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Reaction of Alkyne with W–S Systems: Synthesis and Characterization of Dinuclear W(V) Dithiolene Complex, $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2C_2(COPh)_2)_2]$

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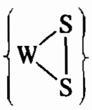
The chemistry of Mo–S systems is full of wonders and anomalies [1–4]. Recently, an interesting reaction of $(Et_4N)_2[Mo_2O_2(\mu\text{-}S)_2(S_2)_2]$ [4] with an activated alkyne, dimethyl acetylene dicarboxylate was reported [5]. In the above reaction the formation of vinyl disulfide, contrary to the expected more symmetrical product, *i.e.* the dithiolene complex, is surprising. This has been explained on the basis of less energy difference between the 4d orbital of Mo and the 3p orbital of S [6, 7]. It has also been observed that with the pure $Mo–S_4$ unit, only cycloaddition takes place and the dithiolene complex is formed [6, 8]. Nothing is known about the reactivity of tungsten–sulfur systems in this regard. Hence, we decided to check the generalization made in the case of Mo–S systems [6] with W–S systems and as the first part of this we report the reaction between $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ (**1**) [9] and dibenzoyl acetylene [10].

Experimental

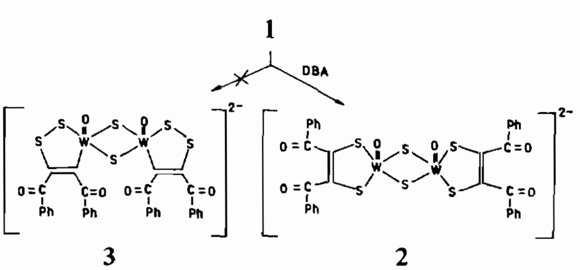
$(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2C_2(COPh)_2)_2]$ (**2**) was obtained by reacting **1** (426 mg, 0.5 mmol) and dibenzoyl acetylene (DBA) (234 mg, 1 mmol) in CH_3CN (15 ml). The dark reddish brown microcrystalline product **2** was obtained by adding EtOH and leaving it standing for two days. The crystals were filtered, washed with EtOH and ether respectively and dried under vacuum (yield, 130 mg, 20%). *Anal.* Calc. for $C_{48}H_{60}N_2O_6S_6W_2$. C, 43.63; H, 4.54; N, 2.12. Found: C, 43.59; H, 4.52; N, 2.04%. IR (KBr): 1660s (ν C=O); 1453s (ν C=C); 960s, 955sh (ν W=O) and 440 m cm^{-1} (ν $W–S_b$). Electronic spectrum (DMF), 382 (ϵ, 1.15×10^4) and 316 nm (3.18×10^4). ^1H NMR (DMSO-d_6), 1.1 (t, cation, CH_3, 24H), 3.2 (q, cation, CH_2, 16H) and 7.2–8.0 δ ppm (m, Ph, 20H).

Results and Discussion

The complex, $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ has side on bound S_2^{2-} ligands, *i.e.*



which on reacting with DBA may give the adduct having a vinyl disulfide ligand or dithiolene ligand. The ^{13}C NMR spectrum (DMSO-d_6) of **2** shows resonances at 6.97 and 51.43 δ ppm for the cation and 137.45, 132.35, 129.02, 127.97 (Ph); 150.45 (C=C) and 193.93 δ ppm (C=O) for the anion. None of these signals represent a carbon directly attached to tungsten [11]. As a check, a tris-dithiolene complex, $(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$ (**4**) was synthesized and ^{13}C NMR of this was compared with that of **2**. It was found that both the spectra are very similar suggesting the presence of the same ligand attached to W**. On the basis of these observations, we propose the formation of **2** containing dithiolene as the ligand (Scheme 1). Insertion of acetylene across the S–S bond rather than the W–S bond may be due to the larger difference in energy of the 5d orbital of W and the 3p orbital of S.



Scheme 1.

2 undergoes one electron irreversible oxidation at 0.97 V (SCE) and decomposes on reduction. XPS of the compound **2** shows a narrow symmetrical peak for S (2p) at 162.6 eV, indicating an effective

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$(Et_4N)_2[W(S_2C_2(COPh)_2)_3]$ was synthesized by reacting $(Et_4N)_2WS_4$ (190.6 mg, $\frac{1}{3}$ mmol), S (21.3 mg $\frac{3}{2}$ mmol) and DBA (234 mg, 1 mmol) in DMF (10 ml) and stirring at room temperature for 12 h. **4 was isolated by adding i-PrOH, then washing with EtOH, CS_2 and ether and drying under vacuum (yield, 165 mg, 37%). *Anal.* Calc. for $C_{64}H_{70}N_2O_6S_6W$: C, 57.39; H, 5.23, N, 2.09. Found: C, 56.65; H, 5.13; N, 1.89%. ^{13}C NMR (DMSO-d_6) 6.96, 51.41 δ ppm (cation); 138.45, 131.56, 128.93, 127.50 (Ph), 159.85 (C=C) and 193.91 δ ppm (C=O).

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mixing and complete loss of individual identity of the different types of sulfur present in the compound. The binding energies for tungsten in **2** are 33.4 ($4f_{7/2}$), 35.6 ($4f_{5/2}$), 246.7 ($4d_{5/2}$), 259.0 ($4d_{3/2}$) and 425.7 ($4p_{3/2}$) eV which are very close to the values found for its parent compound **1***.

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*Binding energies for W in the case of **1** are 33.9 ($4f_{7/2}$), 36.1 ($4f_{5/2}$), 246.7 ($4d_{5/2}$), 260.6 ($4d_{3/2}$) and 426.9 ($4p_{3/2}$) eV.

References

1 A. Müller, S. Sarkar, R. G. Bhattacharyya, S. Pohl and M. Dartman, *Angew. Chem., Int. Ed. Engl., 17,* 535 (1978).

2 A. Müller, W. O. Nolte and B. Krebs, *Inorg. Chem., 19,* 2835 (1980).

3 E. D. Simhon, N. C. Baenziger, M. Kanatzidis, M. Draganjac and D. Coucouvanis, *J. Am. Chem. Soc., 103,* 1218 (1981).

4 W. Clegg, N. Mohan, A. Müller, A. Neumann, W. Rittner and G. M. Sheldrick, *Inorg. Chem., 19,* 2066 (1980).

5 T. R. Halbert, W.-H. Pan and E. I. Stiefel, *J. Am. Chem. Soc., 105,* 5476 (1983).

6 D. Coucouvanis, A. Hajikyriacou, M. Draganjac, M. G. Kanatzidis and O. Ileperuma, *Polyhedron, 5,* 349 (1986).

7 J. Bernholc and N. A. W. Holzwarth, *J. Chem. Phys., 81,* 3987 (1984); J. Bernholc and E. I. Stiefel, *Inorg. Chem., 25,* 3876 (1986).

8 M. Draganjac and D. Coucouvanis, *J. Am. Chem. Soc., 105,* 139 (1982).

9 S. Sarkar and M. A. Ansari, *J. Chem. Soc., Chem. Commun.,* 324 (1986).

10 E. R. Lutz and W. R. Smithey Jr., *J. Org. Chem., 16,* 51 (1951).

11 E. O. Fischer, T. Selmayr, F. R. Kreissl and U. Schubert, *Chem. Ber., 110,* 2574 (1977); E. O. Fischer, T. Lother, G. Huttner, P. Friedrich, F. R. Kreissl and J. O. Besenhard, *Chem. Ber., 110,* 3397 (1977).