reduction of $[Cr(bipy)_3]^{3+}$ to $[Cr(bipy)_3]^{2+}$ as discussed earlier.

When a solution of the bis complex was electrolyzed at −0.80 V, 1 electron/molecule could be passed. The resulting solution was deep red with visible absorption maxima at 470 and 562 nm. A polarogram of this solution is shown in Figure 2. The limiting diffusion current of the anodic wave at $E_{1/2} = -0.49$ V was half that of the original cathodic wave at −0.72 V. The appearance of an anodic wave at $E_{1/2} = -0.49$ V after a one-electron reduction was described previously for solutions of this complex in the presence of free bipyridine. In the previous case, however, the limiting diffusion current of the anodic wave appearing after electrolysis was *equal* to that for the cathodic wave at −0.72 V. The appearance of the anodic polarographic wave at −0.49 V in the reduced solution was apparently due to $[Cr(bipy)_3]^{2+}$. This assumption is based on the position of the anodic wave and the visible absorption spectrum of the reduced solution. In order to substantiate this assumption, the reduced solution was rapidly oxidized with oxygen gas as described previously, in the anticipation of obtaining $[Cr(bipy)_3]^{3+}$ from the $[Cr(bipy)_3]^{2+}$ of the reduced solution. On contact with the oxygen-saturated solution, the reduced solution became yellow and after adjusting the solution to pH 3.5, the polarogram shown in Figure 2 was obtained. It contained a cathodic wave with $E_{1/2}$ of −0.49 V. The polarographic and cyclic voltammetric response to the solution between −0.20 and −0.80 V, as a function of temperature and pH, were similar to those previously observed for a solution of $[Cr(bipy)_3]^{3+}$ under similar conditions.

The above experiments showed conclusively the presence of $[Cr(bipy)_3]^{2+}$ in a solution of $[Cr(bipy)_2(H_2O)_2]^{3+}$ which had been electrolyzed by 1 electron/molecule at −0.80 V. Since no free bipyridine was initially available when the $[Cr(bipy)_2(H_2O)_2]^{3+}$ was reduced, the $[Cr(bipy)_3]^{2+}$ must have been formed by ligand exchange between two molecules of the bis complex forming a tris and a mono complex. The suggested reaction sequence is described by reactions 6–8.

$$[Cr(bipy)_2(H_2O)_2]^{3+} + e^- \rightleftarrows [Cr(bipy)_2(H_2O)_2]^{2+} \quad E = -0.72 \text{ V} \quad (6)$$

$$[Cr(bipy)_2(H_2O)_2]^{2+} + 2H_2O \rightleftharpoons [Cr(bipy)(H_2O)_4]^{2+} + bipy \quad (7)$$

$$[Cr(bipy)_2(H_2O)_2]^{2+} + bipy \rightleftharpoons [Cr(bipy)_3]^{2+} + 2H_2O \quad (8)$$

The equilibrium constant for reaction 8 has been shown earlier to be about 10^4. We have not definitely established that the ligand exchange produces only the mono complex, $[Cr(bipy)(H_2O)_4]^{2+}$. Although it is conceivable that some $[Cr(H_2O)_6]^{2+}$ could also be formed, the data presently available suggest this is not the case. It would seem that one conclusive test would be to determine the amount of tris complex formed by reaction 8. If reaction 7 is correct, we should obtain as a maximum half as much $[Cr(bipy)_3]^{2+}$ as we had $[Cr(bipy)_2(H_2O)_2]^{3+}$ initially. If the ligand-exchange reaction results in formation of $[Cr(H_2O)_6]^{2+}$, we should obtain as a maximum two-thirds as much $[Cr(bipy)_3]^{2+}$ as we had $[Cr(bipy)_2(H_2O)_2]^{3+}$ initially. As stated earlier the anodic wave at $E_{1/2} = -0.49$ V resulting from the reduction of $[Cr(bipy)_3]^{3+}$ gave a diffusion current constant of 1.25 for the $[Cr(bipy)_3]^{2+}$ species. Using this value the concentration ratio of $[Cr(bipy)_3]^{2+}$ to original $[Cr(bipy)_2(H_2O)_2]^{3+}$ was calculated to be 0.5:1. This ratio definitely suggests that the products of the reduction are the tris and the mono complexes.

Acknowledgment.—The authors wish to thank Mr. Edward Branley and Mr. Harry Rees of Louisiana State University in New Orleans for adapting the Scallette pulse counter to the integrator output of the Beckman Electroscan instrument and Mrs. Hilda Z. Jung for preparation of the figures.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
UTAH STATE UNIVERSITY, LOGAN, UTAH 84321

Electron Spin Resonance Active Molybdenum(V) Complexes in Dimethylformamide

BY G. R. LEE AND J. T. SPENCE*

Received March 21, 1972

Complexes of molybdenum(V) with 8-hydroxy-, 8-mercapto-, and 8-aminoquinoline and 3,4-dimercaptotoluene in anhydrous dimethyformamide have been investigated. Each ligand forms a 100% esr active complex in the ratio 1:1 (ligand to Mo(V)). The g values and hyperfine splittings and the visible absorption bands have been determined and the formation constants estimated for each complex. The results indicate the affinity of Mo(V) for ligands of comparable structure is $S^- > O^- > NH_2$ and suggest considerable electron delocalization for the thiol complexes. Possible implications for molybdenum containing enzymes are discussed.

Results

Recently, esr signals attributed to molybdenum(V) have been reported for a number of enzyme systems.[1-3] Because of this, there is considerable interest in model esr active molybdenum(V) complexes. In aqueous solution, however, Mo(V) complexes generally exist as esr inactive dimers, sometimes in equilibrium with rather small amounts of esr active species (monomers or triplets).[4-6] In certain polar, nonaqueous solvents,

(1) J. T. Spence, *Coord. Chem. Rev.*, **4**, 475 (1969).
(2) F. M. Pick, M. A. McGartoll, and R. C. Bray, *Eur. J. Biochem.*, **18**, 65 (1971).
(3) H. J. Cohen, I. Fridovich, and K. V. Rajagopalan, *J. Biol. Chem.*, **246**, 374 (1971).
(4) J. T. Spence and M. Heydanek, *Inorg. Chem.*, **6**, 1489 (1967).
(5) T. Huang and G. P. Haight, Jr., *J. Amer. Chem. Soc.*, **92**, 2336 (1970).
(6) T. Huang and G. P. Haight, Jr., *ibid.*, **93**, 611 (1971).

however, molybdenum(V) complexes that are essentially 100% esr active can be prepared, greatly facilitating the systematic study of their solution esr spectra.

An investigation of molybdenum(V) complexes with 8-hydroxy-, 8-mercapto-, and 8-aminoquinoline, and 3,4-dimercaptotoluene in anhydrous dimethylformamide (DMF) is reported here.

Results

When $(NH_4)_2MoOCl_5$ is added to solutions of the ligands in DMF complex formation occurs, as determined by both esr and absorption spectra analysis. In all cases, visible absorption bands and esr spectra different from those observed for the ligand or Mo(V) alone are observed (Table I).

TABLE I
VISIBLE ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF COMPLEXES

Mo(V) complex	λ_{max}, nm	ϵ
8-hydroxyquinoline	615	455
	455	3220
8-mercaptoquinoline	672	2630
	530	6600
8-aminoquinoline	453	600
3,4-dimercaptotoluene	712	4100
	610	4030
	400	3650

In order to determine the stoichiometry of the complexes, continuous variations plots were made for each ligand at a characteristic absorption peak where the absorbance of the ligand is negligible (Figure 1). As

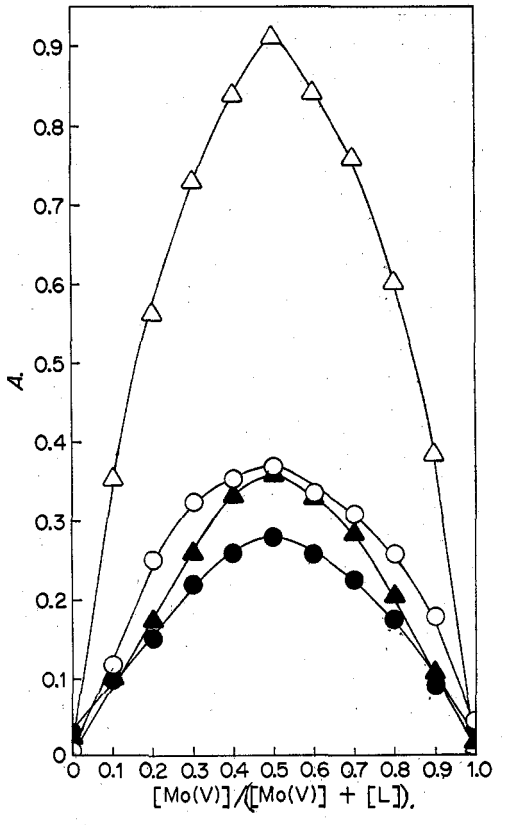

Figure 1.—Continuous variations plots: △ 8-mercaptoquinoline, $C_T = 5.00 \times 10^{-4}$ M, $\lambda = 530$ nm, 1-cm cells; ○ 8-aminoquinoline, $C_T = 2.00 \times 10^{-3}$ M, $\lambda = 453$ nm, 1-cm cells; ▲ 8-hydroxyquinoline, $C_T = 2.00 \times 10^{-3}$ M, $\lambda = 615$ nm, 1-cm cells; and ● 3,4-dimercaptotoluene, $C_T = 2.00 \times 10^{-3}$ M, $\lambda = 400$ nm, 0.1-cm cells. $T = 25°$.

can be seen, 1:1 complexes are formed for all ligands. Estimates of the formation constants were made from these plots, giving the results in Table II. The forma-

TABLE II
FORMATION CONSTANTS

Mo(V) complex	K_f	log K_f
8-hydroxyquinoline	1.35×10^4	4.13
8-mercaptoquinoline	8.84×10^4	4.95
8-aminoquinoline	4.08×10^3	3.61
3,4-dimercaptotoluene	1.46×10^4	4.16

tion constants were estimated from the equation

$$K_f = \frac{[C]}{[Mo(V)][L]} = \frac{A/A_m C_m}{(C_m(1 - A/A_m))^2}$$

where A = absorbance of solution at maximum in plot, A_m = extrapolated maximum absorbance at same point, and C_m = total concentration of all molybdenum species or all ligand species at same point.

Since the complexes are partially dissociated at the concentrations used for the continuous variations plots, all molar absorptivities and esr spectra were obtained from solutions in which the ligand–metal ratio was 5:1.

Representative esr spectra of the complexes are seen in Figures 2 and 3 and their esr parameters are

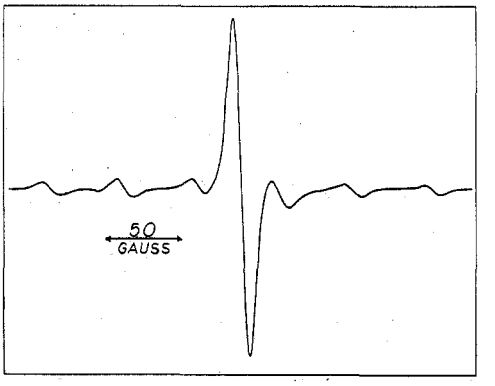

Figure 2.—Room temperature esr spectrum of Mo(V)–8-hydroxyquinoline complex, signal level 10, modulation amplitude 800, 5 min sweep time, attenuation 2.70. $g = 1.950$.

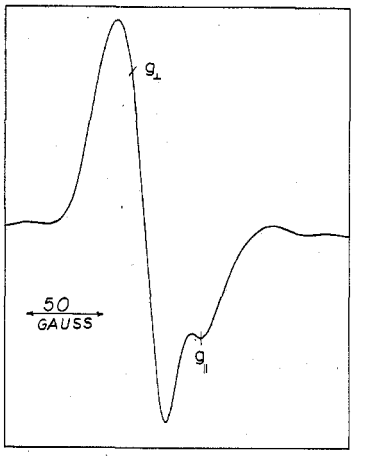

Figure 3.—Liquid-nitrogen temperature esr spectrum of Mo(V)–8-hydroxyquinoline complex, signal level 32, modulation amplitude 800, 5 min sweep time, attenuation 2.25. $g_{\parallel} = 1.935$ and $g_{\perp} = 1.965$.

TABLE III
ESR PARAMETERS

Mo(V) complex	g^a	$g_{\|}{}^b$	$g_{\perp}{}^b$	$g_{av}{}^b$	A, Gauss^a
8-hydroxyquinoline	1.950	1.935	1.968	1.957	48.8
8-mercaptoquinoline	1.971	2.002	1.950	1.967	40.3
8-aminoquinoline	1.945	1.969	1.933	1.945	50.0
3,4-dimercaptotoluene	1.992	1.975	2.004	1.994	30.6

[a] Room temperature. [b] 77°K.

found in Table III. All the esr spectra are similar in shape, differing mainly in g values and hyperfine splittings. Quantitative analysis of the number of spins present, performed by double integration of the esr spectra, using $K_3Mo(CN)_8$ as a standard, indicated the complexes are, within the error of the method, completely esr active. In all cases, the hyperfine splittings, due to the presence in naturally occurring molybdenum of approximately 25% isotopes of nuclear spin $^5/_2$, are easily observed.

In the case of 8-hydroxyquinoline, if a DMF solution containing Mo(V) and a fivefold excess of ligand is heated at 95° for 6 hr, a change in the visible spectrum occurs. By comparison, molybdenum(V) and this ligand in aqueous solution initially form a 2:2 complex (dimer). When this aqueous 2:2 complex is heated with excess ligand, a 4:2 (ligand–metal) complex is formed. Therefore, it is likely the change in the spectrum upon heating the DMF solution containing excess ligand is due to the formation of a 2:1 complex. Heating a DMF solution of the 1:1 complex in the absence of excess ligand produces no change in the visible spectrum. The esr spectrum of this new species, however, is almost identical with that of the 1:1 complex.

With 8-mercaptoquinoline and 3,4-dimercaptotoluene, heating in the presence of excess ligand produces complex changes, in both the visible and the esr spectra. In particular, the esr signal decreases considerably in intensity and appears to be a mixture of at least two signals. This may be due to partial reduction of the Mo(V) complex to an esr inactive Mo(IV) species by the thiol ligand, in addition to some 2:1 complex formation, giving a mixture of species.

Heating of the 1:1 8-aminoquinoline complex with excess ligand produced no changes in the visible or esr spectra.

Discussion

The values of the formation constants indicate the affinity of Mo(V) for ligands of comparable structure is $S^- > O^- > NH_2$.

The g values and hyperfine splittings of the thiol ligands are in agreement with other Mo(V)–thiol complexes reported in the literature.[5,7] The higher g values and lower A values of thiol complexes have been interpreted for Mo(V)–dithiolene complexes as indicating significant electron delocalization onto the ligands.[8]

Since the g values reported for molybdenum signals from the enzymes are all very near to 1.97 and the hyperfine splittings near 37 G,[1,7] it is likely that each Mo(V) is coordinated to sulfur at the active site.

It is perhaps also of significance that all reported complexes containing one thiol per Mo(V) have g values in the range 1.97–1.98, while those with two or more thiols bound per Mo(V) have g values of 1.99–2.01,[1,5,7,8] suggesting that Mo(V) in the enzyme may be bound by only one sulfur. This suggestion is at best tentative, however, since the local environment could produce similar effects.

Experimental Section

Materials.—$(NH_4)_2MoOCl_5$ was prepared according to the method of Palmer.[9] 8-Hydroxyquinoline was obtained from Eastman Kodak Company, 8-mercapto- and 8-aminoquinoline from Pfalz and Bauer, Inc., and 3,4-dimercaptotoluene from Aldrich Chemical Company, Inc. The ligands were used without further purification. Spectral grade dimethylformamide was dried and stored over Linde 4-A molecular seive. $K_3Mo(CN)_8$ was prepared from $K_4Mo(CN)_8$ by the procedure of Bucknall and Wardlaw[10] and $K_4Mo(CN)_8$ by the method of Van de Poel and Neumann.[11]

Methods.—In order to minimize atmospheric oxidation of Mo(V), all solutions were prepared under helium using deaerated solvent. This was particularly important in the cases of 8-aminoquinoline and 3,4-dimercaptotoluene, which give complexes especially susceptible to air oxidation. For esr and absorption spectra measurements, samples were withdrawn using gas-tight syringes and transferred to cells or tubes that had been flushed with helium.

Absorption spectra were obtained with a Cary 15 recording spectrophotometer and the continuous variations data with a Beckman DU spectrophotometer equipped with a constant-temperature compartment.

Esr spectra were obtained with a Varian V-4500 esr spectrometer equipped with 100 kc field modulation. The g values were determined by comparison with 2,2-diphenylpicrylhydrazyl as standard. Quantitative estimation of spins was accomplished by double integration of the signals and weighing of the paper representing the area under the absorption curve. As a standard, $K_3Mo(CN)_8$, which is 100% monomeric, was used.

Acknowledgment.—This work was supported by U. S. Public Health Service Grant GMO8347, National Institute of General Medical Sciences, and by Research Career Development Award 5-K3-GM22,643 to Jack T. Spence.

(7) R. C. Bray and L. S. Meriwether, *Nature (London)*, **212**, 467 (1966).
(8) A. Davidson, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Amer. Chem. Soc.*, **86**, 2799 (1964).
(9) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge Press, Cambridge, England, 1954, p 408.
(10) W. R. Bucknall and W. Wardlaw, *J. Chem. Soc.*, 2981 (1927).
(11) J. Van de Poel and H. M. Neumann, *Inorg. Syn.*, **11**, 53 (1968).