Crown Thioether Chemistry. Synthesis and Structure of Bis(1,4,7-trithiacyclononane)ruthenium Bis(trifluoromethanesulphonate), the First Homoleptic Thioether Complex of Ruthenium

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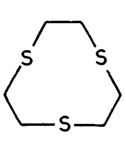
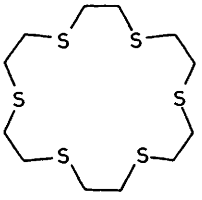
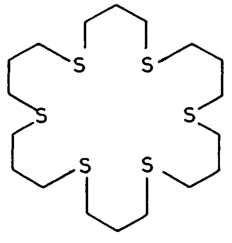
1,4,7-Trithiacyclononane (9S3) reacts with ruthenium(III) tris(trifluoromethanesulphonate) to yield $[Ru(9S3)_2](CF_3SO_3)_2$, the first reported homoleptic thioether complex of ruthenium(II).

Our interest in the co-ordination chemistry of thio crown ethers such as 1,4,7,10,13,16-hexathiacyclo-octadecane (hexathio-18-crown-6, 18S6), 1,4,7-trithiacyclononane (trithio-9-crown-3, 9S3), and 1,5,9,13,17,21-hexathiacyclotetracosane (hexathio-24-crown-6, 24S6)[1] has led us to investigate the utility of this class of ligands for ruthenium. In addition to representing an extension of thio crown ether chemistry to second-row elements, such complexes may exhibit novel photophysical behaviour induced by the homoleptic thioether environment. We report herein the synthesis and characterisation of $[Ru(9S3)_2](CF_3SO_3)_2$, the first homoleptic thioether complex of ruthenium.


9S3


18S6


24S6

Reaction of 9S3 (prepared as previously described[1,2]) (1.5 mmol) with $Ru(CF_3SO_3)_3$ (0.5 mmol) in methanol (6 ml) at reflux under N_2 for 72 h yielded a pale yellow solution. After filtration and removal of the solvent pale yellow crystals separated, which were washed with CH_2Cl_2 (3 ml), and recrystallised from MeOH to yield colourless prisms {yield: 180 mg, 47%; ^{1}H n.m.r. (CD_3NO_2) δ 3.01, sym. mult. (16 peaks); *cf.* $[Co(9S3)_2](ClO_4)_3$[3]}. A suitable crystal was selected and an *X*-ray data set was collected.†

In each of the two centrosymmetric $[Ru(9S3)_2]^{2+}$ cations per asymmetric unit the metal ion is bound by six thioether groups from two 9S3 ligands (Figure 1). (As metrical parameters of the two complexes are virtually the same, the two will be discussed together.) The resulting co-ordination sphere is almost perfectly octahedral with chelating S–Ru–S angles of 87.6—87.8°, and nonchelating S–Ru–S angles (*i.e.*, between sulphur atoms from different 9S3 molecules) of 92.20—92.38°. Ruthenium–sulphur distances range from 2.3306(6) to 2.3437(6) Å. Few Ru–thioether complexes have been structurally characterised, but Ru–S distances in the ranges 2.262(1)—2.333(1) and 2.340(1)—2.393(2) Å were recently reported for *cis*-dichloro(1,4,8,11-tetrathiacyclotetradecane)ruthenium(II),[4] and several mixed sulphoxide–thioether complexes of ruthenium(II),[5] respectively.

Examination of the torsional angles of the ligand reveals the apparent origin of the peculiar stability of this and other 9S3 complexes. The presence of a nine-membered ring constrains the donor atoms of the free ligand to positions that fortuitously correspond closely to those required for complex

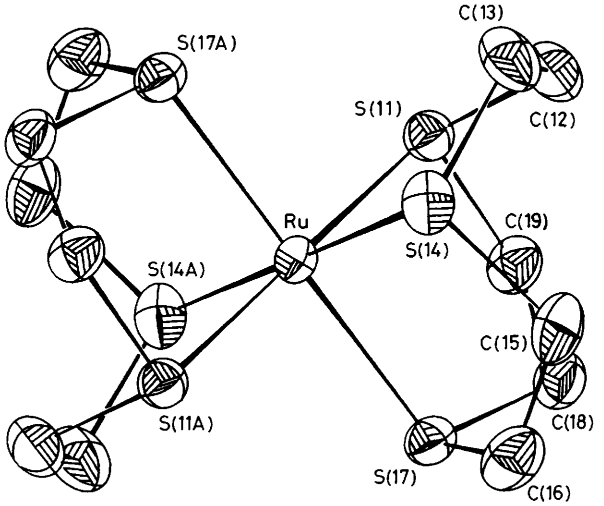


Figure 1. CHEMGRAF drawing of the $[Ru(9S3)_2]^{2+}$ cation showing thermal ellipsoids at 50% probability level (hydrogen atoms are omitted for clarity). Ligand atoms from molecule 1 are numbered sequentially around the ring [S(11), C(12), *etc.*].

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† *Crystal data:* $C_{14}H_{24}F_6O_6RuS_8$, M_r = 759.9, triclinic, space group $P\bar{1}$, a = 7.677(5), b = 9.465(3), c = 18.423(3) Å, α = 83.61(2), β = 88.48(4), γ = 83.05(4)°, U = 1320.46 Å^3, Z = 2, D_c = 1.91 g cm^{-3}. A crystal (0.7 × 0.25 × 0.4 mm) was sealed in an *X*-ray capillary, and 10 031 unique data with $2\theta \leqslant 64°$ were collected on an Enraf–Nonius CAD4 diffractometer with Mo-K_α radiation (λ = 0.71 069 Å). Three standard reflections measured every hour showed no decay. Calculations were performed with the CRYSTALS crystallographic programs on a VAX 11/750 computer, with atomic scattering factors from the usual source. An empirical absorption correction was applied. The Ru atoms were found from a three-dimensional Patterson map, and the remaining non-hydrogen atoms were found by Fourier syntheses. Approximately half of the hydrogen atoms were also found; all hydrogen atoms were included at calculated positions and a group isotropic thermal parameter was refined. Full-matrix least squares refinement based on 6917 data with $I > 3\sigma(I)$ converged to R = 4.03% (R_w = 4.82%) for 321 parameters. The highest peak in the final difference map was 2.5 e/Å^3, and was found next to the sulphur atom [S(2)] of one of the trifluoromethanesulphonate anions, which appears to be slightly disordered. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

formation.[6] As a consequence, complexation necessitates relatively small changes in the torsional angles of 9S3 {<12° for $[Ru(9S3)_2]^{2+}$}; in essence, the enthalpic price of arranging donor atoms for complexation has been paid during synthesis of the ligand.

Electrochemical investigation of the complex suggests a particularly strong interaction between Ru^{II} and the six thioether donor atoms. Cyclic voltammetry reveals no oxidation wave before the ligand oxidation wave at +1.8 V *vs.* normal hydrogen electrode (N.H.E) ($MeNO_2$ or MeCN; Au or glassy carbon electrodes). This redox potential indicates that 9S3 interacts much more strongly with Ru^{II} than with Ru^{III}, and it emphasises the ability of thioethers generally to stabilise low oxidation states.[1]

Further evidence for the strength of the ruthenium(II)–thioether interaction is provided by the optical spectrum of $[Ru(9S3)_2]^{2+}$. The bands at 29 590 and 34 250 cm^{-1} (assigned to the d–d transitions ${}^1A_{1g}$–${}^1T_{1g}$ and ${}^1A_{1g}$–${}^1T_{2g}$, respectively) yield $10Dq = 30\,700$ and $B = 290$ cm^{-1} {*cf.* $[Ru(en)_3]^{2+}$ (en = ethylenediamine):[7] $10Dq = 28\,100$, $B = 420$ cm^{-1}, and $[Ru(H_2O)_6]^{2+}$: $10Dq = 19\,800$, $B = 490$ cm^{-1}}.[8] Thus, compared with amines and water, the 9S3 thioether donor set imposes a much stronger ligand field and nephelauxetic effect.

In addition to showing the efficacy of the thio crown ether approach for complexation of second-row transition metal ions, the present results illustrate the particularly strong interaction between Ru^{II} and thioethers, and provide a benchmark for future structural studies of this interaction.

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References

1 J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1202; J. R. Hartman, E. J. Hintsa, and S. R. Cooper, *J. Am. Chem. Soc.*, 1986, **108**, 1208; *J. Chem. Soc., Chem. Commun.*, 1984, 386; E. J. Hintsa, J. R. Hartman, and S. R. Cooper, *J. Am. Chem. Soc.*, 1983, **105**, 3738; S. C. Rawle, J. R. Hartman, D. J. Watkin, and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1986, 1083.

2 D. Sellman and L. Zapf, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 807.

3 H.-J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1986, **25**, 2400.

4 T.-F. Lai and C.-K. Poon, *J. Chem. Soc., Dalton Trans.*, 1982, 1465.

5 D. P. Riley and J. D. Oliver, *Inorg. Chem.*, 1986, **25**, 1821, 1825.

6 R. S. Glass, G. S. Wilson, and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068; W. N. Setzer, C. A. Ogle, G. S. Wilson, and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.

7 H. Schmidtke and D. Garthoff, *Helv. Chim. Acta*, 1966, **49**, 2039.

8 E. Mercer and R. R. Buckley, *Inorg. Chem.*, 1965, **4**, 1692.