

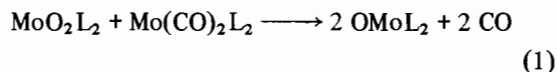
**Oxo Transfer from Mo(VI) to Mo(II) and W(II).
 Synthesis of W(VI) Dithiocarbamate Complexes^a**

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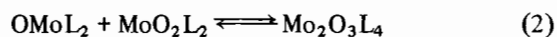
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The theory that the transfer of oxo groups may be involved in the mechanism of action of most molybdoenzymes^{1,2} prompted our previous studies of oxo-transfer reactions between³ Mo(VI) and Mo(IV) and between⁴ Mo(VI) and tertiary phosphines. As a continuation of this study, we now report the transfer of oxo groups from Mo(VI) to Mo(II) and W(II). The latter reaction yields *cis*-dioxotungsten(VI) complexes which have not been previously prepared. The chemistry of these complexes may give insight into the reasons for the inactivity of tungsten-substituted molybdoenzymes.

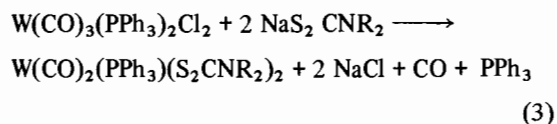
Reaction between the complexes MoO₂L₂ and Mo(CO)₂L₂ [L = S₂CNEt₂, S₂P(*i*-Pr)₂]^{5,6} in CH₂Cl₂ (eq. 1) results in the



rapid formation of 2 mol of the Mo(IV) complexes, OMoL₂, which were characterized by comparison of their ir spectra with spectra of known^{4,7} samples. If excess MoO₂L₂ was used, the purple color of Mo₂O₃-L₄ (formed as in eq. 2)³ was observed.



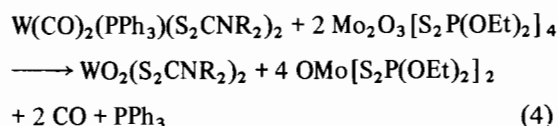
The ease with which oxo transfer occurred between Mo(VI) and Mo(II) suggested that an analogous reaction between Mo(VI) W(II) might yield OMoL₂ and OWL₂, thus providing a method of synthesizing the previously unknown W(IV) complexes. To this end, we prepared the new W(II) dithiocarbamate complexes W(CO)₂(PPh₃)(S₂CNR₂)₂ (R = Me, Et, *n*-Pr) according to eq. 3.



Although this general method has been used previously⁸ for the synthesis of the analogous Mo(II) complexes, we have extended the reaction to other dithio-

late ligands for both molybdenum and tungsten and have developed a more reliable preparation of W(CO)₃(PPh₃)₂Cl₂ (ref. 9). The synthesis and characterization of this series of complexes will be described in a forthcoming publication. We have not as yet been successful in attempts to prepare the phosphine-free complexes, W(CO)₂(S₂CNR₂)₂ or W(CO)₃(S₂CNR₂)₂.

Reaction of W(CO)₂(PPh₃)(S₂CNR₂)₂ with exactly 2 mol of the Mo(V) complex Mo₂O₃[S₂P(OEt)₂]₄ gave WO₂(S₂CNR₂)₂ according to eq. 4.



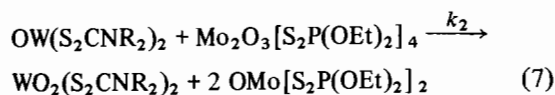
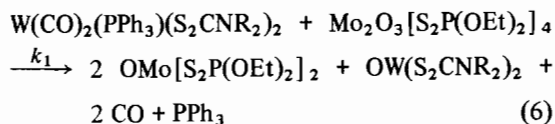
The white W(VI) complexes were isolated by evaporation of the reaction mixture to dryness and trituration of the residue with ether to remove pink OMo[S₂P(OEt)₂]₂, which was characterized by its ir and visible spectra⁷. Previously¹⁰, we suggested that Mo₂O₃[S₂P(OEt)₂]₄ dissociates *via* the equilibrium in eq. 5 even though MoO₂[S₂P(OEt)₂]₂ could not be



isolated, and now we further suggest that it is this Mo(VI) species which oxidizes the W(II) complex. Eq. 4 thus provides further indirect evidence for the validity of eq. 5.

Attempts to use MoO₂(S₂CNEt₂)₂ and MoO₂[S₂P(*i*-Pr)₂]₂ as reagents for the synthesis of W(VI) species were less successful because the tungsten complexes possessed similar solubility to OMo(S₂CNEt₂)₂ and OMo[S₂P(*i*-Pr)₂]₂. However, oxo transfer took place as evidenced by color changes in the reaction mixtures and isolation of impure products.

Reaction of *equimolar* amounts of Mo₂O₃[S₂P(OEt)₂]₄ and W(CO)₂(PPh₃)(S₂CNR₂)₂ did *not* yield OW(S₂CNR₂)₂ as had been expected but instead gave equal amounts of WO₂(S₂CNR₂)₂ and the starting W(II) complex. This result suggests that if OW(S₂CNR₂)₂ is formed in the reaction sequence (eq. 6), then Mo₂O₃[S₂P(OEt)₂]₄ must react much more rapidly with this compound (eq. 7) than with W(CO)₂(PPh₃)(S₂CNR₂)₂, *i.e.* $k_2 \gg k_1$.



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TABLE. Spectral Properties of $\text{WO}_2(\text{S}_2\text{CNR}_2)_2$.

Complex	Infrared ^a	Visible ^b
$\text{WO}_2(\text{S}_2\text{CNMe}_2)_2$	889, 934	305 (7059)
$\text{WO}_2(\text{S}_2\text{CNEt}_2)_2$	890, 933	305 (6810)
$\text{WO}_2[\text{S}_2\text{CN}(\text{n-Pr})_2]_2$	895, 935	305 (6303)

^aTerminal W=O stretching frequencies in cm^{-1} as KBR pellets.

^bPeak positions in nm with molar absorptivity in parentheses. Solvent was 1,2-dichloroethane.

Characterization of $\text{WO}_2(\text{S}_2\text{CNR}_2)_2$

For R = Me and Et, the complexes gave satisfactory elemental analyses for C,H,N. So far, we have been unable to obtain an analytically pure sample of the n-propyl derivative but its ir spectrum indicates relatively high purity. The tungsten-oxygen stretching frequencies in the ir spectra of these complexes appear at ~ 890 and $\sim 930 \text{ cm}^{-1}$ (exact values are given in the Table). Except for a shift to higher energy of $\sim 20 \text{ cm}^{-1}$ in the metal-oxygen stretching frequencies, these spectra were virtually identical to the well-characterized, analogous molybdenum species. As noted above, the W(VI) complexes are white solids and their UV spectra (Table) contain a band at $\sim 305 \text{ nm}$. The analogous molybdenum complexes are yellow with a band at $\sim 380 \text{ nm}$ which was postulated to be due to a molybdenum-oxygen transition.³ Therefore, if this band is due to a metal-oxygen transition in both systems, it is shifted to significantly higher energy in the tungsten complexes.

$\text{WO}_2(\text{S}_2\text{CNMe}_2)_2$ is reasonably stable in dry solvents, but decomposition occurs in the presence of H_2O . The analogous diethyl and di-n-propyl complexes appear to decompose even in dry solvents and so must be isolated quickly during their preparation in order to be obtained pure. Decomposition is accompanied by the appearance of very broad bands at $\sim 800 \text{ cm}^{-1}$ in the ir spectra of isolated solids and could be due to instability of either the tungsten-dithio-carbamate or the tungsten-oxo moiety. This lack of stability is consistent with the utter failure of our attempts to prepare $\text{WO}_2(\text{S}_2\text{CNR}_2)_2$ from Na_2WO_4 in aqueous solution using methods similar¹¹ to those employed for $\text{MoO}_2(\text{S}_2\text{CNR}_2)_2$. Attempts to reduce $\text{WO}_2(\text{S}_2\text{CNMe}_2)_2$ using tertiary phosphines have so far yielded only uncharacterized products. This situation contrasts with the analogous molybdenum complex which cleanly transfers an oxo group to PR_3 forming OPR_3 and $\text{OMo}(\text{S}_2\text{CNMe}_2)_2$.⁴ These differences are further supplemented by the apparent inability of $\text{WO}_2(\text{S}_2\text{CNR}_2)_2$ to interact with other complexes *via* well-characterized oxo transfer. Thus, $\text{WO}_2(\text{S}_2\text{CNMe}_2)_2$ does *not* react at all with $\text{OMo}(\text{S}_2$

$\text{CNEt}_2)_2$ or $\text{W}(\text{CO})_2(\text{PPh}_3)(\text{S}_2\text{CNMe}_2)_2$ and only reacts slowly with $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$ to yield ill-characterized products, even though $\text{MoO}_2(\text{S}_2\text{CNMe}_2)_2$ reacts rapidly with all three species under mild conditions.

The lack of reactivity of the *cis*- WO_2 complexes with respect to clean oxo transfer may be a significant factor in the inactivity of a variety of tungsten-substituted molybdo-enzymes, *e.g.*, nitrogenase¹², nitrate reductase¹³, sulfite oxidase¹⁴, and xanthine oxidase¹⁵. The last three molybdo-enzymes, in their native state, all exhibit an EPR signal attributable to Mo(V) during their catalytic cycle^{2,16}, indicating the involvement of the higher oxidation states of molybdenum in the various catalyzed processes. Thus, the inactivity of the tungsten-substituted oxidases could result from the inability of W(VI)=O to undergo oxo transfer to substrate, while in the reductases, either the apparent instability of W(IV) or the difficulty in removing oxo from tungsten to reactivate the catalytic site may be responsible for the lack of activity.

Acknowledgment

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