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The Preparation and Structure of $[Me_4N][ReS(SCH_2CH_2S)_2]$, a Monomeric Re(V) Dithiolate-complex with a Terminal Sulphido-ligand

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Although the tetrahedral species $[MS_4]^{n-}$ (M = V, Mo, W, Re, n = 1, 2, 3) are known [1], five- and six-coordinate monomeric complexes with terminal sulphido-groups are comparatively rare for these elements [2, 3]. In the course of a systematic study of thiolato-complexes of molybdenum and rhenium we have prepared the anionic species $[ReS(SCH_2CH_2S)_2]^-$. This represents the first non-tetrahedral monomeric rhenium complex with a terminal sulphido-ligand.

The complex was prepared by reaction of $K_2[ReCl_6]$ with excess of 1,2-ethanedithiol in refluxing methanol in the presence of triethylamine. Addition of tetraalkylammonium or tetraphenylphosphonium salts induced crystallisation of the complex as a brown crystalline solid. The analogous oxo-complex $[ReO(SCH_2CH_2S)_2]^-$ was previously prepared directly from $Na[ReO_4]$ [4] but we have found it more conveniently prepared from $[ReOCl_3(PPh_3)_2]$ by reaction with an excess of dithiolate dianion in refluxing methanol in 80–90% yield. Partial substitution of the oxo-group by terminal sulphide can be achieved by reaction of the oxo-complex with P_2S_5 but the ensuing mixture is difficult to separate.

The terminal sulphido-group undoubtedly arises from dealkylation of the dithiolate ligand. Although generation of sulphide by dealkylation is well documented for monodentate thiols this is the first example of its occurrence with a dithiol. The reaction does not proceed with 1,3-propanedithiol and large amounts of ethylene (30% based on Re present) are generated during sulphide formation. The sulphido-complex is also formed in reactions of $[ReCl_4(PPh_3)_2]$ and $[ReCl_2N(PPh_3)_2]$ with ethanedithiol, whereas with arylthiols the nitrogenous ligands are retained to give crystalline products in good yield [5].

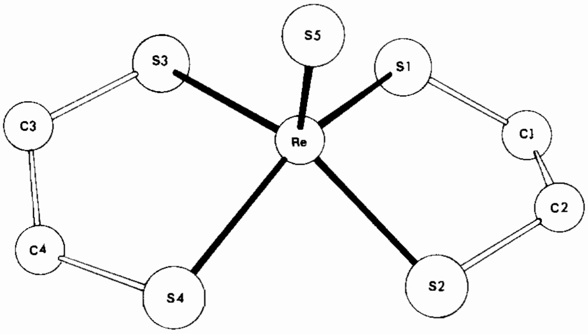

Fig. 1. Perspective view of $[ReS(SCH_2CH_2S)_2]^-$ showing atom-labelling scheme. Some important bond lengths (Å) and angles (°) are: Re–S1, 2.290(2); Re–S2, 2.312(2), Re–S3, 2.308(2); Re–S4, 2.285(2); Re–S5, 2.104(2); S1–Re–S5, 110.1; S2–Re–S5, 108.6(1); ∠S3–Re–S5, 106.2(1); ∠S4–Re–S5, 111.5(1); ∠S1–Re–S4, 138.4(1); ∠S2–Re–S3, 145.2(1); ∠S1–Re–S3, 83.8(1); ∠S3–Re–S4, 85.0(1); ∠S4–Re–S2, 82.0(1); ∠S1–Re–S2, 84.8(1)

Experimental

All reactions were carried out in dry solvents under nitrogen. $K_2[ReCl_6]$ [6] and $[ReOCl_3(PPh_3)_2]$ [7] were prepared by literature methods.

Tetraphenylphosphinium Bis(1,2-ethanedithiolato)-sulphidorhenium(V)

$K_2[ReCl_6]$ (1.0 g, 2.0 × 10^{-3} mol), $HSCH_2CH_2SH$ (1.20 g, 1.3 × 10^{-2} mol) and Et_3N (0.85 g, 8.4 × 10^{-3} mol) were heated in methanol under reflux (20 ml) for 3 h. After cooling and filtering small amounts of brown precipitates, $[Ph_4P]Br$ (3.0 g) was added, giving the complex as a brown microcrystalline solid. $[Me_4N][ReS(SCH_2CH_2S)_2]$ was prepared analogously using $[Me_4N]Br$, $[Ph_4P][ReO(SCH_2CH_2S)_2]$ was prepared analogously starting from $[ReOCl_3(PPh_3)_2]$.

Crystals of the complex $[Me_4N][ReS(SCH_2CH_2S)_2]$ suitable for X-ray structure determination were obtained from dichloromethane–diethylether. *Crystal Data* monoclinic space group $P2_1/c$, a = 9.539(2), b = 15.123(3), c = 21.815(3) Å, β = 93.58(1)°, V = 3140.9(9) Å^3; Z = 8. 4718 reflections collected, 3329 used to give R value of 0.029; Mo-K_α radiation, Nicolet R3m diffractometer.

An ORTEP view of the molecule is presented in Fig. 1 together with selected bond lengths and angles. The structure of the $[ReS(SCH_2CH_2S)_2]^-$ anion has overall approximately square pyramidal geometry

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with the terminal sulphido-ligand occupying the apical site. The Re atom is displaced 0.4 Å above the plane of mercaptide sulphurs, with an Re–S distance of 2.104(2) Å. The mercaptide sulphurs are symmetrically disposed about the Re, the chelated ligand imposing little or no distortion. The structure is analogous to that of $[TcO(SCOCH_2S)_2]^-$ and other square pyramidal Re complexes such as $[ReOX_4]^-$ and $[ReN(S_2CNEt_2)_2]$, all with the strongly π-bonding ligand in the apical site.

A band at 517 cm^{-1} in the i.r. spectrum of the anion is assigned to ν(Re–S), compared to the values of 486 and 501 cm^{-1} (Raman) found in ReO_3S^-. The cyclic voltammetry of the species $[ReY(SCH_2CH_2S)_2]^-$ (Y = O, S) in CH_3CN with Pt electrode and $[Bu^n_4N][BF_4]$ support electrolyte was examined over the range +1.9 V to –2.2 V *vs.* S.C.E. Both complexes oxidised irreversibly at +0.73 (oxo) and +0.8 volts (sulphido) respectively. The oxo-complex did not reduce below –2.2 volts *vs.* S.C.E whereas the sulphido-complex reduced in quasi-reversible one-electron process at –1.83 volts. This supports the contention advanced as result of studies of molybdenum dinuclear oxo- and sulphido-complexes that replacement of oxide by sulphide renders the complexes easier to reduce and makes the reduced products more stable.

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