

[Ru{MeC(CH₂EMe)₃}]₂(CF₃SO₃)₂: the first homoleptic hexaseleno- and hexatelluro-ether complexes

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The preparations of the first examples of homoleptic hexaseleno- and hexatelluro-ether complexes, [Ru{MeC(CH₂EMe)₃}]₂(CF₃SO₃)₂ (E = Se or Te) are described; the crystal structure of the former shows both ligands binding facially to the Ru^{II} centre, with the Se-based lone pairs in the *syn* arrangement.

Recently we embarked on a comparative study of the binding characteristics of thio-, seleno- and telluro-ether ligands to transition metal centres and we have shown that to low-valent group 6 and group 7 metal centres E→M donation increases in the order S < Se << Te.¹ Despite this, multidentate telluroether ligands are very rare, and the only reported tritelluroether complex is *fac*-[Mn(CO)₃{MeC(CH₂TeMe)₃}]CF₃SO₃.² We have already reported the synthesis, structures and properties of a range of multidentate and macrocyclic selenoether ligand complexes, and, in light of the prediction that telluroethers will show enhanced donating abilities, we have begun to investigate the synthesis and properties of multidentate telluroethers and their complexes with the platinum group metals. There are no examples with homoleptic hexaseleno- or hexatelluro-ether coordination to octahedral metal complexes. Typically two or more of the six coordination sites are occupied by halogen co-ligands which greatly influence the metal ion properties.³ We report here the preparation, spectroscopic and structural characterisation of the first homoleptic hexaseleno- and hexatelluro-ether complexes, [Ru{MeC(CH₂EMe)₃}]₂(CF₃SO₃)₂ (E = Se or Te).

[Ru(dmf)₆](CF₃SO₃)₃⁴ reacts with 2 mol. equiv. of MeC(CH₂EMe)₃ (E = Se or Te) in refluxing MeOH solution to give yellow coloured solutions containing the hexa-substituted ruthenium(II) species [Ru{MeC(CH₂EMe)₃}]₂(CF₃SO₃)₂.[†] These species can be isolated by addition of Et₂O to the concentrated solutions and filtration. The electrospray mass spectra (MeCN) show peaks with isotope distributions consistent with the doubly charged species [Ru{MeC(CH₂EMe)₃}]₂²⁺ (E = Se, *m/z* centred at 402; E = Te, *m/z* centred at 548). IR spectroscopy shows peaks associated with coordinated triselenoether or telluroether, as well as absorptions characteristic of the CF₃SO₃⁻ anion. The ⁷⁷Se{¹H} and ¹²⁵Te{¹H} NMR spectra of the complexes show single resonances at δ 120 and 204, respectively. Given that pyramidal inversion at an Ru–SeR₂ or Ru–TeR₂ unit is expected to be slow,^{5,6} the observation of only one resonance in each case indicates that each coordinated ligand adopts a *syn* configuration.

Repeated attempts were made to obtain single crystals of one of these compounds suitable for an X-ray crystal structure analysis. Crystals of the selenoether complex were eventually obtained by diffusion of Et₂O into a solution of the complex in MeNO₂. A data set collected at 150 K gave rather broad peaks and did not refine satisfactorily. Data collection was therefore repeated at a slower scan-speed on a second sample at room temperature, yielding better quality data. The crystal structure[‡] shows an ordered centrosymmetric [Ru{MeC(CH₂SeMe)₃}]₂²⁺ cation with the Ru atom occupying a crystallographic inversion

centre, giving a half-cation and one CF₃SO₃⁻ anion in the asymmetric unit. Within the cation the Ru^{II} centre is coordinated to two tridentate, facially bound selenoether ligands, to give a slightly distorted octahedral arrangement with Ru–Se 2.4808(7), 2.4701(7), 2.4781(6) Å (Fig. 1). The Se–Ru–Se angles involved in the six-membered chelate rings are very close to 90°, and the Me substituents are oriented in the propeller-like arrangement associated with the configuration. This is consistent with the *syn* configuration deduced from ⁷⁷Se{¹H} NMR spectroscopy. The Ru–Se distances compare with 2.396(1)–2.465(1) Å in *cis*-[RuCl₂([16]aneSe₄)] ([16]aneSe₄ = 1,5,9,13-tetraselenacyclohexadecane) and 2.465(3)–2.479(3) Å in *trans*-[RuCl(PPh₃)([16]aneSe₄)]⁺.⁶

The electronic spectrum of [Ru{MeC(CH₂SeMe)₃}]₂(CF₃SO₃)₂ shows two d–d transitions, ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g} at 25975 and 29940 cm⁻¹ respectively, as well as intense charge transfer transitions at higher energy. Analysis of the spectrum⁷ leads to approximate values of 10 *Dq* and *B* of 25000 and 250 cm⁻¹, respectively. These values can be compared with {Ru(H₂O)₆}²⁺ (17700 and 425), [Ru(en)₃]²⁺ (25450 and 390)⁷ and [Ru([9]aneS₃)₂]²⁺ ([9]aneS₃ = 1,4,7-trithiacyclonane) (28400 and 290 cm⁻¹).⁸ These data indicate that the selenoether tripod, like [9]aneS₃, is a strong field ligand with a high degree of covalent character in the Ru–Se bonds. The electronic spectrum of [Ru{MeC(CH₂Te-

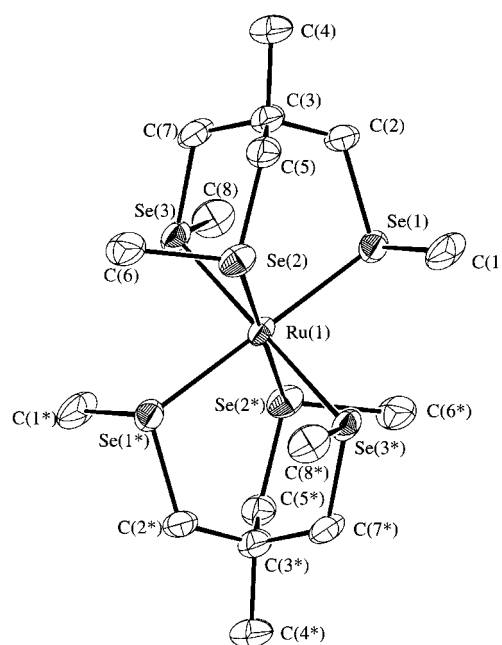


Fig. 1 View of the structure of [Ru{MeC(CH₂SeMe)₃}]₂²⁺ with the numbering scheme adopted. H atoms are omitted for clarity, atoms marked * are related by a crystallographic inversion centre and ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (°): Ru–Se(1) 2.4808(7), Ru–Se(2) 2.4701(7), Ru–Se(3) 2.4781(6); Se(1)–Ru–Se(2) 90.18(2), Se(1)–Ru–Se(3) 89.02(2), Se(2)–Ru–Se(3) 87.56(2)°.

Me)₃}]₂](CF₃SO₃)₂ is less informative since the charge transfer transitions tail into the visible region and completely obscure the metal-centred transitions.

Cyclic voltammetry on [Ru{MeC(CH₂SeMe)₃}]₂](CF₃SO₃)₂ (MeCN solution, 0.1 mol dm⁻³ NBu₄BF₄ supporting electrolyte) shows an irreversible reduction at -2.0 V vs. Fc/Fc⁺ and a quasi-reversible oxidation at 1.18 V vs. Fc/Fc⁺ which is assigned to the Ru^{II/III} redox couple. This oxidation potential is considerably higher than for *trans*-[RuCl₂([16]aneSe₄)] (*E*_{1/2} = 0.32 V vs. Fc/Fc⁺),⁶ reflecting the presence of six soft Se donor atoms around the Ru^{II} centre in the former. [Ru{MeC(CH₂TeMe)₃}]₂](CF₃SO₃)₂ shows no oxidative activity, only an irreversible reduction at -1.52 V vs. Fc/Fc⁺. The relatively high potentials for these processes probably reflect the high stability of the low-spin d⁶ Ru^{II} species within the strong field Se₆ or Te₆ coordination sphere, and strongly suggest that these ligands will be capable of supporting other [ML₆]^{x+} species (L = Se or Te) for a wide variety of metals, thus promoting very different electronic environments at the metal centres.

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Notes and references

† Satisfactory analytical and spectroscopic data were obtained.

‡ *Crystal data*: C₁₈H₃₆F₆O₆RuS₂Se₆, *M* = 1101.42, triclinic, space group *P*1̄, *a* = 8.8436(5), *b* = 11.6692(15), *c* = 8.7056(8) Å, α = 107.369(9), β = 91.648(7), γ = 106.530(7), *V* = 815.62(14) Å³, *Z* = 1, *D*_c = 2.242 g cm⁻³, μ(Mo-Kα) = 73.68 cm⁻¹. Rigaku AFC7S four-circle diffractometer. Data collection at 293 K using Mo-Kα X-radiation (λ = 0.71073 Å), gave 2875 unique reflections (*R*_{int} = 0.0162) which were used in all calculations. The structure was solved using direct methods⁹ and developed by iterative cycles of least-squares refinement¹⁰ and difference Fourier synthesis. While the centrosymmetric cation is ordered, the CF₃SO₃⁻ anion, which occupies

a general position, shows rather high thermal parameters, particularly those associated with the F and O atoms. However, attempts to model this disorder by refining partial site occupancies were not successful, hence the atoms were refined with unit occupancies and high thermal parameters. While low temperature data collection would normally be expected to reduce the thermal motion and improve the structure quality, a data set from a different crystal collected previously at 150 K gave broad peaks and a significantly poorer fit to the data. Anisotropic thermal parameters were refined for all non-H atoms and H atoms were included in fixed, calculated positions. The weighting scheme $w^{-1} = \sigma^2(F_o) + (0.0634P)^2 + 2.2211P$, where $P = (F_o^2 + 2F_c^2)/3$, gave satisfactory agreement analyses. At final convergence, *R*₁ = 0.0539, *wR*₂ = 0.1106 (all data), *R*₁ = 0.0373, *wR*₂ = 0.1011 [*I* ≥ 2σ(*I*)], *S* = 1.032 for 178 parameters. CCDC 182/1245. See <http://www.rsc.org/suppdata/cc/1999/1071/> for crystallographic files in .cif format.

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