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STABILIZATION OF MONOOXOMOLYBDENUM(V) COMPLEXES $[MoO(SR)_4]^{1-}$ USING PEPTIDE THIOLATO AND BULKY AROMATIC THIOLATO LIGANDS

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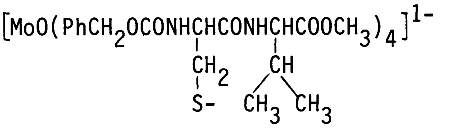
Mononuclear monooxomolybdenum(V) peptide complexes having hydrophobic amino acid residues adjacent to Cys residue, $[MoO(Z\text{-}cys\text{-}Val\text{-}OMe)_4]^{1-}$ and $[MoO(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}OMe)_2]^{1-}$, exhibit large $A_{\parallel}$ values (54.2×10^{-4} cm^{-1} and 56.6×10^{-4} cm^{-1}, respectively) in the EPR spectra. Other monooxomolybdenum(V) complexes having bulky thiolato ligands, $[NEt_4][MoO(tmbt)_4]$ (tmbt = 2,4,6-trimethylbenzenethiolato) and $[NEt_4][MoO(tipbt)_4]$ (tipbt = 2,4,6-triisopropylbenzenethiolato), have been prepared. These have a covalent Mo=O bond as evidenced by the EPR (large $A_{\parallel}$ of 57.6×10^{-4} cm^{-1}), and high ν(Mo-O) (944 cm^{-1}) from Raman spectroscopy on the latter complex). Electrochemical reduction of these complexes results in removal of the oxo ligand.

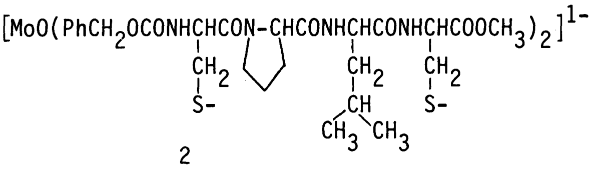
Recently Bray et al. have proposed an active site structure of $[MoO(SR)_4]$ for the $[Fe(CN)_6]^{3-}$-oxidized species (Mo(V)) of the reduced xanthine oxidase (Mo(IV).[1]) Two of these thiolato ligands consist of pterin-dithiolene sulfur atoms and the others come from Cys-thiolato ligands of the protein. Many dioxomolybdenum(VI) and monooxomolybdenum(V) complexes of thiolato ligands have been synthesized as a model complex of molybdoenzymes.[2-7]) In the dioxomolybdenum(VI) model complexes, the thiolato ligand was found to enhance the reactivity of one of the Mo=O groups for oxo-transfer reactions.[8,9]) However, the reductive deoxo reaction of the residual monooxomolybdenum(V) is quite difficult under mild conditions.[6,8]) In this paper we communicate the preparation of Cys-containing peptide monooxomolybdenum(V) complexes and bulky aromatic thiolato complexes and an electrochemical deoxo reaction of the bulky thiolato monooxomolybdenum(V) complex.

Monooxomolybdenum(V) complexes with Cys-containing peptide ligands were synthesized from $MoOCl_3(thf)_2$ and a monodentate peptide, Z-Cys-Val-OMe or a chelating peptide, Z-Cys-Pro-Leu-Cys-OMe. Thus, $[Et_3NH][MoO(Z\text{-}cys\text{-}Val\text{-}OMe)_4]$ (Z = benzyloxycarbonyl) (**1**),[10]) purple microcrystals, and $[Et_3NH][MoO(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}OMe)_2]$ (**2**), deep rose lilac microcrystals, were obtained from the reaction among $MoOCl_3(thf)_2$, the corresponding peptide, and triethylamine in 1,2-dimethoxyethane (DME) under argon atmosphere at 25 °C. Triethylamine was employed to avoid racemization of the Cys-containing peptides. **1** and **2** show a ligand-metal charge transfer band at 530 nm (ε : 1100) or 520 nm (ε: 1300) in acetonitrile. The visible spectroscopic data of unstable mononuclear $[MoO(SR)_4]^{1-}$ with an alkanethiolato ligand have been limited to a brief description of the purple color of a solution of $[MoO(SEt)_4]^{1-}$ or $[MoO(SCH_2Ph)_4]^{1-}$ at -60 °C.[3] The present successful isolation of **1** and **2** is attributable to the bulky peptide ligands which prevent the formation of bi- or polynuclear complexes.



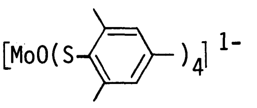
$[MoO(PhCH_2OCONHCHCONHCHCOOCH_3)_4]^{1-}$

1



$[MoO(PhCH_2OCONHCHCON\text{-}CHCONHCHCONHCHCOOCH_3)_2]^{1-}$

2



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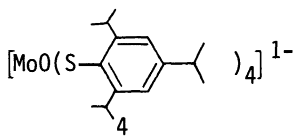

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Table 1. EPR Parameters of Monooxomolybdenum(V) Complexes in Frozen Acetonitrile at 77 K

Complexes	$g_{\parallel}$		$g_{\perp}$	$A_{\parallel}$ x $10^4/cm^{-1}$
$[Et_3NH][MoO(Z\text{-}cys\text{-}Val\text{-}OMe)_4]$ (**1**)	2.0215		1.9736	54.2
$[Et_3NH][MoO(Z\text{-}cys\text{-}Pro\text{-}Leu\text{-}cys\text{-}OMe)_2]$ (**2**)	2.0273	1.9786	1.9634	56.6
$[Et_4N][MoO(tmbt)_4]$ (**3**)		1.9873	(g_{av})	
$[Et_4N][MoO(tipbt)_4]$ (**4**)	2.0196		1.9741	57.6
$[Et_4N][MoO(SPh)_4]$ (**5**)	2.0185		1.9787	52.3

The EPR parameters of **1** and **2** in frozen acetonitrile solution at 77 K are listed in Table 1. The peptide complexes exhibit the same g_{av} values as that reported for $[MoO(SEt)_4]^{1-}$ and $[MoO(SCH_2Ph)_4]^{1-}$ at 77 K. The $A_{\parallel}$ values are relatively large (56.6 x 10^{-4} cm^{-1}) compared with those of the frozen solutions of $[MoO(SEt)_4]^{1-}$ (52.9 x 10^{-4} cm^{-1}) and $[MoO(SCH_2Ph)_4]^{1-}$ (52.8 x 10^{-4} cm^{-1}). This may be due to weakened Mo-S bonds by the ligand bulkiness because of the reduced π-interaction between Mo(V) and sulfur ligand.[3,11] The Raman spectral data for the Mo-O stretching bands are listed in Table 2. **2** shows a relatively higher ν(Mo-O) band (948 cm^{-1}) than conventional $[MoO(SR)_4]^{1-}$ complexes.

The electrochemical properties of the peptide complexes were investigated by cyclic voltammetry in acetonitrile with $[(\underline{n}\text{-}Bu)_4N][ClO_4]$ electrolyte. **1** exhibits a quasi-reversible Mo(IV)/Mo(V) redox couple at -0.61 V (vs. SCE) and an irreversible couple at E_{pa} = +0.93 V (vs. SCE).

Table 2. Raman[a)] and IR Spectral Data of ν(Mo-O) Stretching Bands of **1** - **5**

Complexes	Raman (ν/cm^{-1}) ν(Mo-O)	IR (ν/cm^{-1}) ν(Mo-O)
1	920	-
2	948	-
3	945	938
4	946	944
5	936	934

a) Raman spectra were recorded with 632.8 nm exitation line at 25 °C.

2 shows an irreversible couple at E_{pa} = -0.42 and E_{pc} = -0.73 V (vs. SCE), suggesting that the corresponding Mo(IV) species is very unstable. Further investigation of the peptide monooxomolybdenum(V,IV) complexes having hydrophobic amino acid residues is in progress.

In order to establish the effect of the bulky thiolato ligand on the reactivity of Mo=O group in the low-valent state, $[NEt_4][MoO(tmbt)_4]$ (tmbt = 2,4,6-trimethylbenzenethiolato) (**3**) and $[Et_4N][MoO(tipbt)_4]$ (tipbt = triisopropylbenzenethiolato) (**4**) were synthesized from Na(tmbt) or Na(tipbt), NEt_4Cl, and $MoOCl_3(thf)_2$ in DME. **3** was obtained as deep blue crystals by the recrystallization from acetonitrile (70 % yield). Visible ; 575 nm (ε: 1700). **4** was recrystallized from DME and _n_-hexane to give deep indigo crystals (53 % yield). Visible ; 566 nm (ε: 1200). $[NEt_4][MoO(SPh)_4]$ (**5**) was prepared for the comparison according to the modified method reported by Hanson et al.[3] Visible ; 598 nm (ε: 6600) in acetonitrile. These absorption maxima for **3** - **5** are due to a ligand-metal charge transfer absorption. In general, an increase of the electron donating ability of the thiolato ligands by _o_ or _p_-methyl groups contributes to the red shift of the charge transfer absorption.[3] However, **3** and **4** having bulky 2,4,6-trialkylbenzenethiolato ligands exhibit the blue-shift of the maxima. The bulky groups thus prevent π-conjugation between Mo(V) and sulfur ligand to cancel the electron-donating effect of the alkyl groups.

The EPR parameters of **3** - **5** are listed in Table 1. **4** and **5** exhibited a distinct hyperfine structure with anisotropic pattern. **4** give a high $A_{//}$ value (57.6×10^{-4} cm^{-1}) due to weakened Mo-S bond by the ligand bulkiness. This is consistent with the results from the visible spectra, which indicate weak π-interaction between Mo(V) and sulfur by the ligand bulkiness in **4**. The absence of a clear hyperfine structure for **3** requires further investigations.

In general, the substitution of sulfur ligands with N or O ligands leads to the higher ν(Mo-O)

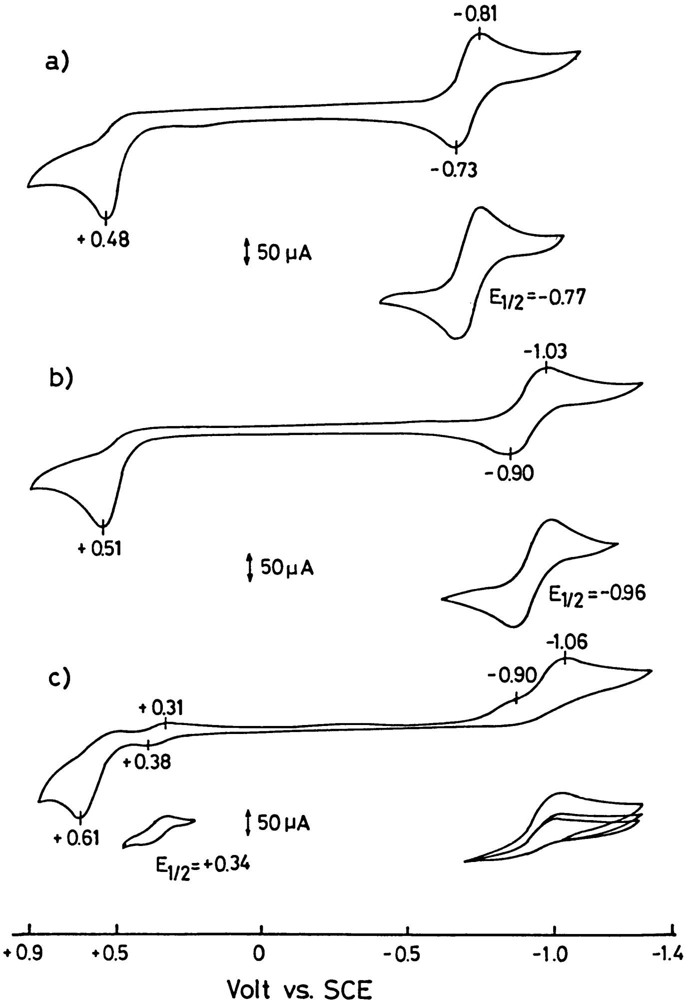

Fig. 2. Cyclic voltammograms of a) $[Et_4N][MoO(SPh)_4]$ (**5**), b) $[Et_4N][MoO(tmbt)_4]$ (**3**), and c) $[Et_4N][MoO(tipbt)_4]$ (**4**) in acetonitrile.

stretching Raman frequency in the case of $MoO_2(L-L)_2$ type.[9,11] The bulky thiolato complexes (**3** and **4**) exhibit higher ν(Mo=O) values (945 - 948 cm^{-1}). The bulky thiolato ligand is less electron-donating to Mo(V) by hindered conjugation and thus enhances Mo=O bonding by π-donation from the oxo ligand.

3 exhibits a quasi-reversible redox couple at $E_{1/2}$ = -0.96 V (vs. SCE) as shown in Fig. 2. **4** has two irreversible peaks at E_{pa} = +0.76 V and E_{pc} = -1.06 V (vs. SCE). The scanning upto -1.3 V results in the appearance of a new quasi-reversible redox couple at $E_{1/2}$ = +0.34 V (vs. SCE), which is due to the formation of a Mo(IV) species since the redox couple of $[Mo^{IV}(tipbt)_4]$ is at +0.32 V (vs. SCE) for Mo(V)/Mo(IV) in DME.[13,14] We speculate that this is due to the formation of $[Mo^{IV}(SR)_4]$ in the electrochemical reduction of the monooxomolybdenum(V) thiolato complexes with bulky ligands. Thus, the Mo(IV) species, $[Mo^{IV}O(tipbt)_4]^{2-}$ has a relatively reactive Mo=O group, although the Mo=O bond in the Mo(V) state is relatively strong as mentioned above. In the Mo(IV) state, the four Mo-S bonds would become stronger and then seem to activate the Mo=O group to result in the deoxo reaction.

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