STUDY OF A MICROWAVE ASSISTED INDUCED ELECTRON TRANSFER REACTION ACROSS METAL-SULFUR BONDS

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***Abstract*—In this paper, we studied and synthesised the induced electron-transfer reactions across metal sulfur bonds. Pioneering work in this area has been done by Taube and co-workers.**

***Index Terms*—Electron Transfer, Tungsten and Molybdenum, Sulfur.**

I. Introduction

This work will certainly be of some help to understand the mechanistic and functional aspects of the recently discovered tungsto-enzyme, formate dehydrogenase. Moreover, this is an entirely new approach in synthetic inorganic chemistry. The field is still in the embryonic stage and many more questions are yet to be answered. Hence, at this stage one then perhaps recalls what **Taube** said, "At this stage, it would be premature to attribute the difference to effects of the kind we are searching for, but it would be equally premature to give up the search at this stage [1-6]."

II. INDUCED ELECTRON TRANSFER REACTIONS

2.1.A. Synthesis of $(Et_4N)_2$ $[W_2O_2(\mu\text{-}S)_2(S_2)_2]$- Method 'A'

$(NH_4)_2WOS_3$ (664 mg; 2mmol) and Et_4NBr (630 mg: 3 mmol) were dissolved in H_2O (20 ml) and iodine (253.8 mg: 2 mmol) was added to it. The mixture was warmed on the water bath for 20 min, then KOH (100 mg; 2.56 mmol) was added to it. After 5 min the solution was filtered and the precipitate was washed with H_2O, EtOH and ether and was recrystallized from CH_3CN/i-ProH (yield, 180mg: 21.12%).

Anal.Calcd. for $C_{16}H_{40}N_2O_2S_6W_2$: C, 22.53; H, 4.69; N.3.28; S, 22.53
Found C, 22.49; H, 4.52; N, 3.08; S. 22.62%

2.1.B. Synthesis of $(Et_4N)_2$ $[W_2O_2(\mu\text{-}S)_2(S_2)_2]$- Method 'B'

$(NH_4)_2WOS_3$ (664 mg; 2mmol) was dissolved in H_2O (30 ml) and solid $(NH_4)_2S_2O_8$ (228.20 mg; 1 mmol) was added shaking the solution vigorously. Solution was stirred for 4 hr and Et_4NBr (630mg; 3 mmol) awas added to it. After 10 min a 25% ammonia solution (5ml) was added to it. This was filtered and the precipitate was wahed and recrystallized as mentioned above (yield, 20 mg; 24%). Analysis was found to be satisfactory [7-10].

2.1.C. Synthesis of $(Et_4N)_2$ $[W_2O_2(\mu\text{-}S)_2(S_2)_2]$- Method 'C'

$(NH_4)_2WOS_3$ (664 mg; 2mmol) and Et_4NBr (630 mg; 3mmol) were dissolved in DMF (20 ml) and warmed at 110^0C for 5 min. C_6H_5-S-S-C_6H_5 (218.34 mg; 1 mmol) or (C_2H_5)2N-CSSSSC-N $(C_2H_5)_2$ (296.54 mg; 1 mmol) or t-butyl hydroperoxide (0.1 ml; 1 mmol) or C_6H_5-O-O-C_6H_5 (186.21 mg; 1 mmol) was added to it. The resulting red solution was left at 110^0C for 1/2 hr. Addition of
i-PrOH (15ml) and ether (30ml) yielded red crystalline product which was washed with H_2O, EtOH and ether and recrystallized from CH_3CN/i-PrOH (Yield, 70%). Analysis was found to be satisfactory.

2.1.D. Synthesis of $(Me_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$

$(NH_4)_2WOS_3$ (668mg; 2 mmol) dissolved in DMF (15 ml). Me_4NCl (219 mg; 2mmol) dissoved in H_2O (5ml) were mixed. This was warmed at 110^0C for 5 min and C_6H_5-S-S-C_6H_5 (216.34 mg; 1.0 mmol) was added to this solution. After 1/2 hr colour of the solution darkened and then became orange. It was then cooled and i-PrOH (20ml) and ether (20ml) was added and left for 1 hr. The yellow product which separated out was washed with H_2O, ethanol, and ether and recrystallized from CH_3CN/i-PrOH (yield, 426 mg; 57.56%).

Anal. Calcd. for $C_8H_{24}N_2O_2S_6W_2$: C, 12.97 H, 3.24; N. 3.78 S, 25.94

Found: C, 12.85; H, 3.25; N, 3.16; S. 25.80%

2.1.E. Synthesis of $(Et_4N)_2[WS(WS_4)_2]$- Method 'A'

To a solution of $(NH_4)_2WS_4$ (1.044g; 3mmol) and Et_4NBr (630mg; 3mmol) in H_2O (30ml), $(NH_4)_2S_2O_8$ (228.20mg; 1 mmol) was added, stirring the solution vigorously. Some red precipitate was thrown out immediately. Further stirring for 1 hr gave some more product, which was filtered, washed with EtOH and ether and was recrystallized from CH_3CN/i-PrOH (Yield, 310 mg; 30%)

Anal. Calcd. For $C_{16}H_{40}N_2S_9W_3$: C, 17.45; H, 3.63; N, 2.54; S, 26.18

Found: C, 17.52; H, 3.42; N 2.50; S. 26.10%

2.1.F. Synthesis of $(Et_4N)_2[WS(WS_4)_2]$- Method 'B'

$(NH_4)_2WS_4$ (1.644g; 3mmol) and Et_4NBr (630 mg; 3 mmol) were dissolved in DMF (15 ml) and the solution was warmed at 110^0C for 5 min. $(C_6H_5S)_2$ (218.34 mg; 1 mmol) was added to the above solution with shaking. It was then cooled to room temperature. Addition of i-PrOH (20 ml) and either (50 ml) yielded a dark red crystalline product, which was washed and recrystallised as mentioned above (yield, 605 mg; 58%)

2.1.G. Synthesis of $(Et_4N)_2[WO(WS_4)_2]$

$(NH_4)_2WS_4$ (1.004g; 3mmol) dissolved in DMF (15 ml) and Et_4NBr (630 mg; 3 mmol) dissolved in H_2O (5ml) were mixed and heated at 110^0C for 15 min. To the above solution C_6H_5-S-S-C_6H_5 (218 mg; 1 mmol) was added and heated for a further 10 min. The resulting solutioni was cooled at room temperature and i-PrOH (10 ml) and ether (50 ml) were added to it. The orange product that separated out was washed with water, EtOH and finally with ether (yield, 410 mg, 40%)

Analysis and spectral results are similar to that of the same compound reported earlier.[11]

III. REACTIVITY OF THE SYNTHESIZED COMPLEXES

1.1. Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DBA or Synthesis of $(Et_4N)_2$- $[W_2O_2(\mu\text{-}S)_2(S_2C_2(COPh)_2)_2]$

Dibenzoyl acetylene (DBA) 234 mg; 1 mmol) was dissolved in CH_3CN (5ml) and added to a solution of $[Et_4N]_2W_2O_2S_6$ (426 mg; 0.5 mmol) in CH_3CN (10ml) and stirred for 5 min. When the colour of the solution changed from orange to green, it was cooled to room temperature, and EtOH was added dropwise till the solution became turbid. It was filtered, and the filtrate was kept at room temperature for 2 days. Dark red needle-shaped crystals separated out, which were washed with EtOH and ether and dried under vacuum (yield, 130 mg; 19.7%)

Anal. Calcd. 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%

1.2. B. Reactivity of $(Et_4N)_2[W_2O_2S_6]$ with DMAC or Synthesis of $(Et_4N)_2$- $[W_2O_2(\mu\text{-}S)_2(S_2C_2(COOMe)_2)_2]$

To a solution of $(Et_4N)_2[W_2O_2(\mu\text{-}S)_2(S_2)_2]$ (426 mg; 0.5mmol) in CH_3CN (10ml) dimethyl acetylene dicarboxylate (DMAC), (0.13 ml; 1 mmol) was added the solution was shaken well. The colour of the solution changed immediately from yellow to brown to green. After 5 hr absolute ethanol was added dropwise till it became turbid. It was left at room temperature For 2 days the precipitate thus formed was washed with EtOH and ether and vacuum dried (yield, 230 mg; 42.91%).

Anal. Calcd. for $C_{28}H_{52}N_2O_6S_6W_2$: C, 31.34; H, 4.85; N, 2.61.

Found : C. 31.62; H, 4.76; N, 2.52%

3.2. Synthesis of $(Et_4N)_2[W(S_2C_2)(COPh)_2)_3]$

$(Et_4N)_2WS_4$ (190.6mg; 1/3 mmol), sulfur (21.33 mg, 3/2 mmol) and dibenzoyl acetylene (234 mg; 1 mmol) were taken in DMF (10 ml) and the solution was stirred for 12 hr. The colour of the solution changed from red to brown to greenish brown. Addition of iso-propanol till the solution became turbid, and leaving it at room temperature for 24 hr gave greenish brown crystals, which were washed with EtOH, CS_2 and ether, and dried under vaccum, yield 165 mg (37%).

Anal. Calcd for $C_{64}H_{70}N_2O_6S_6W$: C, 57.39; H, 5.23; N, 2.09.
Found: C., 56.64; H, 5.13; N. 1.89%

3.3. Synthesis of $K_4[W_2O_2(\mu\text{-}S)_2(CN)_6].3H_2O$

A suspension of $(Et_4N)_2[W_2O_2S_6]$ (852 mg; 1 mmol), potassium ferricyanide (2g; 30.7 mmol) in H_2O (10 ml) was stirred for 10 min. The colour of the solution changes from green to brown and finally to bright yellow. Addition of i-PrOH (20 ml) gave some oily mass, which was recrystallised from H_2O and EtOH. Yellow crystals thus formed were washed with ethanol and ether, and dried in vacuum; yield 600 mg (73.89%).

Anal. Calcd. For $C_6H_6N_6O_5S_2K_4W_2$: C, 8.67; H, 0.72, N, 10.12
Found: C, 9.20; H., 0.81; N, 10.05;

Ⅳ. INDUCED ELECTRON TRANSFER REACTIONS CONCEALED UNDER LIGAND BASED REDOX PROCESSES

4.1.A. Synthesis of $[WO(S_2)(S_2CNEt_2)_2]$-Method 'A'

A Solution of $(Et_2NH_2)_2WOS_3$ (444mg; 1 mmol) in DMF (10 ml) was stirred with CS_2 (2ml) for 36 hr in the presence of air. This solution was filtered and i-PrOH (50 ml) was added to it. This was kept at room temperature for 24 hr. Brown crystalline product was thrown out, which was purified by flash chromatography on silica gel using $CHCl_3$ and petroleum ether (60:40) as eluent (yield, 390 mg; 70%)

Anal. Calcd. For $C_{10}H_{20}N_2OS_6W$: C, 21.43; H, 3.57; N, 5.00.
Found: XC, 21.60; H, 3.60; N. 4.72%

4.1.B. Synthesis of $[WO(S_2)(S_2CNEt_2)_2]$-Method 'B'

$(NH_4)_2WO_2S_2$ (316 mg; 1 mmol) was dissolved in DMF (15 ml) by warming it on a hot plate. The solution was cooled and tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added to it. The solution was filtered, and i-PrOH (10 ml), ehter (200 ml) were added to it. Keeping the solution in the refrigerator for 4 days, yielded brown crystalline product. The crystals were washed with i-PrOH, ether and dried under vacuum (yield, 55mg (9.82%). Analysis was found to be the same as in method 'A'.

4.1.C. Synthesis of $[WO(S_2)(S_2CNPr_2)_2]$

A solution of $(Pr_2NH_2)_2WOS_3$ (500 mg; 1 mmol) in DMF (10ml) was stirred with CS_2 (2.5ml) for 40 hr in the presence of air at room temperature. The solution was poured into water (150 ml). The oily material was extracted in $CHCl_3$ and was purified by flash chromatography on silica gel using $CHCl_3$: petroleum ether mixture (50:50) (Yield, 230 mg; 37.95%) as eluent.

Anal. Calcd. for $C_{14}H_{28}N_2S_6OW$: C, 27.27; H, 4.54; N, 4.54
Found: C, 27.10, H, 4.60; N, 4.60%

4.1.D. Synthesis of $[WS(S_2)(S_2CNEt_2)_2]$

$(Et_2NH_2)_2WS_4$ (460 mg; 1 mmol) was dissolved in DMF (10ml) and CS_2 (2ml) was added to it. The resultant red solution was stirred in the presence of air at room temperature for 36 hr. The solution was filtered and i-PrOH (50ml) and ether (10 ml) were added to ti. Keeping the resulting solution at 25^0C for 24 hr resulted in the separation of green crystalline product. This was washed with H_2O, EtOH, either and dried under vacuum. The compound was purified by flash chromatography on silica gel using $CHCl_3$; petroleum ether (60%40) as eluent (yield, 282 mg; 48.92%).

Anal. Calcd. For $C_{10}H_20N_2S_7W$: C, 20.83; H, 3.47; N, 4.86.

Found: C, 20.86; H, 3.72; N. 4.52%

4.1.E. Synthesis of (Et_2NH_2) [$WO(S_2)_2(S_2CNEt_2)$]- Method 'A'

$(Et_2NH_2)_2WS_4$ (460mg; 1 mmol) was dissolved in DMF (5 ml) and CS_2 (1 ml) was added to it. The resulting and solution was stirred for 16 hr in the presence of air. Addition of i-PrOH (50 ml) and ether (180 ml) and on keeping it at room temperature overnight resulted in the separation of reddish brown crystalline product which was washed with H_2O, i-PrOH and finally with ether and recrystallized from acetone/petroleum ether (yield, 260 mg; 47.37%).

Anal. Calcd. for $C_9H_{22}N_2OS_6W$: C, 19.63, H, 4.00, N, 5.09
Found : C. 19.25, H, 3.75; N, 5.05%

4.1.F. Synthesis of (Et_2NH_2) [$WO(S_2)_2(S_2CNEt_2)$]- Method 'A'

$(NH_4)_2WS_4$ (348 mg; 1 mmol) was dissolved in DMF(10 ml) and heated upto 130^0C and to this tetraethylthiuram disulfide (296.54 mg; 1 mmol) was added. The solution was cooled to room temperature. To this iso-propanol (20 ml) and ether (150 ml) were added. Further cooling of the resultant solution to 5^0C and keeping it at the same temperature for 24 hrs gave reddish brown crystalline product along with microcrystalline red product. The reddish brown product was extracted in acetone (20ml) and was precipitated by adding petroleum ether (20 ml) Yield, 60 mg; 10.9%). The analytical data was identical with that of the compound obtained from method 'A'.

V. THERMALLY INDUCED ELECTRON TRANSFER REACTIONS

5.1.A. Synthesis of [$W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2$]-Method 'A'

To a solution of $(Et_2NH_2)_2WOS_3$ (888mg; 2 mmol) in DMF (10 ml), CS_2 (2ml) was added and the mixture was refluxed for 4 hr. Addition of i-PrOH (10 ml) and ether (100 ml) to the cold solution caused a precipitation of a small amount of green brwon product that was filtered off and the filtrate was kept overnight at room temperature to yield the desired product as yellow needles. The product was washed with H_2O, EtOH and ether and purified chromatographically using CH_2Cl_2/pet. ether (80:20) as eluent (yield, 290 mg; 38%)

Anal. Calcd. for $C_{10}H_{20}N_2O_2S_6W_2$: C, 15.78, H, 2.63; N, 3.68
Found: C, 15.90; H, 2.81, N, 3.48%

5.1.B. Synthesis of [$W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2$]-Method 'B'

To a hot solution (130^0C) of $(NH_4)_2WO_2S_2$ (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 25^0C. Addition of i-PrOH (20ml) and ether (160 ml) and keeping it at 5^0C for 48 hr, yielded yellow product which was purified as described above (yield, 320 mg 45%)

5.1.C. Synthesis of [$W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2$]-Method 'A'

A Solution of $(Et_2NH_2)WS_4$ (920 mg; 2 mmol) DMF (10ml) and CS_2 (2 ml) was refluxed for 4 hr under dry nitrogen atmosphere and in the absence of light. To the cold solution (25^0C), i-PrOH (10ml) and ether (100ml) were added. A small amount of dark brown product was precipitated out that was filtered off. The filtrate was left at room temperature for 24 hr to yield the desired compound as dark red needle shaped crystals. The compound was washed with H_2O, EtOH and ether and purified chromatographically using CH_2Cl_2/pet. ether (75:25) as eluant (yield 220 mg; 28%).

5.1.D. Synthesis of [$W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2$]-Method 'B'

Tetraethylthiuram disulfide (296 mg; 1 mmol) dissolved in DMF (5ml) was added to a solution of $(NH_4)_2WS_4$ (696 mg; 2 mmol) in DMF (10 ml) at 130^0C under dry nitrogen atmosphere. To the cold solution (25^0C) i-PrOH (10 ml) and ether (250 ml) were added and kept at 5^0C for 25 hr. The crude product thus obtained was washed and purified as described above (yield, 96 mg; 12%). Analysis was found to be satisfactory.

5.1.E. Synthesis of $[W_2OS(\mu\text{-}S)_2(S_2CNEt_2)_2]$

The same procedure as for the preparation of $[W_2S_2(\mu\text{-}S)_2\text{-}(S_2CNEt_2)_2]$ (method A) was followed, except that the reaction was carried out in the presence of air. The desired compound was obtained as major product (234 mg 30%) after chromatographic purification. However, if method B was followed for synthesis of $[W_2S_2(\mu\text{-}S)_2\text{-}(S_2CNEt_2)_2]$ in the presence of air, the desired product is obtained in low yield (90 mg; 12%)

Anal. Calcd. For $C_{10}H_{20}N_2OS_2W_2$: C, 15.46; H, 2.57; N, 3.60
Found: C, 15.78; H, 2.50; N, 3.72%

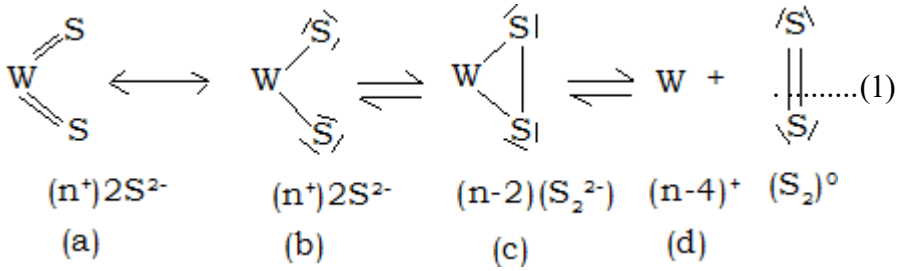
VI. DISPROPORTIONATION REACTION OF [WO(S2)(S2CNET2)2] OR SYNTHESIS OF [W2O2(μ-S)2(S2CNET2)2] BY THERMAL INDUCTION

$[WO(S_2)(S_2CNEt_2)_2]$ (560mg; 1 mmol) was dissolved in DMF (10 ml) and warmed on a water bath for 1 hr. The colour of the solution faded from brown to yellow. The yellow compound was isolated by precipitating it by adding i-PrOH (20ml) and ether (200ml) to the solution and recrystallising from CH_2Cl_2/pet. ether (yield, 265 mg; 70%)

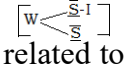
VII. DISPROPORTIONATION REACTION OF (ET2NH2) [WO(S2)(S2CNET2)2] OR SYNTHESIS OF [W2O2(μ-S)2(S2CNET2)2] BY THERMAL INDUCTION

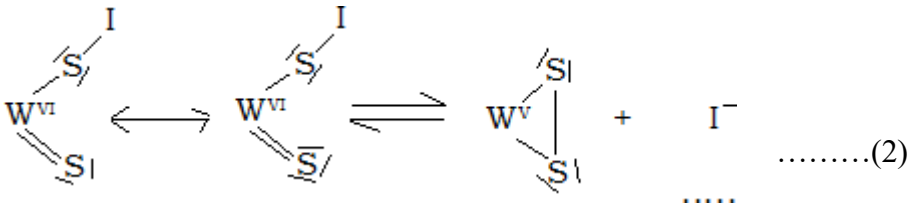
(Et_2NH_2) $[WO(S_2)(S_2CNEt_2)_2]$ (550 mg; 1 mmol) was dissolved in DMSO (10 ml) and warmed on a water bath for 30 min. The colour of the solution changed from red brown to yellow. The reaction mixture was poured into water (100 ml). The solid obtained was filtered, washed with EtOH, CS_2 and ether, dried and recrystallized from CH_2Cl_2/pet. ether. The compound thus obtained gave satisfactory elemental analysis.

The electronic spectrum of WS_4^{2-} shows the lowest energy charge transfer band at 393 nm.[12] The corresponding absorption for W_4S^{2-} is at 467 nm. This difference in abosrption may be taken as a qualitative guideline to understand any difference in the reactivity of these thiometallates when electron transfer reactions are under consideration. Intramolecular electron transfer across W-S bond may be schematically shown as Follows:

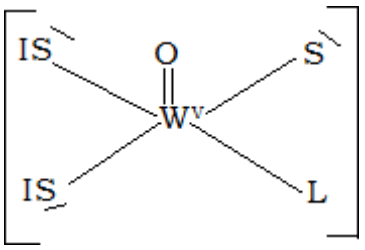


Structures (1a) and (1b) simply show the resonating forms of the tungsten sulfide attachment. The structure 1b is attained under the extreme reaction conditions imposed on the system.

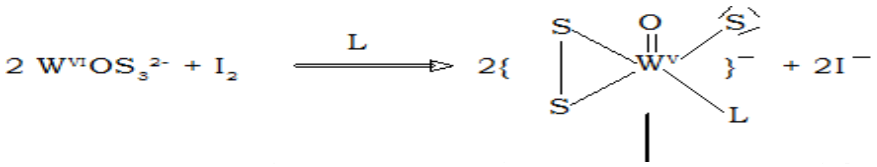
This could be achieved by several means (vide supra). This form is ready to interaction with the external oxidant. Electrophilic attack by iodine might give the intermediate like  . The energy level of this intermediate could change in such a manner that the frontier orbitals related to tungsten and sulfur might comes close in energy and the electron transfer from sulfur to tungsten, followed by sulfur-sulfur bond formation might take place. The formation of disulfide is reminiscent of the reaction of iodine with RS^- to R-S-S-R. The process can be viewed as follows:

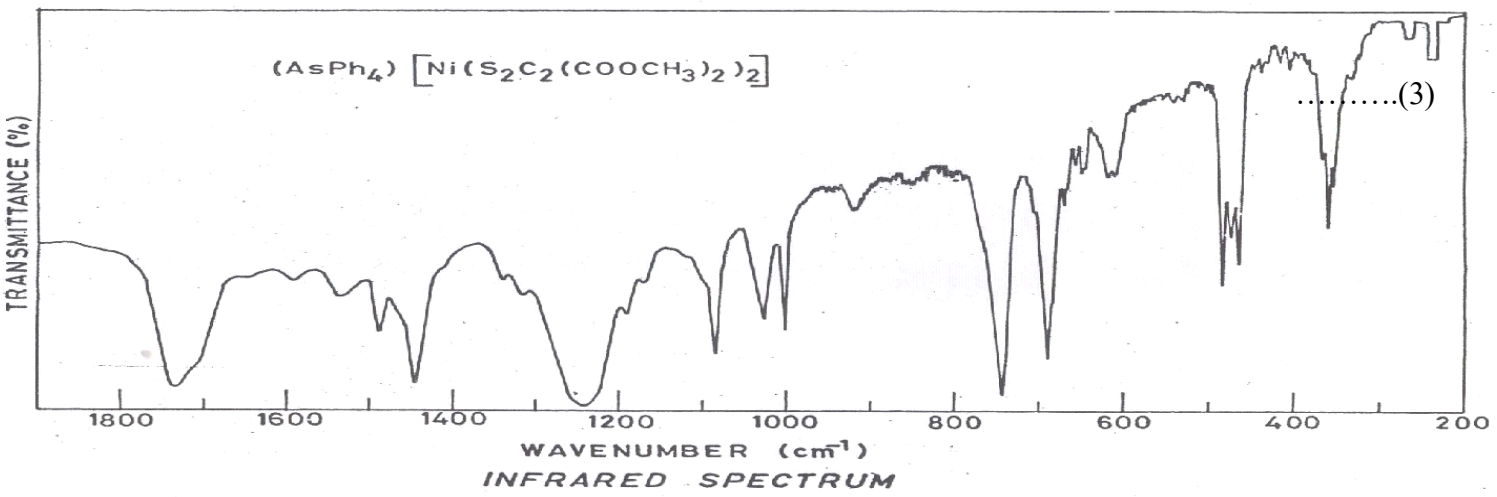


If this happens to be the cause of the reaction occurring, an intermediate, monomeric, pentavalent tungsten species could be identified in the progress of the reaction. The intermediate pentavalent species arising from the reaction might have the structure:



The coordination of the solvent (L) in this structure is in confirmed with the known stable pentavalent complexes of molybednum and tungsten.[13-15] The presence of an intermediate, monoeric, species of this type has been shown by E.S.R. spectroscopy (vide infra). This species might dimerise to give the desired product as shonw below:





overall process involved is the $4e^-$ oxidation of $4S^{2-}$ coordinated to W(VI), and the formation of two S_2^{2-} ligands.

$(Et_4N)_2[W_2O_2S_2(S_2C_2(COOMe)_2)_2]$

VIII. CONCLUSION

The electronic spectrum of $K_4[W_2O_2(m\text{-}S)_2(CN)_6].3H_2O$ has many absorptions in the uv region at 325, 268, 238 and 210 nm which may be attributed to charge transfer transitions originating from coordinated cyanide. The absorption at 428 nm can be assigned to charge transfer from bridged sulfido groups to tungsten (V). It is important to note that in the complex, $[W_2O_2(m\text{-}S)_2(S_2CNEt_2)_2]$ an absorption appears at 415 nm. Hence the absorption in the range 415-420 nm in sulfido-bridged complexes, studied here may be mainly originating from the bridged sulfido groups to tungsten (V) charge transfer.

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