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One Pot Synthesis of Dinuclear Tungsten(V) Compounds Containing $[W_2XY(\mu\text{-}S)_2]^{2+}$ (X=O, S; Y=O, S) Cores by Thermally Induced Internal Electron-Transfer Processes

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Synopsis. New synthetic methods for the preparation of dimeric tungsten(V) complexes are described containing the core $[W_2XY(\mu\text{-}S)_2]^{2+}$ (X=O,S; Y=O,S). The synthesized complexes have been characterized by a variety of spectroscopic techniques. $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ has been found to react with cyanide to give $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$.

The tungsten-sulfur chemistry has received far less attention contrary to molybdenum-sulfur systems, partly due to the importance of molybdenum-sulfur systems in biology[1,2] and in catalysis[3,4] and partly due to the facile reactivity of molybdenum systems in terms of synthetic methodology. Recent observations place tungsten parallel to molybdenum in its biological aspects[5] as well as in its catalytic role.[6,7] Thus, there is a surge of new synthetic strategies to explore tungsten-sulfur chemistry.[8–10] But the synthesis of dinuclear tungsten(V)-sulfur complexes invariably involve multistep procedures.[8,10,11] Our present approach to form $[W_2O_2(\mu\text{-}S)_2]^{2+}$ core using externally induced, internal electron transfer reaction,[12] prompted us to search for a one-pot synthetic strategy for this type of complexes. In this paper we report the synthesis of a series of complexes containing $[W_2O_2(\mu\text{-}S)_2]^{2+}$, $[W_2OS(\mu\text{-}S)_2]^{2+}$ and $[W_2S_2(\mu\text{-}S)_2]^{2+}$ core with diethyl dithiocarbamate as ligand invoking intramolecular electron transfer.

Experimental

All the reactions were carried out under dry nitrogen atmosphere and in the absence of light unless otherwise specified. Solvents used were of analytical grade and were distilled before use but not degassed. Pyridine-d_5 (Aldrich) was used as received. Ammonium tetrathiotungstate, oxotrithiotungstate and dioxodithiotungstate were prepared by literature procedure.[13] Diethylammonium tetrathiotungstate and oxotrithiotungstate were prepared by our own method described below.

Infrared spectra were recorded on Perkin Elmer-580 spectrometer as KBr or CsI pressed pellets and referenced to polystyrene bands. Electronic spectra were recorded on Shimadzu UV-190 double beam spectrometer. NMR spectra were taken on Varian EM-390, 90 MHz spectrometer. XPS measurements were done on ESCALAB 510 photoelectron spectrometer using Al$K\alpha$ X-ray line (1486.6 eV) radiation. Binding energies were computed taking C ($1s_{1/2}$) binding energy (285.0 eV) as standard. Carbon, hydrogen, and nitrogen analyses were carried out at Microanalytical Laboratory, I.I.T, Kanpur (India) and sulfur was estimated as $BaSO_4$.

Synthesis of $(Et_2NH_2)_2WS_4$. Tungstic acid (5 g) was dissolved in a mixture of H_2O (10 ml) and Et_2NH (15 ml) by refluxing for 1 h. The solution was filtered and H_2S was passed rapidly for 4 h at 60 °C. The reaction mixture was cooled to obtain yellow crystals, which were washed with 2-propanol and ether. Found: C, 20.71; H, 5.42; N, 6.25%. Calcd for $C_8H_{24}N_2S_4W$: C, 20.86; H, 5.21; N, 6.08%. IR(KBr): ν(W-S) 460 cm^{-1}. Electronic spectrum: λ_{max} (in water) 387 (ε 7400 dm^3 mol^{-1}cm^{-1}) and 277 nm (8100).[13] Yield: 7.36 g (80%).

Synthesis of $(Et_2NH_2)_2WOS_3$. Tungstic acid (5 g) was refluxed in a mixture of H_2O (10 ml) and Et_2NH (10 ml) for 1.5 h, filtered, into which H_2S was passed rapidly for 30 min. at 60 °C. The solution was cooled and to this 2-propanol (50 ml) and ether (20 ml) were added. The yellow orange oily mass obtained was recrystallized from methanol/ether. Found: C, 20.71; H, 5.32; N; 6.28%. Calcd for $C_8H_{24}N_2OS_3W$: C, 21.62; H 5.40; N, 6.30%. IR(KBr) ν(W=O) s, 880, ν(W-S) 450 cm^{-1}. Electronic spectrum λ_{max} (in water) 375 (ε 1400 dm^3 mol^{-1}cm^{-1}), 332 (6150), and 270 nm (6200).[13] Yield: 6.48 g (73%).

Synthesis of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (1): Method A. To a solution of $(Et_2NH_2)_2WOS_3$ (888 mg, 2 mmol) in DMF (10 ml), CS_2 (2 ml) was added and the mixture was refluxed for 4 h. Addition of 2-propanol (10 ml) and ether (100 ml) to the cold solution, precipitated a small amount of green brown product, which was filtered off and the filtrate was kept overnight at room temperature to yield **1** as yellow needle shaped crystals which were washed with water, ethanol and finally with ether. The compound was recrystallized from dichloromethane/petroleum ether. Found: C, 15.90; H, 2.81; N, 3.48; S, 25.31%. Calcd for $C_{10}H_{20}N_2O_2S_6W_2$: C, 15.78; H, 2.63; N, 3.68; S, 25.26%. IR(KBr): ν(C=N) 1550, ν(W=O) 985, 970, $\nu(WS_2W)$ 470, 338. Electronic spectrum: λ_{max} (in CH_2Cl_2) 415 (ε 200 dm^3 mol^{-1}cm^{-1}), 332 (1500), and 296 nm (7600), ^{1}H NMR ($CDCl_3$): δ=3.54 (CH_2, q), 0.95 (CH_3, t). Yield: 290 mg (38%).

Method B. To a hot solution (130 °C) of $(NH_4)_2WO_2S_2$[13] (632 mg, 2 mmol) in DMF (10 ml), tetraethylthiuram disulfide (296 mg, 1 mmol) dissolved in DMF (5 ml) was added and the solution was cooled to 25 °C immediately. Addition of 2-propanol (20 ml) and ether (100 ml) yielded 340 mg (45%) of **1**, which was recrystallized as in method A.

Synthesis of $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (2): Method A. A solution of $(Et_2NH_2)_2WS_4$ (920 mg, 2 mmol) in DMF (10 ml) and CS_2 (2 ml) was refluxed for 4 h under nitrogen atmosphere and in the absence of light. To the cold solution (ca. 25 °C), 2-propanol (10 ml) and ether (100 ml) were added. A small amount of dark brown product precipitated. This was filtered off and the filtrate was left at room temperature for 24 h to yield compound **2** as dark red needle shaped crystals, which were washed with water, ethanol, and ether. The crude product was recrystallized from dichloromethane/petroleum ether and further purified by chromatography.[14] Found: C, 15.43; H, 2.40; N, 3.68; S, 28.43%. Calcd for $C_{10}H_{20}N_2S_8W_2$: C, 15.15; H, 2.52; N, 3.53; S, 28.28%. IR (KBr): ν(C=N) 1545, ν(W=S) 535, 525, $\nu(WS_2W)$ 460, 332. Electronic spectrum: λ_{max} (in CH_2Cl_2) 420 (ε 2200 dm^3 mol^{-1}cm^{-1}), 382 (6500), and 292 nm (30100), ^{1}H NMR ($CDCl_3$): δ=3.74 (CH_2, q), 1.08 (CH_3, t). Yield: 220 mg (ca. 28%).

Method B. Tetraethylthiuram disulfide (296 mg, 1 mmol) dissolved in DMF (5 ml) was added to a solution of $(NH_4)_2WS_4$ (696 mg; 2 mmol) in DMF (10 ml) at 130 °C under nitrogen atmosphere. The reaction mixture was cooled immediately to room temperature and 2-propanol (10 ml) and ether (250 ml) were added and kept in the refrigera-

Table 1. Binding Energy (eV) Observed by XPS

Compound	W(4f$_{7/2}$)	W(4f$_{5/2}$)	S(2p)	S(2s$_{1/2}$)	W(4d$_{5/2}$)	W(4d$_{3/2}$)
$[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$	33.9	36.1	163.3	227.0	245.7	259.4
$[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$	33.6	35.7	162.8	227.0	245.2	258.0

tor overnight. The crude product thus obtained was purified by chromatography as described in method A. The analytical results and spectral data are in agreement with those shown in method A. Yield: 96 mg (12%).

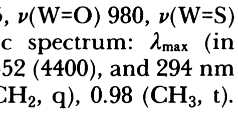
Synthesis of $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (3). The same procedure for the preparation of **2** (method A) was followed except that the reaction was carried out in the presence of air. The major product **3** (234 mg, 30%) was obtained after chromatographic purification.[15] However, if method B for synthesis of **2** is followed in the presence of air, **3** is obtained in low yield (90 mg, 12%).[16] Found: C, 15.78; H, 2.50; N, 3.72; S, 26.68%. Calcd for $C_{10}H_{20}N_2OS_3W_2$: C, 15.46; H, 2.57; N, 3.60; S, 26.80%. IR(KBr): ν(C=N) 1555, ν(W=O) 980, ν(W=S) 540, $\nu(WS_2W)$ 465, 335. Electronic spectrum: λ_{max} (in CH_2Cl_2) 418 (ε 700 dm^3 mol^{-1} cm^{-1}), 352 (4400), and 294 nm (27400). ^{1}H NMR ($CDCl_3$): δ=3.62 (CH_2, q), 0.98 (CH_3, t). Yield: 90 mg (12%).

Reaction of 3 with KCN. A suspension of **3** (776 mg, 1 mmol); KCN (65 mg, 1 mmol) and Et_4NBr (210 mg, 1 mmol) in chloroform (50 ml), ethanol (15 ml) and water (5 ml) was refluxed for 96 h. The solvents were evaporated under vacuum and the residue was washed with water, methanol and diethyl ether. The bright yellow residue was dried in vacuo and recrystallized from dichloromethane/petroleum ether (yield: 544 mg, 73%). The compound showed identical results to that of **1** in elemental and spectral analysis. The washings gave positive test for thiocyanate.

Results and Discussion

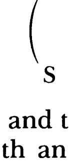
Tungsten(V)-sulfur complexes have generally been prepared by multi-step synthesis.[8,10] Here we report new synthetic methods for their efficient one step preparation. Gradual heating of diethylammonium thiotungstates (WOS_3^{2-}, WS_4^{2-}) with excess CS_2 in DMF affords desired compounds with the overall reaction as shown in Eq. 1:

$$2[(Et_2NH_2)_2WXS_3] + 4\,CS_2 \xrightarrow[\text{DMF}]{\text{reflux}}$$



$$+ (Et_2NCS_2)_2 + 4\,H_2S \qquad (1)$$

X=O, S;



$= S_2CNEt_2^-$

The formation of H_2S and tetraethylthiuram disulfide (TLC comparison with an authentic sample) as by-products of the reaction suggests the above stoichiometry of the reaction.

In the synthesis of $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (**2**), $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$ (**3**) is formed as by-product of the reaction, probably as a result of **2** hydrolyzing with traces of moisture present in the reaction medium. The characterization of tetraethylthiuram disulfide as by-product shows that the reaction is a thermally induced redox reaction.

Spectral Studies. The IR, NMR, and electronic spectral studies of these complexes demonstrate the following important points. The strength of tungsten–oxygen bond is greater than that of molybdenum analogues[17] but the reverse has been observed for metal-sulfur bonds. Similar down field shifts of both methyl and methylene protons are observed by the replacement of oxygen by sulfur in the NMR studies. In the electronic spectral studies as expected, the intraligand transitions[18] and ligand to metal charge-transfer transitions[19] are observed. However the intensities of some of these transitions are not as high compared to similar tungsten(V) dimeric complexes.[10,11] Even using other substituted dithiocarbamates, the relative intensities of these transitions differ.[10,11] We do not have any explanations to offer for this discrepancy. The mixing of the orbitals especially between the metal and oxygen/sulfur might control the components of the electric dipolemoment. In the present case, especially with the oxo species probably there is not considerable charge redistribution during the transition for which the intensity of the band is weak.

XPS results have been tabulated in Table 1. In the spectra of $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ and $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ a broad band around 163 eV is observed. In the first case, a resolution of the broad band (FWHM 2.87 eV) gives two sets of S(2p) binding energies at 163.1 and 163.5 eV. Thus a distinction can be made between the sulfur attached to two tungstens (163.5 eV) and the sulfur attached to one tungsten and one carbon atom (163.1 eV).[20] For the all sulfur compound **2**, S(2p) band is broader (FWHM 3.1 eV). This extra broadness for this compound compared to **1** suggests the presence of three different types of sulfur, S_{term}, S_{bri}, and S_{dtc}. For tungsten, the XPS shows considerable difference between the binding energies of W(4d$_{5/2}$) as well as W(4d$_{3/2}$) in $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ and $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$. The former compound **1** shows more formal positive charge on the metal than the all sulfur compound **2**. This difference may be attributed to the difference in electron population across W=O and W=S bonds. The oxygen being more electronegative withdraws more electron from the metal compared to its sulfur analogue.

Comparison of X-ray powder diffractogram of **1** with its molybdenum analogue $[Mo_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$ suggests that both the compounds are isostructural.[21]

The treatment of **3** with one equivalent of cyanide results in the substitution of terminal sulfur with oxygen affording **1** in high yield, as shown in Eq. 2.

$$\underset{\mathbf{3}}{[W_2OS(\mu\text{-}S)_2\,(S_2CNEt_2)_2]} + CN^- \xrightarrow[H_2O]{96\text{ h}} \underset{\mathbf{1}}{[W_2O_2(\mu\text{-}S)_2\,(S_2CNEt_2)_2]} + SCN^- \qquad (2)$$

After extracting **1** from the reaction mixture, the residue was acidified and treated with iron(III) chloride solution. It gave red color, thus confirming the formation of SCN^-. Attempt to replace the bridging sulfur was not successful, by increasing the quantity of CN^- and the reaction time. This suggests that bridging sulfur atoms are more strongly bound with the metal centers than the terminal ones.

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15) Chromatography on silica gel (dichloromethane pet. ether mixture 75 : 25) yielded first the minor product, **1** (50 mg, 6%) and then the desired compound as major product and then a third compound **3** (15 mg, 2%).

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