similar solid-state structures,‡ an ORTEP view of [V{TeSi(SiMe$_3$)$_3$}$_4$] is shown in Fig. 1. The geometry of the MTe$_4$ units is distorted from T_d symmetry and is best described as a flattened tetrahedron, with the two larger Te–M–Te angles measuring 115.79(9) and 114.73(9)° for M = V, and 114.94(5) and 114.79(5)° for M = Mo. For comparison, the cores of the homoleptic thiolates [V(SCMe$_3$)$_4$][9] and [Mo(SC$_6$H$_2$Pr$^i_3$-2,4,6)$_4$][12] are also flattened tetrahedra, while those in [M(SCMe$_3$)$_4$] (M = Mo,[13] W[14]) are elongated tetrahedra (four larger and two smaller angles). The four smaller Te–M–Te angles are between 102 and 110° in the two tellurolate structures. The M–Te bond lengths are in the range 2.550(3)–2.570(3) Å (M = V) and 2.562(1)–2.582(1) Å (M = Mo). The M–Te–Si angles span the range 116–122° and are typical for metal complexes of this ligand.

Structurally characterized V–Te bonds are rare; the bridging telluride [(dppe)(CO)$_3$V]$_2$Te [dppe = 1,2-bis(diphenylphosphino)ethane] [V–Te 2.514(3), 2.522(3) Å][15] and the tellurolates [(Me$_3$Si)$_2$N]$_2$TeR [R = Si(SiMe$_3$)$_3$, V–Te 2.6758(9) Å; SiPh$_3$, V–Te 2.675(2) Å][16] are the only other examples. That the V–Te distances in [V{TeSi(SiMe$_3$)$_3$}$_4$] compare favourably with those in the bridging telluride, in which the V–Te bond order is between two and three, is probably indicative of some multiple bond character in the homoleptic tellurolate (resonance structure **B**). Nonetheless, factors such as coordination number and oxidation state of the central metal must not be overlooked. For instance, the Mo–Te bond lengths in [Mo{TeSi(SiMe$_3$)$_3$}$_4$] are shorter than the Mo–Te double bonds in [(Me$_3$P)$_4$Mo(Te)$_2$] [Mo–Te 2.597(1) Å].[17] Similar observations are made on comparing the formally single

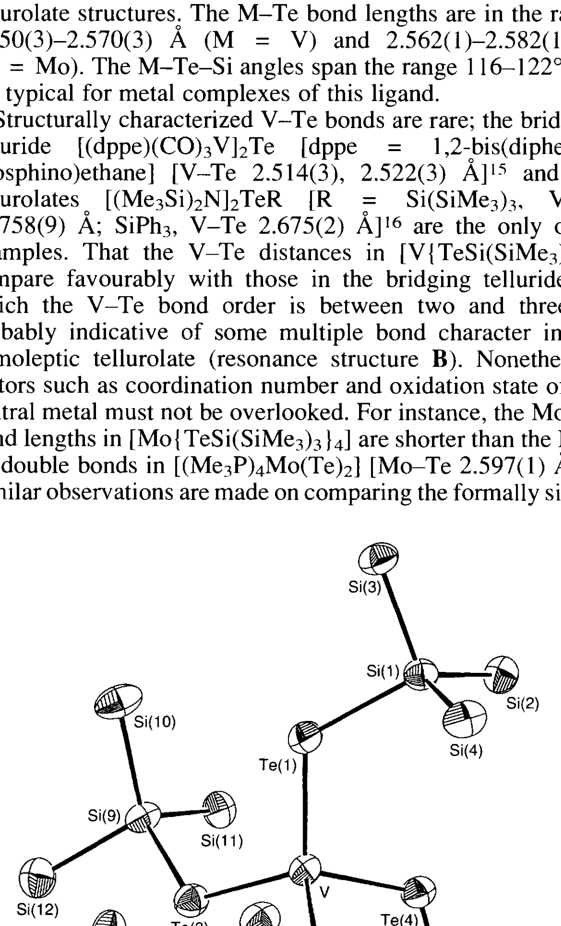
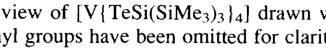


Fig. 1 ORTEP view of [V{TeSi(SiMe$_3$)$_3$}$_4$] drawn with 50% probability ellipsoids; methyl groups have been omitted for clarity



$$\underset{\mathbf{A}}{\mathrm{M{-}TeR}} \longleftrightarrow \underset{\mathbf{B}}{\overset{-}{\mathrm{M}}{=}\overset{+}{\mathrm{Te}}\mathrm{R}}$$

M–Te bond lengths in [M{TeSi(SiMe$_3$)$_3$}$_4$] (M = Zr, Hf) to the M–Te double bonds in [M{TeSi(SiMe$_3$)$_3$}$_2$(Te)(dmpe)$_2$] (M = Zr, Hf)[5,6] and [(η^5-C$_5$Me$_4$Et)$_2$M(Te)(NC$_5$H$_5$)] (M = Zr,[18] Hf[19]). It has been suggested[20] that the low-spin electronic configuration in the [Mo(SR)$_4$] compounds mentioned above is due to weak S(p$_\pi$)–Mo(d$_\pi$) interactions that lift the degeneracy of the e-symmetry HOMO in a T_d MoS$_4$ core; it is reasonable that analogous electronic factors are operating in [Mo{TeSi(SiMe$_3$)$_3$}$_4$].[21]

Preliminary investigations into the reactivity of these tellurolates suggest that both compounds are susceptible to reductive elimination of Te$_2$[Si(SiMe$_3$)$_3$]$_2$. For example [V{TeSi(SiMe$_3$)$_3$}$_4$] reacts with 2 equiv. of dmpe [dmpe = 1,2-bis(dimethylphosphino)ethane] eliminating disilylditelluride and forming *trans*-[V(dmpe)$_2${TeSi(SiMe$_3$)$_3$}$_2$]. [Mo{TeSi(SiMe$_3$)$_3$}$_4$] is also reduced on treatment with dmpe giving ditelluride and a black powder whose insolubility in common solvents has hampered characterization. Treatment of a hexanes solution of [Mo{TeSi(SiMe$_3$)$_3$}$_4$] with CO (1 atm) formed Mo(CO)$_6$ (IR) and ditelluride. Further reactivity studies with both homoleptic tellurolates are currently being pursued.

Footnotes

† *Syntheses*: standard inert atmosphere techniques were employed for all manipulations using dry, oxygen-free solvents.

[V{TeSi(SiMe$_3$)$_3$}$_4$]: a hexanes solution (20 ml) of HTeSi(SiMe$_3$)$_3$[22] (951 mg, 2.53 mmol) was added to a magnetically stirred, cold (−40 °C) hexanes solution (15 ml) of [V{N(SiMe$_3$)$_2$}$_2${TeSi(SiMe$_3$)$_3$}][16] (944 mg, 1.26 mmol). The mixture turned from golden brown to red–orange. The reaction was gradually warmed to room temp. and stirred for a total of 20 h before the volatile materials were removed under reduced pressure. The solid was extracted into HMDSO (*ca.* 40 ml) and the orange–brown solution filtered from some insoluble material. Concentration of the fltrate to *ca.* 20 ml followed by cooling to −35 °C for 24 h afforded 420 mg of black crystals of the product which were isolated by filtration (22% yield based on V). Mp 180–181 °C (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.69 br s ($\Delta\nu_{1/2}$ *ca.* 70 Hz). IR: 1306w, 1257m (sh), 1242s, 855s (sh), 836vs, 745w (sh), 723w, 687m, 622m cm^{-1}. μ_{eff} = 1.56 μ_B (C$_6$D$_6$). EIMS: 1553 (M$^+$). Anal. Calc. for C$_{36}$H$_{108}$Si$_{16}$Te$_4$V: C, 27.86; H, 7.01. Found: C, 26.01; H, 7.26%.

[Mo{TeSi(SiMe$_3$)$_3$}$_4$]: a cold (−70 °C) hexanes solution of HTeSi(SiMe$_3$)$_3$ (1.58 g, 4.20 mmol) was added to a magnetically stirred, cold (−70 °C) hexanes solution of [Mo(C$_6$H$_4$Me-2)$_4$] (480 mg, 1.04 mmol). The black solution was allowed to warm to room temp. and after 1 h the volatile materials were removed under reduced pressure. The black solid was dissolved in HMDSO and the solution filtered. Concentration followed by cooling to −40 °C allowed for isolation of 1.18 g (71%) of black crystalline product. Mp 117–126 °C (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.79 (s). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ 10.9 (s). UV–VIS (hexanes, $\lambda_{\max}$): 212 tailing to 700 nm. IR: 1258 (sh), 1242s, 874 (sh), 836vs, 738m, 687m, 622m cm^{-1}. Anal. Calc. for C$_{36}$H$_{108}$MoSi$_{16}$Te$_4$: C, 27.08; H, 6.82. Found: C, 27.63; H, 6.87%.

‡ *X-Ray crystallography*: [V{TeSi(SiMe$_3$)$_3$}$_4$]. *Crystal data*: C$_{36}$H$_{108}$Si$_{16}$Te$_4$V, M = 1551.96, monoclinic, space group $P2_1/c$, a = 22.4951(3), b = 15.5037(3), c = 22.6211(4) Å, β = 105.037(3)°, U = 7619.11(34) Å^3, Z = 4, D_c = 1.35 g cm^{-3}, Mo-Kα, λ = 0.710 73 Å, T = −131 °C. Red-brown crystals were grown from HMDSO at −35 °C. A hemisphere of data (0.3° ω scans at 20 s per frame) was collected using a Siemens SMART diffractometer/CCD area detector. The raw data were integrated and the unit-cell parameters refined [5731 reflections with $I > 10\sigma(I)$] using SAINT. Preliminary data analysis and a semiempirical ellipsoidal absorption correction were performed using XPREP. Of the 30 406 reflections measured, 11 251 were unique and 4915 had $I > 3\sigma(I)$ and were used in the refinement. Redundant reflections (R_{int} = 9.6%) were averaged. The structure was solved by direct methods using the TEXSAN package and refined upon $|F|$ using standard least-squares and Fourier techniques. A two-site disorder involving the three silicon atoms attached to Si(9) was modelled and refined to occupancies of 0.841 and 0.159 for the major and minor rotamers respectively. All non-hydrogen atoms [except for Si(17)–Si(19)] were refined with anisotropic thermal parameters; hydrogen atoms were introduced at idealized positions and included in F_c but not refined. Neutral atom scattering factors were used and anomalous dispersion effects were included in F_c. The final residuals for 527 variables refined against 4915 data were R = 0.0508, R_w = 0.0582, and GOF = 1.55.

[Mo{TeSi(SiMe$_3$)$_3$}$_4$]. *Crystal data*: C$_{36}$H$_{108}$Si$_{16}$Te$_4$Mo, M = 1596.97, monoclinic, space group $P2_1/c$, a = 22.491(6), b = 15.511(4), c = 22.641(9) Å, β = 105.007(10)°, U = 7629.16(19) Å^3, Z = 4, D_c = 1.39 g cm^{-3}, Mo-Kα, λ = 0.710 73 Å, T = −114 °C. Crystals were grown from HMDSO at −35 °C. Data were collected in the range $+h$, $+k$, $\pm l$ on an Enraf-Nonius CAD4 diffractometer in the ω scan mode to a $2\theta_{\max}$ of 45°. An absorption correction based on Ψ scans was applied to the data. Of the 12 196 reflections measured, 10 416 were unique and 7137 with $I > 3\sigma(I)$ were used in the refinement. Redundant reflections (R_{int} = 7.86%) were averaged. The structure was solved and refined as above. The final residuals for 514 variables refined against 7137 data were R = 0.0407, R_w = 0.0681, and GOF = 2.68. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/259.

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