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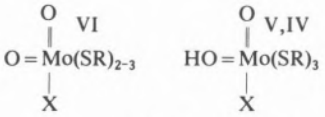
MODELS FOR THE MOLYBDENUM CENTERS OF THE MOLYBDENUM HYDROXYLASES

Recent EXAFS and EPR results indicate the Mo centers of sulfite oxidase and assimilatory nitrate reductase in their oxidized (Mo(VI)) and reduced (Mo(V), Mo(IV)) states have ligand sets as follows [1]:

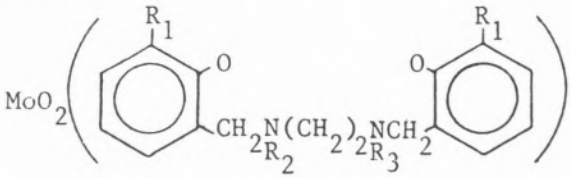


(SR = thiolate S, X = O, N or thioether S)

Most $Mo(VI)O_2L_n$ complexes (L = ligand(s) with O, N or S coordinating groups) give oxo-Mo(V) dimers upon one-electron reduction:

$$1/2\ H_2O + MoO_2L_n \xrightarrow{e^-} 1/2\ Mo_2O_3L_{2n} + OH^- \qquad (1)$$

A number of MoO_2L_n complexes having sterically bulky ligands which prevent such dimer formation upon reduction have been synthesized in this laboratory:

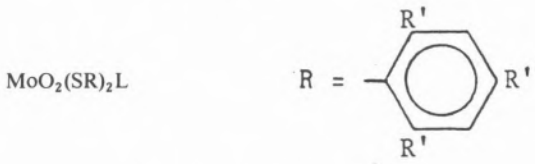


$R_1 = t\text{-Bu},\ R_2 = R_3 = H$
$R_1 = t\text{-Bu},\ R_2 = R_3 = Me,\ Et$
$R_1 = H,\ R_2 = R_3 = Me,\ Et$
$R_1 = t\text{-Bu},\ R_2 = H,\ R_3 = Me,\ Et$

$MoO_2[SC(R_1)_2CH_2N(CH_2)_2\ NCH_2C(R_1)_2S]$

$R_2 \qquad R_2$

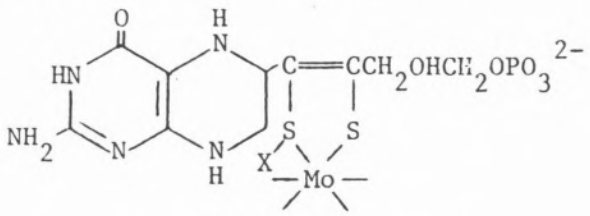
$R_1 = Me,\ Et,\ R_2 = H$
$R_1 = H,\ R_2 = Me$



R' = Me, *i*-Pr; L = en, bpy, phen

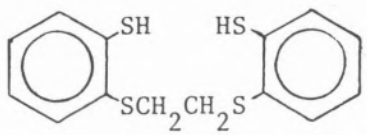
One-electron electrochemical reduction of these complexes gives Mo(V) monomeric products with structures dependent on the presence and the number of protons on the amino groups of the ligands. In some cases, the oxo-Mo(V) complexes and the oxo-Mo(IV) complexes have also been synthesized. Structures, electrochemical properties and EPR spectra of the complexes have been obtained. Their relevance as models for the enzyme Mo centers will be discussed.

Recent work has identified a novel reduced pterin with a sulfur side chain, obtained from the Mo-cofactor of the Mo hydroxylases, for which a Mo-binding site has been proposed [2]:



X = Me, if present.

As possible models for Mo coordination of this kind, MoO_2(dttd), MoOCl(dttd) and MoO(PPh_2Et)(dttd) have been synthesized ($dttdH_2$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane).



$dttdH_2$

MoO_2(dttd) has been determined by X-ray crystallography to have substantially distorted octahedral geometry, with the thioether groups approximately *trans* to the oxo groups. MoO_2(dttd) is reduced electrochemically to MoO(dttd) without dimer formation. MoOCl(dttd) and MoO(dttd) form a reversible couple, but neither can be oxidized electrochemically to MoO_2(dttd). While the oxo-Mo(V) dimer, $Mo_2O_3(dttd)_2$, is thermodynamically stable, it is not formed in the coulometric reduction of MoO_2(dttd) because the comproportionation reaction is very slow:

$$MoO_2(dttd) + MoO(dttd) \longrightarrow Mo_2O_3(dttd)_2 \quad slow \qquad (2)$$

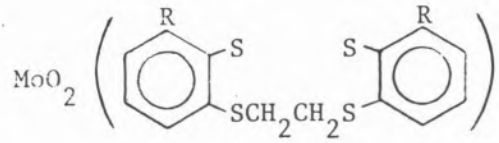
As a result, MoO_2(dttd) reacts with PPh_2Et to give $OPPh_2Et$ and the Mo(IV) complex without dimer formation, while MoO(dttd) reacts with Me_2SO to give MoO_2(dttd) and Me_2S:

$$MoO_2(dttd) + PPh_2Et \longrightarrow MoO(dttd) + OPPh_2Et \quad (slow) \quad (3)$$

$$MoO(dttd) + Me_2SO \longrightarrow MoO_2(dttd) + Me_2S \quad (fast)$$

MoO_2(dttd) thus catalyzes the reduction of Me_2SO to Me_2S, mimicking the Mo enzyme, biotin sulfoxide reductase.

The electrochemical properties and EPR spectra of the complexes have been determined, and the properties of similar complexes having bulky groups on the ligand will be reported:



R = Me, Et, *i*-Pr

The plausibility of an unsaturated thiolate-thioether ligand as a model for the Mo binding site in the Mo-pterin ligand will be discussed.

REFERENCES

[1] S.A. CRAMER, L.S. SOLOMONSON, M.W.H. ADAMS, L.E. MORTENSON, *J. Am. Chem. Soc.*, **106**, 1467 (1984).

[2] J.L. JOHNSON, K.V. RAJAGOPALAN, *Proc. Natl. Acad. Sci. USA*, **79**, 6856 (1982).

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STRUCTURAL AND ^1H AND ^{31}P NMR SPECTROSCOPIC STUDIES OF B_{12} COMPOUNDS: A NEW CRYSTALLINE FORM OF VITAMIN B_{12}

Coenzyme B_{12} (5'-deoxyadenosylcobalamin) can be considered to be an «organic radical carrier» much as the heme group in hemoglobin is a dioxygen carrier [1]. In both types of protein systems, the conformation of the protein influences the ability of the metal center to bind the carried species (radical or dioxygen) [2-4]; therefore, the relationship between the structure at the metal center and its carrying function is both intriguing and important. FINKE [5] has pointed out the need for a greater understanding of the structural factors that influence Co-C homolysis. Until recently, X-ray structural information was available for only one organometallic B_{12} compound, namely coenzyme B_{12} itself [6]. This structure established that the 5'-deoxyadenosyl group was attached to the cobalt *via* the 5'-carbon atom. This was the first demonstration of the existence of a naturally occurring alkyl organometallic compound.

Methyl B_{12} (methylcobalamin) is a biologically active coenzyme and is essential for human metabolism [3]. At the First International Bio-Inorganic meeting, we presented the first report of the