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Communications

Concealed Induced Internal Electron-Transfer Reaction in the Synthesis of $[WO(S_2)(S_2CNEt_2)_2]$ from $(Et_2NH_2)_2WOS_3$ and CS_2 with O_2[1]

Sir:

Intramolecular redox reactions induced by external oxidants are known in cobalt chemistry.[2a] Recently similar redox reactions were reported with tetrathiomolybdate(VI)[2b] and oxotrithiotungstate(VI),[3] where both metal-based and bonded-sulfide-based redox reactions occur. In contrast the reaction between tetraalkylthiuram disulfide and tetrathiotungstate(VI) to yield $[WS(S_2)(S_2CNR_2)_2]$ is accounted for by an entirely ligand-based redox process.[4] In this communication we report this last type of electron-transfer reaction, which is actually an induced electron-transfer reaction but paradoxically looks similar to a purely ligand redox process.

The diethylammonium salt of oxotrithiotungstate, $(Et_2NH_2)_2WOS_3$ has tungsten in its hexavalent oxidation state. In the presence of O_2, this salt reacts with CS_2 to give $[WO(S_2)(S_2CNEt_2)_2]$. The stoichiometry of this reaction has been established[5] as shown in reaction 1. Reaction 1 requires stirring

$$(Et_2NH_2)_2WOS_3 + 2CS_2 + {}^1/_2O_2 \rightarrow [WO(S_2)(S_2CNEt_2)_2] + H_2S + H_2O \quad (1)$$

of $(Et_2NH_2)_2WOS_3$ (444 mg, 1 mmol) in DMF and CS_2 (2 mL) for 36 h in the presence of air under ambient conditions. The product is isolated in 70% yield (by adding 2-propanol (50 mL)/diethyl ether (20 mL) and allowing the mixture to stand for 24 h) as brown crystals after washing successively with H_2O (10 mL), ethanol (20 mL), and diethyl ether (20 mL). The product has been purified by "flash chromatography" on silica gel using chloroform/petroleum ether (80:20) as eluant.[6] The molybdenum analogue of this compound, which is well-known, has been synthesized by several different procedures.[4,7] The formation of $[WS(S_2)(S_2CNEt_2)_2]$ can also be effected by the procedure of reaction 1 using the corresponding salt of tetrathiotungstate(VI). This product is identical with the one formed by using tetraalkylthiuram disulfide as oxidant.[4] Both $[WO(S_2)(S_2CNEt_2)_2]$ and $[WS(S_2)(S_2CNEt_2)_2]$ display analytical[8] and spectral[9] data consistent with their formulation.

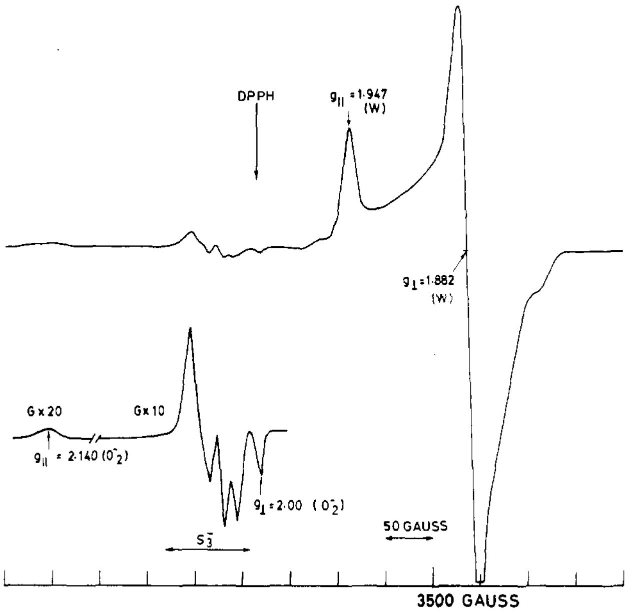

Figure 1. First derivation X-band (ν = 9.300 GHz) EPR spectra of the reaction mixture after 1 h reaction time in DMF at 77 K.

$[WO(S_2)(S_2CNEt_2)_2]$ of reaction 1 maintains hexavalent tungsten, suggesting purely a ligand redox reaction. The conversion of two S^{2-} ligands to one S_2^{2-} ligand and the uptake of two electrons by ${}^1/_2O_2$ as electron acceptor furnish an electron-balanced reaction. Does said reaction involves any redox participation of tungsten? The likely participation of lower valent tungsten in this reaction is indicated by the observation of an EPR active W(V) ($g_{\parallel} = 1.947$, $g_{\perp} = 1.882$, $\langle g \rangle$ solution = 1.897) species[10] formed during the course of the reaction (Figure 1). The EPR signal appears within 5 min of the addition of CS_2 into the DMF solution of $(Et_2NH_2)_2WOS_3$ at room temperature in air,

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(1) Dedicated to Professor R. P. Rastogi, on the occasion of his 60th birthday.

(2) (a) Taube, H. *Electron Transfer Reactions of Complex Ions in Solutions*, Academic: New York, 1970; pp 73–98 and references therein. (b) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

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

(4) Pan, W.-H.; Halbert, T. R.; Hutchings, L. L.; Stiefel, E. I. *J. Chem. Soc., Chem. Commun.* **1985**, 927.

(5) The reaction byproduct, H_2S, has been quantitated by absorbing it in ammoniacal cadmium chloride to precipitate CdS followed by iodometric titration.

(6) Final yield of the pure compound was found to be 70%.

(7) (a) Dirand-Colin, J.; Ricard, L.; Weiss, R.; Schappacher, M. *J. Less-Common Met.* **1977**, *54*, 91. (b) Dirand-Colin, J.; Ricard, L.; Weiss, R. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 661. (c) Leonard, K.; Plute, K.; Haltiwanger, R. C.; DuBois, M. R. *Inorg. Chem.* **1979**, *18*, 3246. (d) McDonald, J. W.; Newton, W. E. *Inorg. Chim. Acta* **1980**, *44*, L81.

(8) Anal. Calcd for $C_{10}H_{20}N_2OS_6W$: C, 21.43; H, 3.57; N, 5.0. Found: C, 21.66; H, 3.60; N, 4.42. Calcd for $C_{10}H_{20}N_2S_7W$: C, 20.83; H, 3.47; N, 4.86. Found: C, 20.86; H, 3.32; N, 4.52.

(9) The infrared spectrum in KBr disk of $[WO(S_2)(S_2CNEt_2)_2]$ shows bands at 940 (ν(W═O)) and 552 (ν(S—S)) cm^{-1}. The electronic spectrum in CH_2Cl_2 displays bands at 485 (ϵ 1800), 438 (2400), 340 (sh), and 320 (9350) nm. ^1H NMR ($CDCl_3$): δ 1.1 (t, CH_3), 1.21–1.61 (t, CH_3), 3.48 (q, CH_2), 3.61–4.0 (q, CH_2). For $[WS(S_2)(S_2CNEt_2)_2]$, IR (KBr): 550 (ν(S—S)), 500 (ν(W═S)) cm^{-1}. Electronic spectrum in CH_2Cl_2 shows bands at 600 nm (ϵ 3480), 380 (10 800), and 360 (9800). ^1H NMR ($CDCl_3$): δ 1.18 (t, CH_3), 1.26–1.68 (t, CH_3), 3.48 (q, CH_2), 3.7–4.05 (q, CH_2).

(10) Kon, H.; Sharpless, N. E. *J. Phys. Chem.* **1966**, *70*, 105.

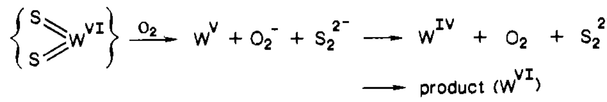
0020-1669/88/1327-0763$01.50/0

gains maximum intensity after 8 h, starts decaying, and disappears after 20 h. The observed reaction does not take place if it is carried out in an inert atmosphere, eliminating H^+ as an alternative electron acceptor.[11] The disappearance of the EPR active species after 20 h might be due to (i) dimerization of EPR-active W(V), (ii) oxidation of W(V) to W(VI), or (iii) further reduction of W(V) to W(IV). Possibility i seems likely as no dimeric W(V) compound could be isolated under the reaction conditions within 40 h.[12] For possibility ii the oxidation of W(V) to W(VI) should lead to the formation of the product immediately after the disappearance of EPR signal (20 h after the reaction is started). However, workup at this stage gives the product, $[WO(S_2)(S_2CNEt_2)_2]$, in low yield (~30%).[13] Thus to increase the formation of the product to 70% (final yield), the last 16 h, when the solution is EPR silent, is essential (total reaction time 36 h). This gives indirect support to possibility iii and suggests that electron transfer from the S^{2-} ligand to W(VI) takes place to produce W(IV) via a kinetically competent W(V) species. Proof for the acceptance of one electron by oxygen to generate O_2^- in situ is furnished by observing an EPR signal due to O_2^-[14] ($g_\parallel = 2.14$, $g_\perp = 2.00$) (Figure 1). In addition an EPR signal due to S_3^- ($\langle g \rangle = 2.028$) is also seen.[15,16] Thus, internal and external oxidants share one electron each donated by two S^{2-} ligands with the formation of one S_2^{2-}.

When the W(V) EPR signal was at a maximum (after 8 h) an aliquot of the reaction mixture was treated with an excess of solid KO_2 and then subjected to EPR measurements at room temperature. The W(V) EPR signal disappeared after 4 h compared to 12 h for the KO_2-untreated aliquot. The disappearance of the W(V) EPR signal more quickly in the presence of KO_2 than in its absence is consistent with the reduction of W(V) to W(IV) by O_2^-, which is a moderate reducing agent in aprotic media.[17] Recently, the reduction of Mo(V) to Mo(IV) by O_2^- has also been reported.[18] Attempts to isolate the intermediate W(V) species as a solid failed. However, under identical reaction conditions, the corresponding dimethylammonium salt of WOS_3^{2-} gave a brown product that shows an EPR signal characteristic of W(V) ($\langle g \rangle = 1.879$). This compound $[WO(S_2CNMe_2)_3]$[19] in CH_2Cl_2 solution containing 5% v/v DMSO reacts slowly with $K^+O_2^-$ to give $[W^{IV}O(S_2CNMe_2)_2]$.[20]

The concentration of W(V) at 8 h reaction time was estimated to be 22% of the total tungsten by weighing a cutout absorption curve. The concentration of W(V) remains more than 10% between the 5th and the 13th hour of the total reaction period of 36 h. Stability of the W(V) species for hours under the experimental conditions is not expected. This can be explained by the generation of W(V) species from W(VI) followed by further reactions between W(V), O_2^-, and/or several other species that are generated as side products.[16] However, the long time stability of W(V) species establishes a kinetically competent reaction for its generation over the other side reactions.

Thus, we suggest that the main electron-transfer pathway can be described as in (2).



(2)

The last step of oxidation of W(IV) to the product is achieved by aerial oxygen in the presence of polysulfide, which is a byproduct of the reaction.[20] The entire process of this ligand to metal electron flow is controlled by the external oxidant, oxygen, functioning as an electron acceptor. The role of tungsten is to function as an electron sink, which is very similar to the role of molybdenum in the substrate reduction phase of xanthine oxidase turnover.[21]

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Registry No. $(Et_2NH_2)_2WOS_3$, 112296-52-3; $[WO(S_2)(S_2CNEt_2)_2]$, 108556-13-4; CS_2, 75-15-0; O_2, 7782-44-7.

Department of Chemistry
Indian Institute of Technology
Kanpur 208016, India

Mohammad A. Ansari
Jayanthi Chandrasekaran
Sabyasachi Sarkar*

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[11] (a) The reaction does not take place in H_2S atmosphere. (b) As suggested by one of the reviewers, incubation of the reaction mixture under an inert atmosphere (N_2) for 20 h followed by exposing the mixture to air takes a further 36 h to complete the reaction. This eliminates direct anaerobic reduction of W(VI) to W(IV) under the reaction conditions with the oxidation of W(IV) by aerial oxygen to W(V) as a side reaction.

[12] Thermal reaction of the product or keeping it for weeks in solution gives the W(V) dimer, $[W_2O_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$: Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Bull. Chem. Soc. Jpn.* in press.

[13] Workup of the reaction mixture at this stage gives mostly the unreacted starting material.

[14] (a) Eastland, G. W.; Symons, M. C. R. *J. Phys. Chem.* **1977**, *81*, 1502. (b) Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. T. *Inorg. Chem.* **1983**, *22*, 2577.

[15] Seel, F. In *Sulfur, its Significance for Chemistry for Geo-, Bio-, and Cosmosphere and Technology*; Muller, A., Krebs, B., Eds; Elsevier: Amsterdam, 1984; pp 78–84.

[16] (a) The formation of S_3^- suggests the involvement of many side reactions associated with the main reaction. It is well-known that aerial oxygen oxidizes sulfide to elemental sulfur especially in the presence of transition-metal ions. Furthermore, S_2^{2-} reacts with elemental sulfur to produce higher polysulfides, which in polar solvents like DMF may dissociate to generate radicals like S_3^-. This process may be more complicated in the presence of W(V) and O_2^-. (b) We have checked the reaction of elemental sulfur in the presence of KO_2 in DMF by EPR, which shows the formation of S_3^-.

[17] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, Chichester, Brisbane, Toronto, 1980; pp 490–491.

[18] Hasegawa, K.; Imamura, T.; Fujimoto, M. *Inorg. Chem.* **1986**, *25*, 2154.

[19] The compound has been tentatively identified as $[WO(S_2CNMe_2)_3]$ on the basis of elemental analysis and IR and EPR spectroscopy.

[20] $[W^{VI}O(S_2)(S_2CNEt_2)_2]$ on reacting with CN^- produces $[W^{IV}O(S_2CNEt_2)_2]$, which is more stable than its molybdenum analogue. This compound on prolonged stirring with polysulfide or elemental sulfur reverts back to $[W^{VI}O(S_2)(S_2CNEt_2)_2]$ (see ref 7c,d). The possibility that the last step in the mechanism of reaction 1 involves an oxidation, parallel to this type of reaction, is not excluded.

[21] Hughes, M. N. *The Inorganic Chemistry of Biological Processes*, 2nd ed.; Wiley: New York, 1981; pp 171–177 and references therein.

Cobalt(III) Complexes of 1,3-Propanediamine-*N*,*N*′-diacetic-*N*,*N*′-di-3-propionic Acid and 1,3-Propanediamine-*N*-3-propionic-*N*,*N*′,*N*′-triacetic Acid

Sir:

For (diamine-*N*,*N*′-diacetato-*N*,*N*′-di-3-propionato)metal(III) complexes, three geometrical isomers, differing in the number (2, 1, or 0) of six-membered carboxylate rings lying in the G plane, are possible: trans(O_5) (I), trans(O_5O_6) (II), and trans(O_6) (III) (Figure 1a). On the other hand, the unsymmetrical ligand 1,3-propanediamine-*N*-3-propionate-*N*,*N*′,*N*′-triacetate (1,3-pdp3a) can form only two geometrical isomers upon coordination, trans(O_5) (I) and trans(O_5O_6) (II) (Figure 1b).

We report the synthesis of the ligand 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionate (1,3-pddadp) in good yield along with small amounts of 1,3-pdp3a and the earlier reported[1,2] 1,3-propanediaminetetraacetic acid (H_4pdta). Two isomers of [Co(1,3-pddadp)]$^-$ and one of [Co(1,3-pdp3a)]$^-$ were isolated and

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[1] Dwyer, F. P.; Garvan, F. L. *J. Am. Chem. Soc.* **1959**, *81*, 2955.

[2] Van Saun, C. W.; Douglas, B. E. *Inorg. Chem.* **1969**, *8*, 1145. Ogino, H.; Takahashi, M.; Tanaka, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 424.

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