

Crown Thioether Chemistry. Synthesis and Structure of the d^0 Re^{VII} Complex $[\text{ReO}_3(9\text{S3})]^+$ (9S3 = 1,4,7-Trithiacyclononane)

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The first crown thioether complex of a d^0 ion, $[\text{ReO}_3(9\text{S3})]^+$, has been prepared by reaction of NH_4ReO_4 with 1,4,7-trithiacyclononane (9S3) in acidified MeCN and characterized by X-ray, IR, Raman, and ^{17}O NMR methods.

Owing to their weak σ -donor and moderate π -acid character thioethers generally stabilise lower oxidation states of metal ions.¹ Accordingly, most thioether co-ordination complexes involve d^n ions with $n \geq 5$. Consonant with this generalization, the recently reported $[\text{Re}(\text{CO})_3(9\text{S3})]^+$ cation² (9S3 = 1,4,7-trithiacyclononane) formally contains Re^{I} , although few $\text{Re}(\text{thioether})_n$ complexes with $n \geq 3$ are known.³ We report here the first crown thioether complex of Re^{VII} , or indeed of any d^0 ion. The results reported here suggest that the scope of crown thioether chemistry may extend to higher formal oxidation states than has heretofore been considered.

Reaction of NH_4ReO_4 with 9S3 in MeCN containing HBF_4 yields $[\text{ReO}_3(9\text{S3})(\text{BF}_4)]^+$ as a yellow powder.[†] Recrystallisation from nitromethane by ether diffusion gave yellow crystals suitable for X-ray structural analysis.[‡] In the $[\text{ReO}_3(9\text{S3})]^+$ cation three thioether groups and three oxo ligands coordinate facially to Re^{VII} (Figure 1). The ReS_3O_3 co-ordination sphere deviates from octahedral geometry through constriction of the S–Re–S bond angles (average 79.5°) from the octahedral value and corresponding dilation of O–Re–O ones (to 107.4°). These distortions result from the small bite of 9S3 coupled with repulsion between the oxo groups (all $\text{O} \cdots \text{O}$ 2.72 Å).

Metal–ligand bond distances indicate strong Re–O but weak Re–S bonding. While no structural data for Re^{VII} -thioether complexes appear in the literature, comparison with the sum of the ionic radii [$r(\text{Re}^{\text{VII}}) + r(\text{S}^{2-}) = 2.37$ Å]⁴ implies

weak Re–S bonds (average 2.58 Å) in the title compound. In fact, Re–S distances in $[\text{ReO}_3(9\text{S3})]^+$ exceed those in $[\text{Re}(\text{CO})_3(9\text{S3})]^+$ (2.46 Å),² despite the greater covalent radius of Re^0 . Conversely, Re–O bond lengths (average 1.69 Å) indicate significantly stronger Re–O bonding than in $[\text{ReO}_3(\text{L})]^+$ [$\text{L} = 9\text{N3}$ ($9\text{N3} = 1,4,7$ -triazacyclononane), 1.756 Å;⁵ $\text{L} = \text{C}_5\text{Me}_5$ 1.75 Å (estimated)⁶] or even in KReO_4 (1.723 Å),⁷ presumably reflecting greater $\text{Re} \leftarrow \text{O}$ π -donation. Metal–ligand distances therefore suggest that 9S3 tenuously

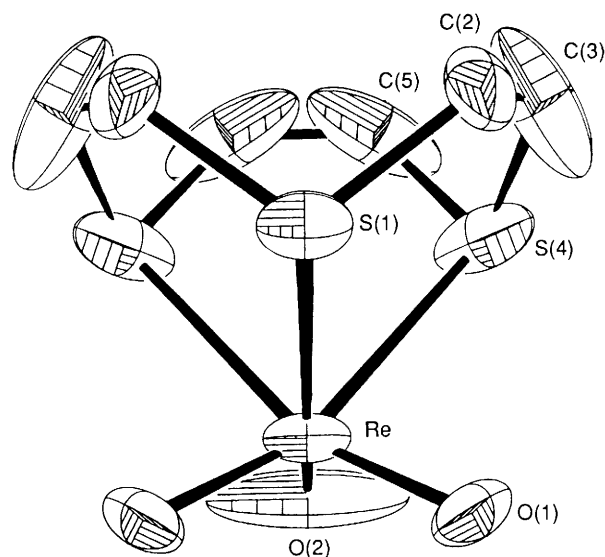


Figure 1. ORTEP view of $[\text{ReO}_3(9\text{S3})]^+$ (tetragonal modification). Selected bond lengths (Å) and angles ($^\circ$): Re–S(1) 2.564(4), Re–S(4) 2.585(5), Re–O(1) 1.687(10), Re–O(2) 1.689(16), S(1)–Re–S(4) $79.9(1)$, S(4)–Re–S(4') $79.2(2)$, S(1)–Re–O(1) $84.3(3)$, S(4)–Re–O(1) $159.1(3)$, S(1)–Re–O(2) $159.5(5)$, S(4)–Re–O(2) $84.3(4)$, O(1)–Re–S(4') $84.7(3)$, O(1)–Re–O(2) $107.3(4)$, O(1)–Re–O(1') $107.4(7)$.

[†] HBF_4 (2.0 ml, 54% in Et_2O) was added dropwise to a mixture of NH_4ReO_4 (0.27 g 1.0 mmol) and 9S3 (0.38 g 2.1 mmol) in 30 ml MeCN. The resulting solution gradually became yellow and after 6 h deposited a pale yellow solid, which was filtered, washed several times with ether, and dried in air. Yield: 0.5 g (97%). Satisfactory elemental analyses were obtained for $\text{ReC}_6\text{H}_{12}\text{S}_3\text{O}_3\text{BF}_4$.

[‡] Crystal data for $[\text{ReO}_3(9\text{S3})(\text{BF}_4)]^+$: $\text{C}_6\text{H}_{12}\text{O}_3\text{S}_3\text{BF}_4\text{Re}$, tetragonal, space group $P4_2/m$ ($C_{4h}/2$), $a = 11.129$ (6), $c = 10.954$ (5) Å, $U = 1356.7$ Å³, $F(000) = 944$, $Z = 4$, $D_c = 2.45$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 9.56$ mm⁻¹, $T = 295$ K, $R(F^2) = 0.054$; $R_w(F^2) = 0.049$. The intensities and lattice parameters of a yellow spherical crystal of $[\text{ReO}_3(9\text{S3})(\text{BF}_4)]^+$, $0.23 \times 0.25 \times 0.28$ mm, were measured on an AED II/Syntex R3 diffractometer. The lattice parameters were obtained from a least squares fit to the setting angles of 41 reflections with $15 < 2\theta < 30^\circ$. An empirical absorption correction was carried out with ψ scans of seven reflections with $8 < 2\theta < 49^\circ$. The structure was solved by standard Patterson and difference Fourier syntheses through use of SHELXTL PLUS, Program for Crystal Structure Determination, G. M. Sheldrick, with scattering factors taken from International Tables for Crystallography, Kynoch, Birmingham, England, 1974. Disorder of the cation across a mirror plane [manifested by eclipsing of the S(1)–C(2)–C(3)–S(4) linkages] and of the BF_4^- anions limits the precision of the structure. 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.

Table 1. Comparison of $[\text{ReO}_3(\text{L})]^+$ complexes.

Ligand	$\delta(^{17}\text{O})$ /ppm ^a	$d(\text{Re}-\text{O})$ /Å	$\nu(\text{Re}-\text{O})$ (Raman)/cm ⁻¹	Ref.
9S3	775	1.69	933, 902 (934, 920, 909)	This work
$\text{Me}_3\text{-}9\text{N3}$	747	—	920, 900	8
9N3	728	1.76	945, ^b 920	5, 8
9N3–H	703	—	920–840	8
C_5Me_5	646	—	909, 878 (907, 889, 874)	6

^a Relative to H_2O . ^b The higher frequency band previously reported is now assigned to a ligand vibration; K. Wiegardt, personal communication.

perches on the hard acid Re^{VII} centre, which it can do by virtue of the charge neutralisation offered by the three strongly bound oxo groups.

^{17}O NMR and vibrational spectroscopic results (Table 1) support this contention. ^{17}O NMR resonances in the Re^{VII} complexes $[\text{ReO}_3(\text{L})]$ (charges omitted) shift to higher field across the series C_5Me_5 , $9\text{N}3\text{-H}$ (the deprotonated form of $9\text{N}3$), $9\text{N}3\text{ Me}_3\text{-}9\text{N}3$, and $9\text{S}3$ (646,⁶ 703,⁸ 728,⁸ 747, and 775 ppm vs. H_2O , respectively) and thereby reflect progressively diminishing electron density at the oxo groups. Similarly Re-O stretching frequencies (Table 1)⁸ increase in the order C_5Me_5 , $\text{Me}_3\text{-}9\text{N}3$, $9\text{N}3$, $9\text{N}3\text{-H}$, and $9\text{S}3$, as the increasing π -acidity of L promotes greater $\text{Re} \leftarrow \text{O}$ π -donation. Thus, like the structural results, ^{17}O NMR chemical shifts and Re-O stretching frequencies indicate especially strong Re-O bonding in $[\text{ReO}_3(9\text{S}3)]^+$, which in turn implies correspondingly weak Re-S interaction.

The title compound represents the first example of a crown thioether complex of a d^0 transition ion, *i.e.*, one that has achieved group valence. Thioethers are generally considered to have weak affinity for metal ions in high oxidation states. Hence the surprising existence of this Re^{VII} -thioether complex raises the possibility that crown thioether chemistry may have greater scope than has been previously suspected.

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