Contribution from the Department of Chemistry,
Virginia Commonwealth University, Richmond, Virginia 23284

Ligand Control of the Redox Properties of Dioxomolybdenum(VI) Coordination Complexes

JOSEPH TOPICH

Received November 5, 1980

Several new *cis*-dioxomolybdenum(VI) coordination complexes have been synthesized incorporating dibasic tridentate Schiff-base ligands derived from 5-substituted salicylaldehydes and *o*-aminophenol, 2-aminoethanol, or anthranilic acid. The synthesis and characterization of these complexes are described. Cyclic voltammetry was used to obtain cathodic reduction potentials (E_{pc}) for the irreversible reduction of the Mo(VI) complexes. The substituent on the salicylaldehyde portion of the ligand causes rather substantial differences in the E_{pc}'s that are observed for the Mo(VI) complexes. Electron-withdrawing substituents cause an anodic shift in E_{pc} while the opposite effect is observed for electron-donating ligand substituents. Within a series of Mo complexes, a potential range of ~200 mV is spanned, and a linear relationship is observed between E_{pc} and the Hammett σ_p parameter for the ligand substituent. In addition to substituent effects within each series, there are structural effects between series that are important. Ligand delocalization and the substitution of a carboxylic acid group for the phenolic oxygen donor atom facilitate Mo complex reducibility. The trends in E_{pc} are also manifested in shifts observed in the low-energy ligand-to-metal charge-transfer transitions, and these are also discussed.

Introduction

Molybdenum is a versatile transition element due to the fact that it possesses a large number of stable and accessible oxidation states. A variety of chemical reactions are catalyzed by molybdenum coordination complexes. Molybdenum compounds provide the active centers for such processes as hydrodesulfurization[1] and for oxygen atom transfer reactions such as olefin epoxidation and deepoxidation.[2] The useful role of molybdenum is not restricted to industrial type catalytic reactions. Nature has incorporated molybdenum into a number of redox enzymes.[3] These include among others aldehyde, sulfite, and xanthine oxidase, nitrate reductase, and nitrogenase. Nitrate reductase and nitrogenase are important reducing enzymes that are involved in the nitrogen cycle of plants. The common feature associated with both the industrial and biological reactions is that the molybdenum serves as the site for a catalytic redox reaction.

The higher oxidation states of molybdenum are dominated by complexes that contain the molybdenum-oxo group. Monooxo- or *cis*-dioxomolybdenum species are observed. Most simple Mo(VI) coordination complexes contain the *cis*-dioxo MoO_2^{2+} cation. Recent EXAFS studies have confirmed the presence of this group as well as sulfur in the vicinity of the molybdenum in the oxidized forms of xanthine oxidase[4] and sulfite oxidase.[5]

Chakravorty[6] has reported on the synthesis and cyclic voltammetry of some *cis*-dioxomolybdenum(VI) complexes that incorporate tridentate Schiff-base ligands that contain nitrogen, oxygen, and/or sulfur donor atoms. Their results show that replacement of one oxygen by a sulfur donor leads to a complex that is easier to reduce and that ligand substituents not directly bonded to the metal also alter the redox properties of the molybdenum. These and other molybdenum complexes can be prepared by several methods depending on whether Na_2MoO_4, MoO_2Cl_2, or $MoO_2(acac)_2$ (acac$^-$ = acetylacetonate monoanion) is used as the source of the MoO_2^{2+} cation. MoO_2(5-H-SAP)[6-8] and MoO_2(5-H-SAE)[6] have been described by others in the literature. Some comment is necessary about the general synthesis of compounds of this type because there is some question about the actual nature and stoichiometry of the isolated product. McAuliffe[9] and Chakravorty[10] have both described a synthesis using 5-H-SAP-H_2 and $MoO_2(acac)_2$ to obtain the *cis*-dioxomolybdenum(VI) complex; however, they suggest different stoichiometries for their products. Chakravorty claims that the two acac$^-$ ligands are displaced and the final stoichiometry of the product is MoO_2(5-H-SAP)(CH_3CH_2OH) with 5-H-SAP^{2-} acting as a tridentate ligand and the ethanol, which was the reaction solvent, bound in the sixth coordination site. The ethanol can be replaced by Me_2SO, DMF, pyridine, etc., and IR data are presented for these adducts. On the other hand, McAuliffe asserts that the 5-H-SAP-H_2 acts as a monoanionic species binding only as a bidentate ligand displacing only one of the acetylacetonate ligands of the $MoO_2(acac)_2$ complex. He presents analytical as well as NMR data to support the stoichiometry of the product as MoO_2(5-H-SAP-H)(acac). The reason for differences between McAuliffe's and Chakravorty's work is unclear. Results to be discussed in a later section support Chakravorty's claim concerning the product obtained by the reaction of $MoO_2(acac)_2$ with 5-H-SAP-H_2. We have shown in a preliminary report[11] that within a particular ligand series (5-X-SAP-H_2) there is a linear correlation between the cathodic reduction potential of the Mo(VI) complex and the Hammett σ_p parameter of the X substituent on the ligand. This paper reports on the extension of this study to include some new Mo(VI) coordination complexes. Trends in cathodic reduction potentials and charge-transfer transitions are discussed in terms of ligand substituent and ligand structural variations.

Experimental Section

Materials. All ligand components (5-X-salicylaldehyde (X = H, Cl, Br, NO_2, CH_3O), *o*-aminophenol, 2-aminoethanol, and anthranilic acid) were obtained from commercial sources and used without further purification. Dimethyl sulfoxide (Me_2SO) and *N,N*-dimethylformamide (DMF) were reagent grade and were dried over type 3A molecular sieves. $Na_2MoO_4{\cdot}2H_2O$ and MoO_2Cl_2 were obtained from

---

[1] Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979; p 390.

[2] Green, M. L. H. " Proceedings of the Climax Third International Conference on the Chemistry and Uses of Molybdenum"; Barry, H. F., Mitchell, P. C. H., Eds., Climax Molybdenum Co.: Ann Arbor, MI, 1979; p 34.

[3] Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1 and references therein.

[4] Tullius, T. D.; Kurtz, D. M., Jr.; Conradson, S. D.; Hodgson, K. O. *J. Am. Chem. Soc.* **1979**, *101*, 2776.

[5] Cramer, S. P.; Gray, H. B.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1979**, *101*, 2772.

[6] Rajan, O. A.; Chakravorty, A. *Inorg. Chim. Acta* **1979**, *37*, L503.

[7] Abbreviations used for ligands: 5-X-SAP-H_2 = *N*-(5-X-salicylidene)-2-aminophenol; 5-X-SAE-H_2 = *N*-(5-X-salicylidene)-2-aminoethanol; 5-X-SAN-H_2 = *N*-(5-X-salicylidene)-2-aminobenzoic acid.

[8] Taylor, R. D.; Todd, P. G.; Chasteen, N. D.; Spence, J. T. *Inorg. Chem.* **1979**, *18*, 44.

[9] Hill, W. E.; Atabay, N.; McAuliffe, C. A.; McCullough, F. P.; Razzoki, S. M. *Inorg. Chim. Acta* **1979**, *35*, 35.

[10] Rajan, O. A.; Adhikari, S.; Chakravorty, A. *Indian J. Chem., Sect. A* **1977**, *15*, 337.

[11] Topich, J. *Inorg. Chim. Acta* **1980**, *46*, L37.

0020-1669/81/1320-3704$01.25/0

Table I. Cyclic Voltammetry, Spectroscopic, and Elemental Analysis Data for *cis*-Dioxomolybdenum(VI) Complexes

Mo complex	E_{pc}, V[a]	ν(Mo=O), cm^{-1}	low-energy LMCT, cm^{-1} (log ϵ)	anal., % found (% calcd) C	H	N
MoO_2(5-NO_2-SAP)(Me_2SO)	−0.97	945, 923	23 697 (3.72)	38.80 (38.97)	3.22 (3.05)	5.91 (6.06)
MoO_2(5-Br-SAP)(Me_2SO)	−1.07	963, 920	23 148 (3.60)	36.11 (36.31)	2.81 (2.84)	2.74 (2.82)
MoO_2(5-H-SAP)(Me_2SO)	−1.09	943, 910	23 697 (3.59)	43.16 (43.18)	3.66 (3.62)	3.36 (3.36)
MoO_2(5-CH_3O-SAP)(Me_2SO)	−1.14	974, 937	22 472 (3.63)	43.12 (42.96)	3.45 (3.83)	3.17 (3.13)
MoO_2(5-NO_2-SAE)$(H_2O)_{1/2}$	−1.06	915	29 674 (4.12)	31.66 (31.32)	2.82 (2.63)	8.19 (8.12)
MoO_2(5-Br-SAE)	−1.24	938, 912	28 249 (3.41)	29.40 (29.22)	2.33 (2.18)	3.99 (3.79)
MoO_2(5-Cl-SAE)	−1.24	940, 912	28 249 (3.41)	33.38 (33.20)	2.53 (2.48)	4.61 (4.30)
MoO_2(5-H-SAE)(H_2O)	−1.27	940, 929	29 070 (3.41)	35.16 (34.97)	3.45 (3.59)	4.68 (4.53)
MoO_2(5-CH_3O-SAE)(H_2O)	−1.28	924	26 667 (3.43)	35.65 (35.42)	3.76 (3.86)	4.46 (4.13)
MoO_2(5-Br-SAN)	−0.84	946	26 882 (3.50)	37.80 (37.70)	2.01 (1.81)	3.34 (3.14)
MoO_2(5-Cl-SAN)$(H_2O)_{1/2}$	−0.84	946	26 882 (3.57)	40.93 (40.93)	2.25 (2.21)	3.37 (3.41)
MoO_2(5-CH_3O-SAN)$(H_2O)_{1/2}$	−0.92	940	25 253 (3.45)	44.31 (44.35)	2.99 (2.98)	3.45 (3.45)
MoO_2(5-H-SAN-H)(acac)	−0.88	941, 914	27 778 (3.63)	48.56 (48.84)	4.03 (3.67)	3.29 (3.00)

[a] Volts vs. Ag/AgCl.

Alfa. MoO_2Cl_2 was stored in a drybox to prevent hydrolysis. $MoO_2(acac)_2$ was prepared according to a literature procedure[12] and characterized by its IR spectrum.

Synthesis. The ligands were obtained via a Schiff base condensation reaction between the appropriate aldehyde and amine. The reactions were run in absolute ethanol. 5-X-SAP-H_2 and 5-X-SAN-H_2 are crystalline solids while 5-X-SAE-H_2 are oils. Three general procedures were used to obtain the *cis*-dioxomolybdenum(VI) complexes depending on the source of the MoO_2^{2+} cation. The following procedures are typical for the syntheses of the *cis*-dioxomolybdenum(VI) complexes starting with Na_2MoO_4, MoO_2Cl_2 or $MoO_2(acac)_2$.

Na_2MoO_4. Since the ligands used for this study are not water soluble, it is necessary to use a two-solvent system when Na_2MoO_4 is used as the source of Mo(VI). In a typical preparation, 1 mmol of Na_2MoO_4 is dissolved in 20 mL of H_2O while 1 mmol of the appropriate ligand is dissolved in 30 mL of Me_2SO. The two solutions are mixed at room temperature, and dilute HCl is added until the pH is ~5–6, at which time the molybdenum(VI) complex precipitates. The complex is filtered, dried, and recrystallized by dissolving in Me_2SO, adding H_2O until the solution just becomes cloudy, and then cooling the solution at 5 °C in a refrigerator.

MoO_2Cl_2. The disodium salt of the ligand (1 mmol) is dissolved in 50 mL of absolute ethanol, and MoO_2Cl_2 (1 mmol) is dissolved in 10 mL of absolute ethanol. The two solutions are mixed at room temperature and stirred for 20 min, after which time the Mo(VI) complex precipitates. The complex is filtered, dried, and recrystallized as previously described.

$MoO_2(acac)_2$. A 1-mmol sample of ligand was dissolved in 100 mL of either dry tetrahydrofuran, ethanol, or ethyl acetate. $MoO_2(acac)_2$ (1 mmol) was added as a solid to the ligand solution, and the reaction mixture was gently refluxed for 30 min. During reflux, the product precipitates. After cooling, the solution is filtered, and the Mo(VI) complex is recrystallized as described above.

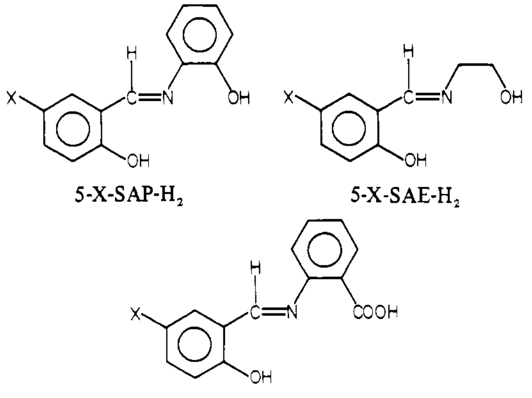
Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Atlantic Microlab, Atlanta, GA.

Physical Measurements. Cyclic voltammetry measurements were made with a homemade potentiostat of conventional design utilizing a three-electrode cell. The working electrode was a Princeton Applied Research Model 9323 hanging mercury drop electrode, and the auxiliary electrode was a coil of Pt wire. A Ag/AgCl (KCl 1 M) reference electrode was employed. All measurements were done in dry and deaerated Me_2SO with LiCl as the supporting electrolyte and with a molybdenum complex concentration $\sim 10^{-3}$ M. UV–visible spectra were obtained by using a Beckman Acta M VII spectrophotometer, and ^1H NMR data were obtained by using a Varian T60 or a JEOL FX-90Q spectrometer.

Results and Discussions

Synthesis. Tridentate Shiff base ligands (see Chart I) have been employed to prepare *cis*-dioxomolybdenum(VI) coordination complexes.

Chart I



5-X-SAP-H_2

5-X-SAE-H_2

5-X-SAN-H_2

X = H, Cl, Br, NO_2, CH_3O

In an effort to clarify the contradictory results of Chakravorty and McAuliffe, 5-H-SAP-H_2 has been reacted with Na_2MoO_4, MoO_2Cl_2, and $MoO_2(acac)_2$ under a variety of experimental conditions, and in all cases the products obtained were identical with each other as determined by elemental analysis and IR and NMR spectroscopy. The product that was isolated has the stoichiometry MoO_2(5-H-SAP)(solvent), and there is no evidence for a coordinated acetylacetonate ligand in the NMR spectrum for the Mo complex obtained from the reaction of ligand with $MoO_2(acac)_2$. Although all the reactions with 5-H-SAP-H_2 led to the same product, one ligand (5-H-SAN-H_2), which was reacted with $MoO_2(acac)_2$, led to a product with the stoichiometry MoO_2(5-H-SAN-H)(acac). The other ligands in this series led to complexes that contained no $acac^-$ as confirmed by elemental analysis and ^1H NMR. The reason for this difference in reaction stoichiometry is unclear. Even when the ligand to metal ratio is greater than 1, the second acetylacetonate ligand was not displaced in the case of 5-H-SAN-H_2. Attempts to prepare the complex MoO_2(5-H-SAN) from Na_2MoO_4 or MoO_2Cl_2 have been unsuccessful. Analytical data for the *cis*-dioxomolybdenum(VI) complexes are presented in Table I. It can be seen that the sixth coordination site in many of the complexes is occupied by a solvent molecule. The IR spectrum for MoO_2(5-H-SAN-H)(acac) is very similar in the carboxylic acid region to the IR spectra for the remaining complexes in this series, indicating that the ligand is binding most likely through the nitrogen and a carboxylic acid oxygen and not through the phenolic oxygen. IR data also indicate that some of the complexes may be oligomers in the solid state due to $Mo{=}O{\rightarrow}Mo$ bridging. However, in donor solvents such as

---

[12] Chen, G. J.-J; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

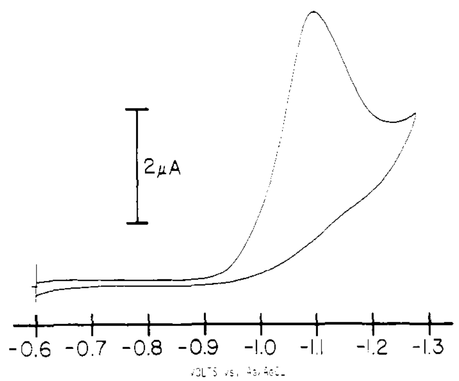


Figure 1. Cyclic voltammogram for MoO_2(5-H-SAP) in Me_2SO. E_{p_c} was measured vs. Ag/AgCl; scan rate was ~100 mV/s.

Me_2SO and DMF the bridge is broken and monomeric complexes with the MoO_2(L)(solvent) stoichiometry are obtained.[13] The complexes are stable in Me_2SO and DMF for extended periods as is evidenced by no significant change in their UV-visible spectra.

Electrochemistry. The redox behavior of the *cis*-dioxomolybdenum(VI) complexes described here has been examined to see how the cathodic reduction potentials of the complexes can be altered through ligand modification. Cyclic voltammetry was used to obtain the cathodic reduction potentials (E_{p_c}). The data are presented in Table I. A truly reversible one-electron transfer will have an E_p value independent of scan rate, a ΔE value of 58 mV, and a ratio of 1.00 for cathodic to anodic peak currents. For all but two of the complexes reported in Table I only a cathodic reduction peak is observed and no reoxidation was seen even as the scan rate was increased. For MoO_2(5-X-SAE) (X = H and CH_3O) a weak anodic oxidation peak was observed. ΔE was approximately 400 mV for these two complexes. This behavior indicates an irreversible redox process is taking place. Electrochemical studies on other *cis*-dioxomolybdenum(VI) complexes[14,15] have generally shown irreversible or quasi-reversible behavior. Spence[14] has shown for a series of molybdenum complexes that Mo(V) monomers are not obtainable by electrochemical reduction of the corresponding Mo(VI) complexes. He also has shown that Mo(V) monomers cannot be oxidized to the corresponding dioxomolybdenum(VI) complexes, most likely due to the difficulty in adding a second oxo group to the Mo in a nonaqueous solvent. The different oxo stoichiometries for the two oxidation states ($Mo^{V}O$ vs. $Mo^{VI}O_2$) is probably a leading contributor to the irreversible redox behavior that is observed in this work and also by others.

Since all the reductions that are observed are irreversible, the data that are presented are for the cathodic reduction potential, which is the potential measured where the cathodic peak current is at its maximum. It must be emphasized that the cylic voltammetry data are for cathodic reduction potentials and not for true reduction potentials, which are obtained from reversible cyclic voltammograms.

The ligands 5-X-SAP-H_2 and 5-X-SAE-H_2 do not show any redox activity in the range of −0.5 to −1.3 V vs. Ag/AgCl. The ligands 5-X-SAN-H_2 show irreversible reductions in the potential range −0.9 to −1.3 V. This reduction is due to the carboxylic acid group present in this ligand system.

The cyclic voltammogram for MoO_2(5-H-SAP) is shown in Figure 1 as a typical example of what is observed. Since the ligands 5-X-SAP-H_2 and 5-X-SAE-H_2 do not show reduction waves in the range where a molybdenum reduction is observed and the reduction for 5-X-SAN-H_2 has been characterized, the assignment of the reduction wave for the molybdenum complexes is straightforward. In the case of the MoO_2(5-X-SAN) complexes, the cyclic voltammograms show two reduction waves. One is associated with a reduction that is essentially into a molecular orbital that is mainly metal in character while the second wave is associated with reduction of the ligand. The second reduction wave that is observed for these Mo complexes occurs either at the same potential or at a potential shifted slightly in the anodic direction with respect to the same reduction wave observed in the free ligands.

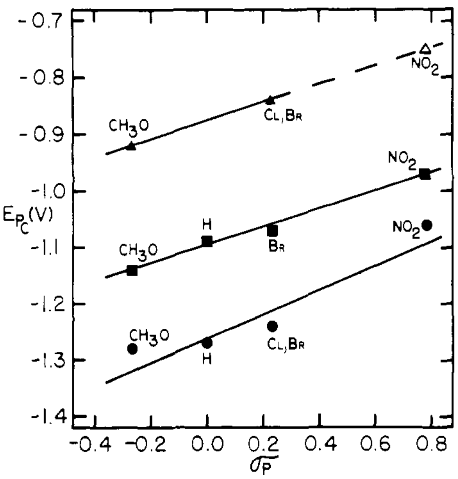


Figure 2. Correlation of E_{p_c} (V) with the Hammett σ_p parameter for the molybdenum(VI) complexes: ●, MoO_2(5-X-SAE); ■, MoO_2(5-X-SAP); ▲, MoO_2(5-X-SAN); △, predicted (X = CH_3O, H, Cl, Br, NO_2).

Substituent Effects. Trends are observed in the cathodic reduction potentials both within a series and between series even though the reductions for the *cis*-dioxomolybdenum(VI) complexes are not reversible. Figure 2 shows cathodic reduction potentials plotted as a function of the Hammett σ_p parameter for the X substituent on the ligands for the three series of molybdenum complexes studies. The magnitude of the Hammett σ_p parameter indicates the relative electron-withdrawing or electron-releasing effect of a particular substituent. The para parameter was chosen because the substituent of interest is para to the salicylaldehyde oxygen donor atom.

Figure 2 shows that the substituent on the ligand has a significant effect on the cathodic reduction potential. The more negative the cathodic reduction potential, the more difficultly is the molybdenum complex reduced. Of the substituents used the NO_2 group is the most electron withdrawing while the CH_3O group is the most electron donating. It is satisfying to note the linear relationship within a series between the cathodic reduction potential and the Hammett σ_p parameter. This shows that in fact the changes in the cathodic reduction potentials are controlled by the various substituents that are found on the ligand. Within a given series, the substituent is the only difference between the complexes. For the series MoO_2(5-X-SAP) the cathodic reduction potential range that is spanned is ~170 mV. The most anodic reduction in this series occurs at −0.97 V, which is for X = NO_2. This is expected since the nitro group is strongly electron withdrawing. The effect of this group, although not intimately linked to the molybdenum, is to draw electron density away from the metal and hence allow the metal to be more easily reduced. The opposite effect is observed when the substituent is CH_3O. In this case, the cathodic reduction potential is the most cathodic of the series. This is to be expected for the electron-donating methoxy group. A range of 216 mV is spanned for the

---

[13] Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 660.

[14] Taylor, R. D.; Street, J. P.; Minelli, M.; Spence, J. T. *Inorg. Chem.* **1978**, *17*, 3207.

[15] Cliff, C. A.; Fallon, G. D.; Gatehouse, B. M.; Murray, K. S.; Newman, P. J. *Inorg. Chem.* **1980**, *19*, 773.

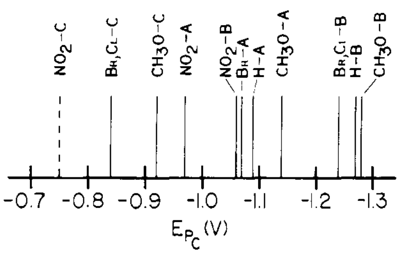


Figure 3. Relative cathodic reduction potentials for the various Mo(VI) complexes: A, MoO_2(5-X-SAP); B, MoO_2(5-X-SAE); C, MoO_2(5-X-SAN) (X = CH_3O, H, Cl, Br, NO_2; NO_2–C predicted).

cathodic reduction potentials for the series MoO_2(5-X-SAE). Again the most anodic E_{p_c} occurs when X = NO_2 and the most cathodic when X = CH_3O. This is analogous to the behavior that was observed for the MoO_2(5-X-SAP) series. Although the range of E_{p_c}'s is larger, the entire range is shifted to more negative potentials. Similar substituent effects have been observed for the reduction of some Mn(III) Schiff base complexes.[16,17]

Structural Effects. The MoO_2(5-X-SAE) complexes are more difficult to reduce than are the corresponding MoO_2(5-X-SAP) complexes. The two ligand systems are similar in that they both contain the ONO donor atom set; however, they differ in that the 5-X-SAP-H_2 ligand has a more extended π system than 5-X-SAE-H_2, which allows for greater electron delocalization. The series MoO_2(5-X-SAN) is not as extensive as the previous two because the complex MoO_2(5-NO_2-SAN) could not be prepared and the complex with 5-H-SAN-H_2 turns out to have the stoichiometry MoO_2(5-H-SAN-H)(acac). One must be cautious in drawing conclusions from a series that contains just three members, two of which (X = Br and Cl) have the same E_{p_c} and σ_p, but some comments are in order. The 5-X-SAN-H_2 ligand shares about the same degree of delocalization as its 5-X-SAP-H_2 counterpart and is more delocalized than the 5-X-SAE-H_2 ligand system. In addition, the 5-X-SAN-H_2 ligand contains the carboxylic acid donor group as compared to the phenolic or hydroxy group of the other two ligands. It is interesting to note that for MoO_2(5-X-SAN) (X = Br and Cl) the cathodic reduction potential occurs at −0.84 V. This potential is the most anodic one that we observe for any of the complexes in the three series. It is more anodic than MoO_2(5-Br-SAP) and MoO_2(5-Br-SAE) by 230 and 400 mV, respectively. If one assumes that there still holds the linear relationship between E_{p_c} and σ_p, which was observed for the other two series, then one can predict a cathodic reduction potential for MoO_2(5-NO_2-SAN) to be −0.75 V. Attempts to synthesize this compound and verify this prediction are in progress. The relative E_{p_c} positions for all the complexes are summarized in Figure 3.

Electronic Spectra. The electronic spectra of the complexes were recorded between 650 and 300 nm in either Me_2SO or DMF as the solvent. There were no significant differences in the spectra in the two solvents. The electronic spectra for the complexes are dominated by ligand to metal charge-transfer (LMCT) and intraligand transitions since Mo(VI) has a $4d^0$ electronic configuration. One can assume that the first electronic excitation observed is a transition from the highest occupied ligand molecular orbital to the lowest unoccupied metal orbital. An examination of the energies of these transitions (Table I) indicates some general trends that parallel the trends observed in the redox behavior. The first electronic transition (LMCT) can be thought of as an internal reduction of the metal, and it seems reasonable to expect some type of correlation with it and E_{p_c}. Martell[18] has observed a correlation between the LMCT bands and the reduction potential in some Co(III) peroxo complexes.

Within a series, the complexes with X = NO_2 have energies for the first electronic transition that are highest while those with X = CH_3O are lowest. For the series MoO_2(5-X-SAP) and MoO_2(5-X-SAE) there is a linear relationship between the energy of the first electronic transition and the Hammett σ_p parameter (except for X = H). Since the nitro complex for the MoO_2(5-X-SAN) series was not made, all that can be said about this series is that the position for the first transition where X = Br or Cl is higher in energy than the same transition for the corresponding methoxy complex. This is in agreement with what is observed for the other complexes described here. It is interesting to observe this type of correlation in the LMCT bands because, in contrast, Taylor found for a series of Mn^{III}(5-X-SALEN) complexes,[17] where the reduction potential was shifted 400 mV on going from X = NO_2 to CH_3O, that within experimental error the position of the d–d transitions was not changed. The results indicate that as the electron-withdrawing capacity of the ligand is increased, the energy difference between the highest occupied ligand orbital and the lowest empty Mo d orbital increases. This is not unexpected if one assumes that the X substituent is changing the electronegativity of the ligand. Jørgensen[19] has demonstrated in the case of simple transition-metal halide complexes that the low-energy charge-transfer transition varies in proportion to the electronegativity of the halide. The more electronegative the ligand, the higher in energy is the LMCT transition. A similar result is observed for the molybdenum complexes reported here. This electronegativity effect manifests itself both in the LMCT transitions and in E_{p_c}. Because of this a correlation is seen between the energy of the first charge-transfer transition and the cathodic reduction potentials for these complexes. It does not appear that any conclusions can be drawn concerning the energies of the charge-transfer transitions between series.

Conclusions

This work has shown that the cathodic reduction potentials for the *cis*-dioxomolybdenum(VI) complexes can be controlled through careful ligand design since a linear relationship is observed between E_{p_c} and the Hammett σ_p parameter for the substituent on the ligand. Besides the substituent effect that is observed within each series, important structural effects are also observed when series are compared. Ligand delocalization and substitution of a carboxylic acid group for the phenolic oxygen donor atom facilitate Mo complex reducibility. The trends observed in E_{p_c} are also manifested in the shifts seen in the LMCT transitions. With these results in hand, additional ligand systems are being considered that incorporate and extend those features that allow for the more facile reduction of *cis*-dioxomolybdenum(VI) complexes.

Acknowledgment. Support of this research by the Research Corp. and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. MoO_2(5-NO_2-SAP)(Me_2SO), 74678-21-0; MoO_2(5-Br-SAP)(Me_2SO), 74678-22-1; MoO_2(5-H-SAP)(Me_2SO), 75908-28-0; MoO_2(5-CH_3O-SAP)(Me_2SO), 74678-23-2; MoO_2(5-NO_2-SAE), 78803-81-3; MoO_2(5-Br-SAE), 78803-82-4; MoO_2(5-Cl-SAE), 78803-83-5; MoO_2(5-H-SAE)(H_2O), 75780-81-3; MoO_2(5-CH_3O-SAE)(H_2O), 78790-93-9; MoO_2(5-Br-SAN), 78790-94-0; MoO_2(5-Cl-SAN), 78790-95-1; MoO_2(5-CH_3O-SAN), 78790-96-2; MoO_2(5-H-SAN-H)(acac), 78790-97-3; Na_2MoO_4, 7631-95-0; MoO_2Cl_2, 13637-68-8; MoO_2(acac)$_2$, 21884-95-7.

---

(16) Coleman, W. M.; Goehring, R. R.; Taylor, L. T.; Mason, J. G.; Boggess, R. K. *J. Am. Chem. Soc.* **1979**, *101*, 2311.

(17) Boggess, R. K.; Hughes, J. W.; Coleman, W. M.; Taylor, L. T. *Inorg. Chim. Acta* **1980**, *38*, 183.

(18) Pickens, S. R.; Martell, A. E. *Inorg. Chem.* **1980**, *19*, 15.

(19) Jørgensen, C. K. *Solid State Phys.* **1962**, *13*, 376.