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Coordination Complexes of Mo(VI) with Tridentate Schiff Base Ligands: Synthesis and Redox Activity

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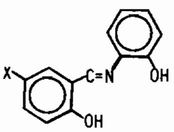
Molybdenum is the only second row transition metal which is essential to living systems. Enzymes such as nitrogenase, nitrate reductase, aldehyde oxidase, *etc.* are believed to have Mo coordinated at the active site [1]. The oxidation state of the Mo varies depending on the nature of the particular enzyme. The actual coordination geometry about the Mo in these enzymes is uncertain. Recent biochemical investigations [2–4] have revealed that all of the Mo enzymes except nitrogenase may have a common Mo cofactor. EXAFS data have shed some light on the nature of the coordination sphere about the Mo. Recent results on xanthine oxidase [5] and sulfite oxidase [6] have established that the Mo coordination environment in these two enzymes are similar and that each contains terminal oxo groups bonded to the Mo. On the other hand nitrogenase [7] has been found to have primarily S ligation with no Mo=O species present. In an effort to expand our knowledge of the coordination chemistry of Mo we have synthesized Mo(VI) complexes using tridentate Schiff base chelates to examine their electronic structure and reactivity as a function of ligand structure. We report here on the synthesis, electronic spectra and redox activity of some new Mo(VI) coordination complexes.

Discussion

Schiff base ligands of the type X = H, Br, NO_2, CH_3O were synthesized to impart various electronic structures to the Mo complexes while at the same time coordinating in an identical manner. Tridentate ligands were employed to obtain *cis*-dioxo-Mo(VI) complexes which would be potentially coordinatively unsaturated. Although much of the chemistry of Mo(VI) is dominated by monomeric complexes, our infrared spectra reveal the possibility of the existence of a mixture of monomer and dimer in the solid state. However in solution the complex is monomeric and most probably the tridentate ligand lies in the equatorial plane of the complex along with one of the oxo ligands while the solvent molecule occupies a labile coordination site trans to the remaining oxo ligand. The metal complexes other than X = H [8] are new. The complexes have been characterized by IR, NMR and UV–vis spectroscopy. Analytical data is presented in Table I.



In DMSO the complexes are stable for some time as the electronic spectra are unchanged. The electronic spectra for the four complexes are very similar and are dominated by charge transfer transitions. The first electronic transition is most likely a ligand to metal charge transfer transition. The energy of this first transition shifts depending on the X-group present on the tridentate Schiff base ligand (Table I). As the X-group becomes more electron withdrawing the energy of the first electronic transition shifts to higher energy. This transition is a measure of the energy difference between the highest occupied ligand molecular orbital and the lowest empty Mo d-orbital. The nature of the Mo d-orbitals are of interest because in a reduction process they are the orbitals that will accept any additional electrons. As Table I and Fig. 1 indicate, the cathodic reduction peak for these complexes becomes more positive as the energy of the first transition shifts to higher energy (except for X = H). It is sometimes difficult to obtain correlations between electronic transitions and redox potentials however in this case the ligands are only slightly changed and the trends observed are most

TABLE I. Cyclic Voltammetry, Electronic Spectral and Elemental Analysis Data for the Mo(VI) Dioxo-Complexes.

	Ep_c[a]	λ[b](nm)	$\nu(cm^{-1})$	log ϵ	C (calculated)	H	N
MoO_2(H-L)·ETOH	−1.09	422	23697	3.59	46.78 (45.30)	3.74 (3.53)	3.64 (3.77)
MoO_2(NO_2-L)·DMSO	−0.97	422	23697	3.72	38.88 (38.97)	3.22 (3.05)	5.91 (6.06)
MoO_2(Br-L)·DMSO	−1.07	432	23148	3.60	36.11 (36.31)	2.81 (2.84)	2.74 (2.82)
MoO_2(CH_3O-L)·DMSO	−1.14	445	22472	3.63	43.12 (42.96)	3.45 (3.83)	3.17 (3.13)

[a] Volts *versus* Ag/AgCl. [b] Lowest energy electronic transition.

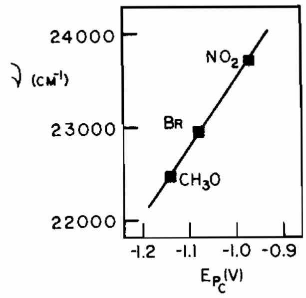


Fig. 1. Correlation of the low energy charge-transfer electronic transition with the cathodic reduction potential (*versus* Ag/AgCl) for MoO_2(X-L) (X = NO_2, Br and CH_3O).

likely a result of ligand 'fine tuning'. Nakamura *et al.* [9] have shown how a variation in the ligand donor atom set affects the reduction potentials of octahedral monomeric *cis*-dioxo-Mo(VI) chelates. They observe that the more sulfur atoms present the easier is the complex reduced. They conclude that the sulfur allows more electron delocalization and hence make it easier for the complex to accept additional electrons. With our complexes we find that the higher the energy of the first electronic transition the easier is the complex reduced (*cf.* complex with X = NO_2). Cyclic voltammetry shows the complexes undergoing an irreversible reduction (Fig. 2). As a result no formal reduction potential can be obtained however trends in the potential of the cathodic reduction peak are still present (Table I). At the scan rate of 2 V/sec the irreversible reduction is most probably due to the formation of a binuclear Mo(V) complex. Binuclear Mo(V) complexes have been studied for many years [1] and their stability make them likely candidates for the products of the reductions discussed above. It is interesting to note for these complexes that the cathodic reduction peak is shifted almost 200 mV on going from X = NO_2 to X = CH_3O. As a comparison the one electron reduction potential for $MoO_2(Et_2dtc)_2$ (Et_2dtc = diethyldithiocarbamate) is –0.83 V [10] and for $MoO_2(OX)_2$ (OX = hydroxyquinoline) is –1.07 V [11] here a difference of approximately 250 mV. In the latter two complexes the change in reduction potential was accomplished by a radical change in the ligating atoms surrounding the metal. In $MoO_2(Et_2dtc)_2$, the metal is complexed by four sulfur atoms in addition to the two oxo ligands. The sulfur atoms are efficient at electron delocalization and because of this it is much easier to reduce this complex as compared to $MoO_2(OX)_2$. The 'harder' oxygen and nitrogen of the 8-hydroxyquinoline are not as efficient at electron delocalization.

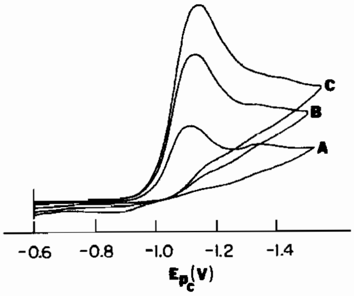


Fig. 2. Cyclic voltammogram for MoO_2 (H-L) in DMSO. Voltages are reported *versus* Ag/AgCl (scan rate: A = 50 mV/sec; B = 100 mV/sec; C = 200 mV/sec).

The Schiff base ligands used in the present study coordinate to the Mo using oxygens and nitrogen, the same donor atoms we find for 8-hydroxyquinoline. For X = H the cathodic reduction peak occurs at −1.05 V for the Mo complex. This is very close to that observed for $MoO_2(OX)_2$. Without changing the basic stereochemistry and the ligand donor atom set around the Mo we have been able to vary the reduction potential of the complex through only a minor ligand modification.

We have already noted the correlation between the energy of the first electronic transition and the cathodic reduction potential (see Fig. 1). If we assume that in all four complexes the energy of the LUMO to be about the same then we find that as the X-group becomes more electron withdrawing, the energy of HOMO drops. This is reasonable, since for simple ligand systems, the more electronegative the ligands, the more stable (with respect to the metal orbital) are the ligand MO's. It appears that for our complexes the ease of reduction is directly related to the electron withdrawing capacity of the ligand. This electron withdrawing capacity is also manifested in the ligand-to-metal charge transfer transition.

This work has shown how it is possible to vary the reduction potential of a Mo(VI) complex without significantly changing the coordinating properties of its ligand. The electronic spectra can be used to obtain a qualitative measure of the ease of reduction. These Mo complexes do not model Mo oxidase enzymes in that they do not readily react with substrates such as triphenylphosphine in an oxygen transfer reaction. Additional ligands are being prepared to extend our range of reduction potentials and allow us to gain more information on ligand structure and metal complex redox activity.

Experimental

The ligands were prepared by the condensation of substituted salicylaldehydes with *o*-aminophenol. The Mo complexes were prepared by the following general procedure: The ligand (0.001 mol) and $NaOCH_3$ (0.002 mol) were dissolved in a minimum amount of DMSO. MoO_2Cl_2 (0.001 mol) was dissolved in a minimum of absolute ethanol. The two solutions are mixed and on cooling the Mo complexes precipitate. They are recrystallized from DMSO/H_2O. NMR and

UV-visible spectra were obtained in DMSO. Cyclic voltammetry was done in DMSO with LiCl as the supporting electrolyte using a potentiostat of conventional design. Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

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