The Preparation and Structures of Trigonal-Bipyramidal Molybdenum and Tungsten Nitrosyl Thiolato-complexes. $[Mo(SPh)_4(NO)]^-$ and $[WCl(SPh)_3(NO)]^-$

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The nitrosonium ion NO^+ is isoelectronic with N_2, and co-ordinated NO is formally analogous to N_2H, the presumed primary intermediate in N_2 protonation. Moreover the position of ν(NO) in the IR spectrum provides a useful probe of the electronic state of the metal. As part of our programme of studying molybdenum and tungsten thiolato complexes we here report the preparation and X-ray crystal structures of the first molybdenum and tungsten nitrosyls with monodentate thiolates. Previously reported mononuclear nitrosyl complexes with sulphur ligands are $[Mo(dtc)_3(NO)]$ [1], $[Mo(dtc)_2(NO)_2]$ [2] (dtc = dithiocarbamate), $[Mo(mnt)_2(NO)]^-$ and $[Mo(mnt)_2(NO)_2]^{2-}$ [3] (mnt = maleonitrile dithiolate). Several cluster nitrosyls with sulphido-ligands have also been reported [4].

The chloro-nitrosyl complex $[MoCl_3(NO)(PPh_3)_2]$ [5] reacts with excess aryl thiol in methanol in the presence of triethylamine to give red $[Et_3NH][Mo(SPh)_4(NO)]$ (*I*). The complexes are most conveniently isolated as the tetraphenylphosphonium salts, and the reaction proceeds analogously for a range of aryl thiols. However the same reaction with t-butyl mercaptan gives $[MoCl(SBu^t)_3(NO)]^-$ even after protracted reaction periods. A more convenient preparation of (*I*) and its analogues is from the polymeric nitrosyl hydroxylamido-complex derived from molybdate and hydroxylamine in aqueous solution [6]. The polymeric species reacts with excess aryl thiolate anion in refluxing methanol to give $[Mo(SPh)_4(NO)]^-$ in good yield.

The tungsten nitrosyl $[WCl_3(NO)(PPh_3)_2]$ does not undergo complete substitution even with aryl thiolates, and under forcing conditions yellow $[WCl(SPh)_3(NO)]^-$ (*II*) is produced. The complex is again isolated as a tetraphenylphosphonium salt.

The complexes are air-stable in the solid and in solution and the conductivity of their nitrobenzene solutions confirms that they are 1:1 electrolytes. The IR spectrum of complex (*I*) shows ν(NO) at 1675 cm^{-1} compared with 1694 cm^{-1} for $[MoCl_4(NO)]^-$ and suggests a relatively electron rich metal site. The ^1H NMR spectrum of $[PPh_4][Mo(SC_6H_4\text{-}4Me)_4(NO)]$ shows two resonances, ratio 3:1, for the methyl substituents on the thiols, suggesting a trigonal bipyramidal geometry. The inequivalence of the thiolate aryl groups persists even on heating the solutions to 50 °C in $CDCl_3$.

In view of the unusual trigonal bipyramidal geometry apparent in solution X-ray crystal structure determinations were carried out for complexes *I* and *II*. Crystal data for *I*, monoclinic, space group $P2_1/n$ with $a = 10.9960(2)$ Å, $b = 16.127(35)$ Å, $c = 18.4950(35)$ Å, $\beta = 105.94(1)°$; $V = 3229.3(11)$ Å^3; $Z = 4$. 4187 reflections collected, 2786 used in solution to give $R = 0.516$. Crystal data for (*II*), monoclinic, space group $P2_1/c$ with $a = 10.809(1)$ Å, $b = 19.677(3)$ Å, $c = 19.250(3)$ Å, $\beta = 105.85(1)°$, $V = 3938.3(9)$ Å^3, $Z = 4$. 4122 reflections collected, 1895 reflections used in solution to give $R = 0.0375$.

The structure of $[Mo(SPh)_4(NO)]^-$ is shown in Fig. 1 together with selected bond-lengths and angles. The geometry about the molybdenum is essentially trigonal bipyramidal with the NO ligand in an axial position. The Mo–N–O system is essentially linear suggesting that the NO ligand is functioning as a formal three electron donor. The overall electron

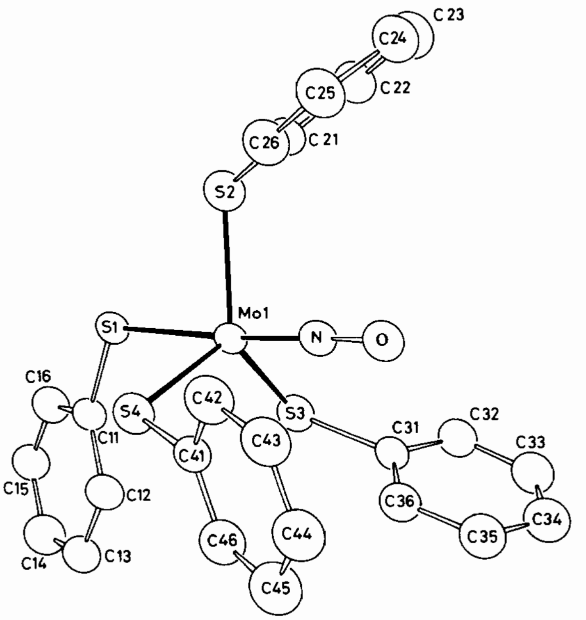

Fig. 1. An ORTEP representation of the structure of $[Mo(SPh)_4(NO)]^-$ showing the atom-labelling scheme. Selected bond lengths (in Å) and bond angles (in °): Mo–N, 1.766(6); Mo–S1, 2.524(2); Mo–S2, 2.337(2); Mo–S3, 2.326(3); Mo–S4, 2.317(2); N–O, 1.188(8). N–$\hat{Mo}$–S1, 175.8; N–$\hat{Mo}$–S2, 93.9(2); N–$\hat{Mo}$–S3, 95.3(2); N–$\hat{Mo}$–S4, 94.6; S2–$\hat{Mo}$–S3, 122.0(1); S3–$\hat{Mo}$–S4, 117.5(1); S2–$\hat{Mo}$–S4, 118.5(1); Mo–$\hat{N}$–O, 178.7(5).

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count for the complex is fourteen, but despite this and the five-co-ordination observed there is no tendency to form thiolato-bridged oligomers. The complex [MoO(SPh)$_4$]$^-$ is also monomeric and it appears that small multiply-bonded ligands such as oxo and nitrosyl militate against bridge formation by utilising metal orbitals for the multiple bonds. The related chloro-species [MoCl$_4$(NO)]$^-$ has a square pyramidal geometry and the change in geometry observed for complex (*I*) presumably reflects the maximisation of π-bonding for the thiolato-ligands in the equatorial plane. The disposition of the three equatorial thiolato-phenyl groups *endo* to an axial substituent appears to be a common feature of the complexes of general type [MXY(SPh)$_3$]$^-$ such as [Re(SPh)$_3$(MeCN)(PPh$_3$)]. The Mo–S distances in the equatorial plane are typical for molybdenum thiolates and are approximately equal (average 2.33 Å), but the Mo–S distance for the axial thiolate is longer at 2.524(2) Å. This difference probably reflects the occupation of axial and equatorial sites rather than any *trans* effect from the NO ligand.

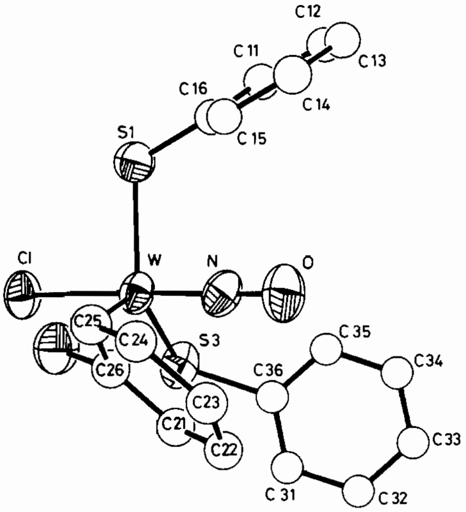

Fig. 2. An ORTEP representation of the structure of [WCl(SPh)$_3$(NO)]$^-$ showing the atom-labelling scheme. Selected bond-lengths (in Å) and bond angles (in °): W–N, 1.755(13); W–S1, 2.328(4); W–S2, 2.315(4); W–S3, 2.320(4); N–O, 1.235(17); W–Cl, 2.490(4). Cl–Ŵ–N, 177.8(4); N–Ŵ–S1, 96.0(4); N–Ŵ–S2, 95.0(4); N–Ŵ–S3, 96.5(4); W–N̂–O, 178.5(11); S1–Ŵ–S3, 119.3(1); S2–Ŵ–S3, 118.8(1); S1–Ŵ–S2, 118.8(1).

The structure of [WCl(SPh)$_3$(NO)]$^-$ (*II*) is shown in Fig. 2 together with selected bond lengths and angles. The overall structure is directly analogous to (*I*) with overall trigonal bipyramidal geometry. The equatorial thiolate aryl groups are again disposed *endo* with respect to the nitrosyl. This configuration, also favoured for the molybdenum complex, permits the sulphur non-bonding electron pairs to be directed away from the concentration of electron density in the metal–nitrogen multiple bond. The thiolate sulphurs of both (*I*) and (*II*) can form bridges to other metal ions to give a range of heteronuclear clusters which will be described in detail elsewhere.

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