Alkylation of $[WS_4]^{2-}$: Synthesis and Structural Characterization of the Ethylthiolatotrithiotungstate(VI) Anion

P. Michael Boorman,* Meiping Wang and Masood Parvez

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Reaction of $[PPh_4]_2[WS_4]$ with ethyl bromide yields the tetraphenylphosphonium salt of the title anion **1**, for which an X-ray structure determination reveals no evidence for an intramolecular redox reaction, but concentrated solutions undergo rapid reactions leading to $[W_3S_9]^{2-}$ and Et_2S_x (x = 1–3).

Sulfur ligated complexes of molybdenum and tungsten continue to be a very active area of research, prompted by the relevance of this chemistry to both biological[1] and industrial[2] catalytic processes. Mononuclear, terminal thiolate complexes of Mo and W are still very rare, especially for the higher oxidation states of these metals.[3] Successful isolation of stable terminal thiolato complexes has usually been achieved by using hindered arylthiolate ligands, and lower oxidation states of the central Group 6 metal.[4] We report here the preparation and structural characterization of a unique, terminal tungsten(VI) alkylthiolate complex, $[PPh_4][WS_3(SEt)]\cdot THF$ **1**, which has been prepared by the alkylation of tetrathiotungstate(VI) under carefully controlled conditions. Conversion of $[WS_4]^{2-}$ to sulfido clusters of higher nuclearity can be provoked by either protonation[5–7] or alkylation.[8,9] The mechanisms of the alkylation reactions, in particular, are incompletely understood, hence the isolation of **1** may be an important step in exploring how the alkylation reactions proceed. The use of thiomolybdate and thiotungstate anions as reagents for the conversion of organic halides to organic disulfides has been reported,[8,10] hence these reactions are of relevance to synthetic organic chemistry as well as to metal sulfide cluster synthesis.

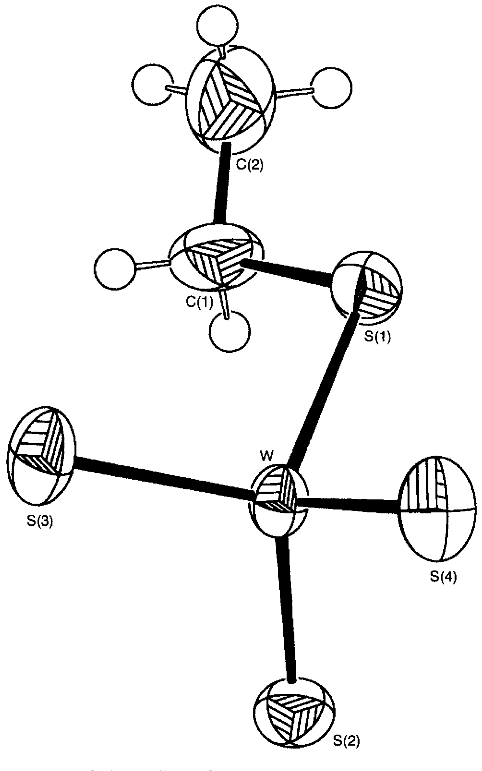

Fig. 1 Structure of the anion of $(Ph_4P)[WS_3(SEt)]\cdot THF$. Selected bond lengths (Å) and angles (°): W–S(1) 2.323(3), W–S(2) 2.163(3), W–S(3) 2.156(3), W–S(4) 2.142(3), S(1)–C(1) 1.86(1), C(1)–C(2) 1.47(2), S(1)–W(1)–S(2) 111.1(1), S(1)–W(1)–S(3), 108.2(1), S(1)–W(1)–S(4) 103.4(1), S(2)–W(1)–S(4) 110.7, S(1)–C(1)–C(2) 110.0(10), W(1)–S(1)–C(1) 105.2(4).

Compound **1** was prepared by the following procedure.† To a suspension of $[Ph_4P]_2[WS_4]$ (0.54 g, 0.54 mmol) in MeCN (50 ml) was added EtBr (0.73 g, 6.7 mmol) at 0 °C. The reaction temperature was allowed to rise to 21 °C and the solution was stirred until all the yellow $[Ph_4P]_2WS_4$ powder reacted and formed a clear, bright red solution. This solution was cooled to 0 °C then reduced in volume to *ca.* 10 ml by pumping. THF (40 ml) was used to extract the red compound from the by-product Ph_4PBr in the sticky residue, a process that was repeated three times. The final red solution was reduced in volume to 5 ml and kept at −20 °C; after 12 h, red crystals were obtained, which were washed with diethyl ether and dried (yield: 0.28 g, 75%).‡

An X-ray diffraction study of a crystal of **1** was undertaken,§ proving its identity as $[PPh_4][WS_3(SEt)]\cdot THF$. The structure of the anion is shown in Fig. 1. The bond lengths and angles show that the anion is correctly described as $[W(=S)_3(SEt)]^-$, with the formal oxidation state of W as +6. There is no indication that an internal redox reaction has begun to occur, as would be suggested by a close S···S(Et) contact. Thus the initial step in the degradation of this anion to $[W_3S_9]^{2-}$ and Et_2S_2 is likely to be a bimolecular process. From ^1H NMR studies of the reaction of $[WS_4]^{2-}$ with ethyl halides we have found that the first step is monoalkylation and this is followed by a series of other steps. Surprisingly, however, there is no tendency by the $[WS_3(SEt)]^-$ anion to undergo a second alkylation reaction. When **1** is dissolved in MeCN it is relatively stable at concentrations of <0.01 mol dm^{-3}; however, at higher concentrations the production of Et_2S_2, Et_2S_3 and Et_2S has been observed, along with a black precipitate believed to be WS_3. The reaction is both temperature and concentration dependent. Attempts to reverse the synthetic alkylation reaction by mixing solutions of **1** and $[PPh_4]Br$ in CD_3CN showed no indication of the formation of EtBr, and hence dealkylation is clearly not a thermodynamically favoured process here. A more detailed study of the reactions of **1** is now underway, including reactions with $[WS_3(SR)]^{2-}$ anions where R is a group other than ethyl.

The relationship between the chemistry of $[WS_4]^{2-}$ and $[MoS_4]^{2-}$ is of interest. To date we have found that the Mo analogue of **1** is too labile to isolate in a pure form, even in dilute solution and at low temperature. MoS_3 is rapidly precipitated from the solution. Another interesting comparison is with the chemistry of Nb and Ta. Here, the $[MS_4]^{3-}$ ions have proved difficult to isolate, whereas several mixed sulfido(thiolato)-metallate anions have been described.[11,12] The other correlation that will be interesting is that between protonation and alkylation reactions of $[WS_4]^{2-}$. The anion $[WS_3SH]^-$ was prepared and characterized by Muller *et al.*,[13] and is widely believed to be an intermediate in the condensation reactions of $[WS_4]^{2-}$ induced by protonation. It is hoped that the alkylation reactions will provide plausible models for these rapid and synthetically important reactions.

We acknowledge the financial support of the NSERC of Canada, and we thank Dr X. Gao and Dr H.-B. Kraatz for helpful discussions.

Received, 31st January 1995; Com. 5/00586H

Footnotes

† All handling procedures were carried out in an atmosphere of dry nitrogen.

‡ Satisfactory elemental analyses were obtained for **1**, although some loss of the solvent THF molecule occurred.

Selected spectroscopic data for **1**: ^{1}H NMR (200 MHz, $CDCl_3$), δ 7.2–7.8 (Ph, 20H), 3.18 (CH_2, 2H), 1.29 (CH_3, 3H). ^{13}C NMR (200 MHz, $CDCl_3$), δ 135.7, 134.5, 130.6, 116.5 (Ph, 6C), 35.9($-SCH_2-$), 17.2 ($-CH_3$). IR (ν/cm^{-1}, polyethylene disc) (W=S) 525(s), 491(2), (W–S) 466(m), 455(sh), 374(w). UV–VIS, λ/nm (ε 1×10^3 dm^3 mol^{-1} cm^{-1}) 525(1.3), 443(2.0), 385(6.6), 336(2.8), 296(6.4), 273(16), 240(20).

§ *Crystal data* for **1**: $C_{26}H_{25}PS_4W\cdot 1THF$, $M = 752.654$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.360(2)$, $b = 19.346(10)$, $c = 17.330(3)$ Å, $\beta = 96.19(2)°$, $U = 3120(1)$ Å^3, $D_c = 1.602$ g cm^{-3}, $Z = 4$, $F(000) = 1496\ e$, $T = 170$ K. 5704 Unique data were collected using a Rigaku AFC6S diffractometer, Mo-Kα radiation. Final $R = 0.041$ and $R_w = 0.040$ for 3232 observations with $I > 3\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 R. R. Chianelli, *Catal. Rev. Sci. Eng.*, 1984, **26**, 361; M. Rakowski DuBois, *Chem. Rev.*, 1989, **89**, 1; T. R. Halbert, T. C. Ho, E. I. Stiefel, R. R. Chianelli and M. Daage, *J. Catal.*, 1991, **130**, 116.

2 *Molybdenum Enzymes*, ed. T. G. Spiro, Wiley, New York, 1985; *Molybdenum Enzymes, Cofactors and Model Systems*, ed. E. I. Stiefel, D. Coucouvanis and W. E. Newton, *ACS Symp. Ser.*, 535, American Chemical Society, Washington DC, 1993; J. H. Enemark and C. G. Young, *Adv. Inorg. Chem.*, 1993, **40**, 1.

3 I. G. Dance, *Polyhedron*, 1986, **5**, 1037; P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.

4 P. J. Blower, J. R. Dilworth, J. Hutchinson, T. Nicholson and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 2639; P. T. Bishop, J. R. Dilworth, J. Hutchinson and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1986, 967.

5 E. Koniger-Ahlborn and A. Müller, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 573; A. Müller, W. Rittner, A. Neumann, E. Koniger-Ahlborn and R. G. Bhattacharyya, *Z. Anorg. Allg. Chem.*, 1980, **461**, 91; A. Müller, E. Diemann, U. Wienboker and H. Bogge, *Inorg. Chem.*, 1989, **28**, 4046.

6 F. Sécheresse, J. Lefebvre, J. C. Daran and Y. Jeannin, *Inorg. Chem.*, 1982, **21**, 1311; C. Simonnet-Jegat, R. A. Toscano, F. Robert, J.-C. Daran and F. Sécheresse, *J. Chem. Soc., Dalton Trans.*, 1994, 1311.

7 V. P. Fedin, Y. V. Mironov, M. N. Sokolov, Y. I. Mironov and V. E. Fedorov, *Inorg. Chim. Acta*, 1989, **163**, 65.

8 P. Dhar and S. Chandrasekaran, *J. Org. Chem.*, 1989, **54**, 2998.

9 K. Hanewald and G. Gattow, *Z. Anorg. Allg. Chem.*, 1981, **476**, 159.

10 D. N. Harpp and J. G. MacDonald, *Tetrahedron Lett.*, 1984, **25**, 703.

11 D. Coucouvanis, S.-J. Chen, B. S. Mandimitsura and C. G. Kim, *Inorg. Chem.*, 1994, **33**, 4429.

12 D. Coucouvanis, S. Al-Ahmad, C. G. Kim and S.-M. Koo, *Inorg. Chem.*, 1992, **312**, 2996.

13 E. Koniger-Ahlborn, H. Schulze and A. Müller, *Z. Anorg. Allg. Chem.*, 1977, **428**, 5.