It is not difficult to find reasons for expecting the rate of electron self-exchange between two reactants to be governed by a different rate constant when the reaction proceeds in homogeneous solution than when one of the coreactants is bound to a surface in an oligomerized state. Steric factors that decrease the rate of collision between the coreactants when one is confined to a surface as well as differences in the activation energies for the two reaction conditions could act to decrease the rate constant for the surface reaction.

The previously reported values for the homogeneous self-exchange reaction,[5] were both obtained from the measured rates of cross-reactions (rather than the self-exchange reaction itself) combined with the Marcus correlation of rate constants for the two types of reactions.[26] However, there is good reason for doubting the applicability of the unmodified Marcus correlation between cross-reactions and self-exchange reactions that involve structural changes as significant as those that both halves of the Cu(phen)$_2^{2+/+}$ couple undergo upon electron transfer.[27] Indeed, the previous discrepant estimates of k_{ex} for the Cu(phen)$_2^{2+/+}$ couple have been shown to be mutually compatible with a value of k_{ex} near 10^5 M^{-1} s^{-1} if the Marcus correlation is appropriately modified to take account to the possible effects of large structural changes.[27] The resulting agreement between the values of k_{ex} obtained from (recalculated) homogeneous and heterogeneous experiments suggests that, despite the adsorption and oligomerization of Cu(phen)$_2^+$ on the surface of graphite electrodes, its reactivity in undergoing electron exchange with Cu(phen)$_2^{2+}$ in solution is not significantly diminished.

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Registry No. Cu(phen)$_2^+$, 17378-82-4; Cu(phen)$_2^{2+}$, 15823-71-9; Cu(phen)$_2$Cl$_2$, 83043-11-2; graphite, 7782-42-5.

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Solution Equilibria and Redox Properties of Schiff Base Complexes of Oxomolybdenum(V) in Dimethylformamide Solution

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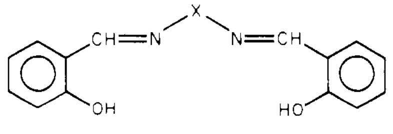
Measurement of spin and free halide concentrations in solutions of *trans*-[MoOL(MeOH)]Br (H$_2$L = H$_2$SALOPHEN, H$_2$SALPN, H$_2$SALEN) and [MoO(SALPN)Cl] in DMF (1–5 mM Mo; 0.1 M Et$_4$NX; X = PF$_6$, Cl, Br) indicates the presence of equilibria between mononuclear and polynuclear species. For [MoO(SALOPHEN)(MeOH)]Br in the presence of 0.1 M PF$_6^-$, the mononuclear cation *trans*-[MoO(SALOPHEN)(DMF)]$^+$ is present at a concentration of about 100 mol % but equivalent solutions of [MoOL(MeOH)]Br (H$_2$L = H$_2$SALPN, H$_2$SALEN) contain low concentrations (ca. 10 mol %) of ESR-silent polynuclear species containing bound bromide. For [MoO(SALPN)Cl] solutions, the concentration of polynuclear species is much higher, being >50 mol % Mo in PF$_6^-$ media and >85 mol% in Cl$^-$ media. The dominant mononuclear species appears to be [MoO(SALPN)Cl]. The electrochemistry of these systems is complicated by the equilibria and an unequivocal interpretation is not possible from the present (quite extensive) data. Examination of the first reduction process for each system suggests that the halide-bound complexes are electroactive, even for [MoO(SALOPHEN)(MeOH)]Br in 0.1 M PF$_6^-$ media where the free bromide concentration is about 100 mol %. For [MoO(SALPN)Cl], reduction of both mononuclear and polynuclear species is observed. The total data appear to reflect the tendency of mononuclear oxomolybdenum(V) species (4d^1) to associate in solution to form binuclear or polynuclear products that are stabilized by spin–spin interactions, whereas the oxomolybdenum(IV) analogues tend to thermodynamically favor mononuclear (low-spin d^2) forms.

Introduction



H$_2$SALEN, X = (CH$_2$)$_2$
H$_2$SALPN, X = (CH$_2$)$_3$
H$_2$SALOPHEN, X = *o*-phenylene

In view of the presence of mononuclear oxomolybdenum centers in certain redox enzymes,[2] detailed study of the redox properties of such centers in low molecular weight species is desirable and several systems featuring [Mo^{V}O] and [Mo^{VI}O$_2$] centers have been examined in some detail.[3] The four crystalline compounds *trans*-[MoOL(MeOH)]Br (H$_2$L = H$_2$SALPN, H$_2$SALEN, H$_2$SALOPHEN) and [MoO(SALPN)Cl] have been isolated in *recrystallizable, soluble* form.[4] The synthetic aspects of this system are somewhat complicated, with polynuclear species of low solubility tending to contaminate the isolated, soluble mononuclear species under certain conditions.[4] This is a particular problem for the chloride complexes. Synthetic,[5,6] ESR,[5-7] and reactivity[8]

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Table I. Free Halide and Spin Concentrations in 4 mM DMF Solutions (0.1 M Et_4NPF_6)

			ESR parameters[d]		
compd	free halide concn,[a] mol %	spin concn,[b] mol %	g	10^4a, cm^{-1}	rel concn, mol %
[MoO(SALOPHEN)(MeOH)]Br	95 ± 3	103 ± 5	1.944	43.7	100
[MoO(SALPN)(MeOH)]Br	86	90	1.943	39.6	100
[MoO(SALEN)(MeOH)]Br	92	89	1.942	42.0	>96
			~1.95		<4
[MoO(SALPN)Cl]	<10	49[c]	1.943	39.2	>96
			~1.95		<4

[a] Reproducibility is ±3 mol % for these free halide estimates. [b] Reproducibility is ±5 mol % for these spin concentration estimates. [c] Less than 15 mol % in DMF (0.1 M Et_4NCl. [d] Determined at a frequency of ca. 9 GHz.

properties of the chloro species [MoOLCl] have been undertaken. This paper reports that dissolution of *trans*-[MoOL(MeOH)]Br and [MoO(SALPN)Cl] in DMF (1–5 mM Mo; 0.1 M Et_4NX; X = PF_6^-, Br^-, Cl^-) leads to equilibria between mononuclear and binuclear or more highly condensed species. The electrochemistry of such solutions is correspondingly complex.

Experimental Section

All solution manipulations were carried out under purified argon or dinitrogen by using standard Schlenk and syringe techniques. Compounds were available from the previous study.[2]

Electrochemistry. The techniques employed were direct-current (dc) and differential-pulse (dp) polarography at a dropping-mercury electrode (DME), cyclic voltammetry (CV) at an inlaid platinum-disk (Beckman 39002A5) working electrode, and controlled-potential electrolysis (CPE) at a platinum-gauze electrode. The latter technique was coupled with coulometry and dc polarographic monitoring of the products of electrolysis. The experiments employed were carried out on a Princeton Applied Research (PAR) Corp. Model 170 instrument. All solutions were flushed with purified solvent-saturated argon prior to obtaining data. Low temperatures were attained via suitable slush baths, and the temperature was monitored inside the cell. The standard calomel electrode (SCE, PAR 9331) was the standard for DMF solutions and was incorporated into a Luggin capillary containing supporting electrolyte and solvent to minimize H_2O contamination. The coulometric ell was adapted from that described by ref 9. Analytical grade dimethylformamide (DMF) was treated[10] with molecular sieves and BaO, twice fractionally distilled under dinitrogen at less than 15 mmHg pressure, and stored in the dark at 5 °C. The salts EtNX (X = PF_6, Cl, Br; Southwestern Analytical Chemistry) were dried at 110 °C under vacuum and employed as the supporting electrolyte (0.1 M).

Polarographic Determination of Free Halide in DMF Solution. DMF solutions of halide, X^-, produce well-defined polarographic waves that correspond to oxidation of the mercury electrode.[11] The oxidation waves at the least positive potential ($E_{1/2} \sim -0.12$ and -0.23 V for X = Cl and Br, respectively) are assigned[11] to the processes

$$\mathrm{Hg} + 3\mathrm{X}^- \rightarrow [\mathrm{HgX}_3]^- + 2\mathrm{e}^- \quad (1)$$

The dc polarographic limiting current is proportional to halide concentration as is the peak current for dp polarography. Quantitative determinations of halide concentration were made by dc and dp polarography (e.g., see Figure 2) on 4×10^{-3}M solutions of the complexes by comparison with those obtained from standard halide solutions in 0.1 M Et_4NPF_6 supporting electrolyte. Initially a linear calibration curve was confirmed in the halide concentration range 10^{-4}–10^{-2} M. Preliminary measurements indicated the approximate concentration of free halide in the test solutions, and standard halide solutions close to that concentration were prepared accordingly. For final halide determinations, polarograms of these standard halide solutions were measured immediately before and after that of each test solution. The purity of the standard halides NaBr (Merck extra pure) and $Ph_4AsCl{\cdot}H_2O$ (Ventron-Alfa) was determined by potentiometric titration with standard $AgNO_3$ solution and found to be 100 ± 1 and 101 ± 1% pure. The reproducibility of the polarographic determinations was established to be ±3%. The precision depends upon the ability to correctly allow for overlap of the mercury oxidation and metal reduction waves (deconvolution techniques were used where necessary) and the assumptions that the background and Faradaic currents are additive and that no bound halide dissociates on the time scale of the determination.

Determination of ESR Intensities. A Varian E9 spectrometer with a double cavity operating in the TE_{104} mode was employed. Bis(*N*-methylbenzothiohydroxamato)copper(II)[12] was employed as the spin standard in DMF solution because of its stability, solubility, and narrow line width. The relative spin concentration of the Mo(V) test solution, Mo_u, compared to that of the standard copper(II) solution, Cu_k, was determined[13a] as

$$\frac{\mathrm{Mo}_u}{\mathrm{Cu}_k} = \left[\left(\frac{A_{u1}G_{k1}M_{k1}P_{k1}{}^{1/2}g_{k1}[S(S+1)]_{k1}W_{k1}{}^2}{A_{k1}G_{u1}M_{u1}P_{u1}{}^{1/2}g_{u1}[S(S+1)]_{u1}W_{u1}{}^2} \right) \times \left(\frac{A_{u2}G_{k2}M_{k2}P_{k2}{}^{1/2}g_{k2}[S(S+1)]_{k2}W_{k2}{}^2}{A_{k2}G_{u2}M_{u2}P_{u2}{}^{1/2}g_{u2}[S(S+1)]_{u2}W_{u2}{}^2} \right) \right]^{1/2}$$

where the subscripts 1 and 2 refer to the cavity in which the particular sample was measured, *G*, *M*, *P*, and *W* are respectively the receiver gain, modulation amplitude, power, and scan width employed, *A* is the area under the ESR absorption curve, *S* is the electron spin, and *g* is the transition probability. *A* was determined by double integration[13b] of the first derivative output of the spectrometer following digitization of data via a light pen interfaced to a DEC-10 computer system. Controls established the precision of measurement to be ±5%.

Results

Free Halide and Spin Concentrations. Substitution of ^{98}Mo ($I = 0$) for the naturally abundant mixture of isotopes removes the six hyperfine lines present in the ESR spectra of the complexes due to the presence of isotopes with $I = 5/2$ and facilitates detection of minor ESR-active components. Dissolution of [MoOL(MeOH)]Br and [MoO(SALPN)Cl] in MeCN or CH_2Cl_2 furnishes solutions containing at least two major ESR-active species. In 4 mM DMF (0.1 M Et_4NPF_6) solutions of *recrystallized* materials, a single species was detected (Table I) for [MoOL(MeOH)]Br (L = SALOPHEN, SALPN) and the relative concentration of a second species was <4% in [MoO(SALEN)(MeOH)]Br (Figure 1) and [MoO(SALPN)Cl]. The total spin concentrations in such solutions are also listed in Table I together with the free halide concentrations determined polarographically.

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Table II. Dc Polarography and Coulometry Data in DMF Solutions (0.1 M Et_4NPF_6)

compd	$E_{1/2}$,[a] V (Mo redn)	slope,[b] mV	i_{lim}, μA (Mo redn)	i_{lim}, μA (Hg oxidn[d])	no. of electrons/ molecule[e]
[MoO(SALOPHEN)(MeOH)]Br	−0.302	68	9.18	9.68	0.50
[MoO(SALPN)(MeOH)]Br	−0.407	70	8.22	8.84	0.47
[MoO(SALEN)(MeOH)]Br	−0.387	87	5.68	9.29	0.49
[MoO(SALPN)Cl]	−0.503	*c*	8.61	0.90	0.82, 0.63[f]
NaBr				10.16	

[a] 4 mM Mo; 25 °C; drop time 1 s. [b] Slope of plot of log $[(i_{lim} - i)/i]$ vs. *E*; theoretical slope for a reversible one-electron process is 59 mV. [c] Nonlinear ($E_{3/4} - E_{1/4} \sim 107$ mV). [d] Wave associated with the oxidation of Hg in the presence of halide. [e] Average of two determinations: ±0.03. [f] Solution was 0.1 M in Et_4NCl for this datum.

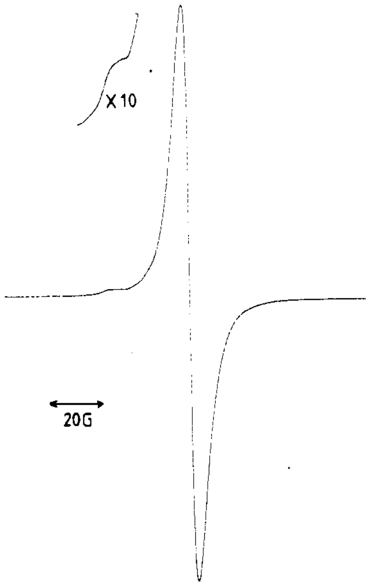

Figure 1. ESR spectrum of a 4 mM solution of *trans*-[MoO(SALEN)(MeOH)]Br (98.23 mol % ^{98}Mo ($I = 0$)) in DMF (0.1 M Et_4NPF_6).

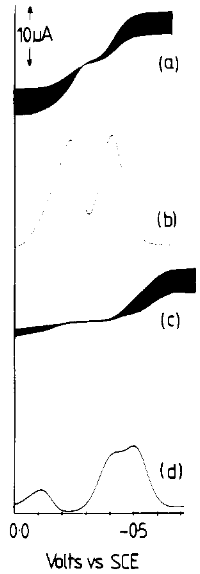

Figure 2. Direct-current (a, c) and differential-pulse (b, d) polarograms for 1 mM solutions of *trans*-[MoO(SALPN)(MeOH)]Br (a, b) and [MoO(SALPN)Cl] (c, d) in DMF (0.1 M Et_4NPF_6) (drop time 1 s).

Electrochemistry. The electrochemistry in DMF at potentials more positive than −0.2 V at Hg (Figure 2) and +0.6 V at Pt was dominated by oxidation processes involving free halide and/or ligand oxidation.[14,15] At potentials more negative than −1.5 V, ligand imine functions are expected to reduce.[16,17] A series of reduction processes were observed at intermediate potentials. Only the first (least negative) process of each complex was examined in detail. Polarography, coulometry, and CV data are collected in Tables II–IV.

***trans*-[MoOL(MeOH)]Br.** The dc and dp polarograms in DMF (0.1 M Et_4NPF_6) for the first reduction process in these compounds are extremely well-defined at Hg electrodes (e.g., Figure 2a,b). A well-defined wave for the oxidation of Hg in the presence of Br^- is also present and is the basis of the analytical procedure for determination of free bromide (vide supra).

L = SALOPHEN. The polarographic limiting currents of the compound reduction and the mercury oxidation waves are very similar (Table II). $E_{1/2}$ is approximately −0.3 V, and the slope of the plot *E* vs. log $[(i_{lim} - i)/i]$ is consistent with a quasi-reversible one-electron reduction.

The CV data in DMF (0.1 M Et_4NPF_6) at Pt electrodes show that the reduction process at Pt is well resolved from any oxidation waves, as bromide oxidation occurs at potentials more positive than +0.6 V. The reduction process occurs at similar potentials at both Pt and Hg electrodes. At a concentration of 1 mM Mo, application of the Nicholson–Shain criteria (Table III) indicates that all data are consistent with a quasi-reversible one-electron reduction. For 4 mM Mo, the response is similar to that at 1 mM, although the data are modified slightly by uncompensated resistance. Importantly, the current ratio $I_{pa}I_{pc}^{-1}$ remains unity at both concentrations within experimental error. Except for the fact that the peak positions are moved to slightly more negative potentials (~30 mV), the electrochemical observations are little changed upon substitution of Br^- for PF_6^- as background electrolyte.

The data are entirely consistent with a simple, one-electron, chemically reversible reduction process that is independent of the electrode (Pt or Hg).

L = SALPN. Apart from the slightly decreased limiting current (Table II), the dc polarographic characteristics at Hg are very similar to those of the SALOPHEN case, as are the CV data for 1 mM DMF solutions in both the Br^- and PF_6^- media (Table III). However at 4 mM concentration in the PF_6^- medium, both the cathodic and anodic peak currents per unit concentration are significantly reduced and the current ratio $I_{pa}I_{pc}^{-1}$ becomes less than unity. Clearly, for this compound, chemical reactions (non first order) are associated with the electron transfer.

L = SALEN. In the PF_6^- electrolyte, the polarographic limiting current per unit concentration is greatly reduced relative to both that of the other two compounds and that of the Hg oxidation wave (Table II). In addition, the slope of the plot of *E* vs. log $[(i_d - i)/i]$ is non-Nernstian. It is apparent that the limiting current is kinetically rather than diffusion controlled for this particular complex. While the CV reductive peak current $I_{pc}C^{-1}$ for 1 mM solutions in the Br^- medium is maintained at the level observed for the other systems at Pt

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Table III. Cyclic Voltammetry Data[a] for the First Reduction Process of [MoOL(MeOH)]Br in DMF (0.1 M Et_4NX) at 20 °C

ligand (L)	concn	electrolyte anion (X^-)	υ	E_{pc}	E_{pa}	ΔE_p	$I_{pc}C^{-1}$	$I_{pa}C^{-1}$	$I_{pa}I_{pc}^{-1}$	$I_{pc}\upsilon^{-1/2}C^{-1}$
SALOPHEN	1	PF_6^-	500	−0.348	−0.247	101	70.2	72.0	1.03	3.14
			200	−0.336	−0.255	81	42.0	46.6	1.11	2.97
			100	−0.330	−0.260	70	29.2	32.9	1.13	2.92
			50	−0.330	−0.266	64	21.5	22.3	1.03	3.05
	4	PF_6^-	500	−0.389	−0.231	158	62.8	65.3	1.04	2.81
			200	−0.371	−0.247	124	42.5	43.5	1.02	3.01
			100	−0.364	−0.253	111	30.5	31.5	1.03	3.05
			50	−0.355	−0.261	97	21.8	22.8	1.05	3.08
	1	Br^-	500	−0.384	−0.285	99	56.8	57.7	1.02	2.54
			200	−0.371	−0.287	84	36.2	38.6	1.07	2.56
			100	−0.367	−0.293	74	26.4	29.3	1.11	2.64
			50	−0.365	−0.294	71	19.9	20.4	1.03	2.81
SALPN	1	PF_6^-	500	−0.477	−0.391	86	64.3	58.6	0.91	2.88
			200	−0.463	−0.396	67	40.2	39.3	0.98	2.85
			100	−0.464	−0.398	66	25.8	26.0	1.01	2.58
			50	−0.465	−0.398	67	20.2	19.1	0.94	2.86
	4	PF_6^-	500	−0.507	−0.348	159	52.0	40.0	0.77	2.33
			200	−0.487	−0.358	129	34.5	26.3	0.76	2.44
			100	−0.477	−0.361	117	25.0	19.3	0.78	2.50
			50	−0.462	−0.358	104	17.5	13.5	0.77	2.48
SALPN	1	Br^-	500	−0.516	−0.380	136	66.6	67.8	1.02	2.98
			200	−0.495	−0.394	101	43.1	43.8	1.02	3.05
			100	−0.487	−0.399	88	31.4	32.7	1.04	3.14
			50	−0.482	−0.404	78	22.8	21.7	1.04	3.22
SALEN	1	PF_6^-	500	−0.476	−0.399	77	46.8	26.5	0.53	2.09
			200	−0.457	−0.394	63	22.8	15.2	0.67	1.61
			100	−0.455	−0.390	65	18.2	13.4	0.73	1.82
			50	−0.449	−0.375	74	12.9	8.8	0.68	1.82
	4	PF_6^-	500	−0.510	−0.393	117	50.3	19.0	0.38	2.25
			200	−0.485	−0.388	97	31.0	12.5	0.41	2.19
			100	−0.465	−0.373	92	21.8	9.8	0.44	2.18
			50	−0.456	−0.371	85	14.5	7.5	0.51	2.05
	1	Br^-	500	−0.518	−0.421	97	64.7	22.9	0.35	2.89
			200	−0.499	−0.420	79	39.4	15.8	0.40	2.79
			100	−0.480	−0.415	65	25.6	10.6	0.41	2.56
			50	−0.472	−0.395	77	17.7	8.9	0.51	2.50

[a] Units: concentration, mM; υ, mV s^{-1}; E_{pc}, V; E_{pa}, V; ΔE_p, mV; $I_{pc}C^{-1}$, μA mM^{-1}; $I_{pa}C^{-1}$, μA mM^{-1}; $I_{pc}\upsilon^{-1/2}C^{-1}$, μA $s^{1/2}$ $mV^{-1/2}$ mM^{-1}.

Table IV. Cyclic Voltammetry Data[a] for [MoO(SALPN)Cl] in DMF (0.1 M Et_4NX) at 20 °C

concn	electrolyte anion (X^-)	υ	E_{pc}^1	E_{pc}^2	E_{pa}	$E_{pc}^1 - E_{pa}$	$E_{pc}^2 - E_{pa}$	$I_{pc}^1C^{-1}$	$I_{pc}^2C^{-1}$	$I_{pa}C^{-1}$
1	PF_6^-	500	−0.443	−0.661	−0.396	47	265	26.0	67.0	31.0
		200	−0.473	−0.637	−0.408	65	229	13.8	26.4	26.8
		100	−0.494	−0.607	−0.418	76	189	11.6	16.6	19.5
		50	−0.500	−0.594	−0.419	81	175	10.0	12.5	13.3

concn	electrolyte anion (X^-)	υ	E_{pc}	E_{pa}	ΔE_p	$I_{pc}C^{-1}$	$I_{pa}C^{-1}$	$I_{pa}I_{pc}^{-1}$	$I_{pc}\upsilon^{-1/2}C^{-1}$
4	PF_6^-	500	−0.637	−0.387	250	61.8	47.3	0.77	2.76
		200	−0.600	−0.410	190	36.3	30.5	0.84	2.56
		100	−0.584	−0.415	169	25.0	21.8	0.87	2.50
		50	−0.569	−0.425	144	17.0	15.5	0.91	2.41
1	Cl^-	500	−0.711	−0.502	209	86.1	71.3	0.83	3.84
		200	−0.664	−0.542	122	55.2	43.9	0.80	3.92
		100	−0.649	−0.562	87	30.2	28.8	0.95	3.02
		50	−0.647	−0.558	89	26.8	24.0	0.90	3.78
5	Cl^-	500	−0.676	−0.404	272	65.0	50.0	0.77	2.90
		200	−0.655	−0.415	240	40.0	31.2	0.78	2.83
		100	−0.630	−0.450	180	30.4	23.2	0.77	3.04
		50	−0.612	−0.455	157	21.0	16.8	0.80	2.97

[a] Units: see footnote to Table III.

electrodes (Table III), the oxidative component $I_{pa}C^{-1}$ is sharply reduced leading to $I_{pa}I_{pc}^{-1}$ = 0.3–0.5 under the conditions examined. These data imply that a chemical reaction is occurring subsequent to electron transfer. At both 1 and 4 mM concentrations in the PF_6^- medium, *both* I_{pa} C^{-1} and $I_{pc}C^{-1}$ are significantly less than for other complexes and the current ratio $I_{pa}I_{pc}^{-1}$ is also less than unity. Clearly, when L = SALEN, the reduction process is not a simple quasi-irreversible one-electron process. Chemical reactions appear to precede and to follow the charge-transfer step.

[MoO(SALPN)Cl]. The dc polarogram (Figure 2) of a 1 mM solution (0.1 M $Et_4N[PF_6]$) shows that the Mo reduction step has an $E_{1/2}$ value of about −0.5 V and is well-defined. However, the wave is more drawn out than expected for a reversible process ($E_{3/4} - E_{1/4}$ is about 107 mV), and a casual inspection of the data might suggest the presence of a slow charge-transfer process. A plot of the limiting current vs. the square root of the Hg column height is linear, passing through the origin (Figure 3). Consequently, at potentials in the limiting current region, the overall process is diffusion con-

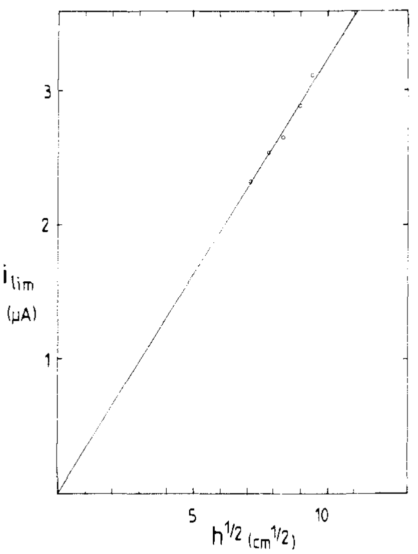


Figure 3. Plot of the net limiting polarographic current, i_{lim}, against the square root of the mercury column height (no back-pressure correction) for a 1 mM solution of [MoO(SALPN)Cl] in DMF (0.1 M Et_4NPF_6).

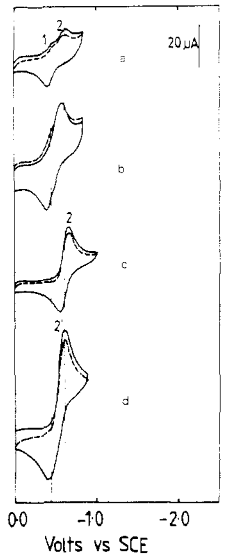


Figure 4. Cyclic voltammograms of [MoO(SALPN)Cl] at platinum in DMF (scan rate, v, 200 mV s^{-1}): (a) 1 mM in 0.1 M Et_4NPF_6, (b) 4 mM in 0.1 M Et_4NPF_6, (c) 1 mM in 0.1 M Et_4NCl, (d) 5 mM in 0.1 M Et_4NCl.

trolled. This contrasts with the situation in the region of $E_{1/2}$, where it is apparently kinetically controlled. Quantitative comparison of the limiting currents for [MoO(SALPN)Cl] (8.61 µA), [MoO(SALOPHEN)(MeOH)]Br (9.18 µA), and NaBr (9.02 µA for the $Na^+ + e^- \rightarrow Na/Hg$ wave) suggests an *overall* one-electron transfer per Mo atom.

The dp polarogram (Figure 2d) clearly reveals the presence of at least two metal reduction processes with similar $E_{1/2}$ values in the -0.4 to -0.6 V range. Consequently the origin of the kinetic control on the rising portion of the dc wave discussed above is not a slow electron-transfer step. The oxidation of Hg in the presence of free Cl^- at about -0.1 V is also clearly seen in Figure 2d.

The CV behavior of [MoO(SALPN)Cl] at Pt in DMF is complex (Table IV). At 1 mM (0.1 M Et_4NPF_6, 20 °C), the reduction process observed by dp polarography is again seen (labeled 1 and 2 in Figure 4a) but only one oxidation peak is resolved on the reverse scan. It appears again that similar processes are occurring both at Pt and at Hg electrodes. The results at 4 mM concentration (Table IV; Figure 4b) show a substantial dependence of peak position and total peak current per unit concentration on Mo concentration. At this higher concentration, a single reduction peak only is observed, although the peak shape suggests that overlapping processes are still contributing to the response. In Cl^- media, peak positions and currents are again concentration dependent in the 1–5 mM Mo range (Table V; Figure 4c,d). Extensive data collection at temperatures in the range +20 to -50 °C confirmed the complexity of the reduction process (e.g., see Figure 5). In particular, note that the combination of low temperature (-48 °C) and faster scan rates reveals a new reduction process (Figure 5b) on the second and subsequent cycles that *corresponds to peak 1* (Figure 4a).

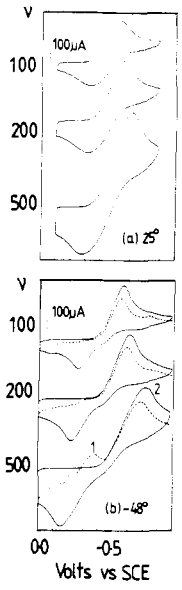


Figure 5. Temperature dependence of the cyclic voltammetry at platinum of a 5 mM solution of [MoO(SALPN)Cl] in DMF (0.1 M Et_4NCl; scan rates v, in mV s^{-1}).

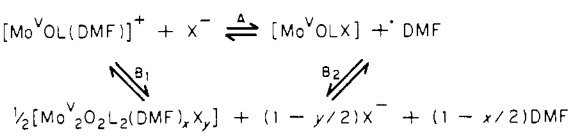
Coulometry. Exhaustive controlled-potential reductive electrolysis coupled with coulometry at potentials slightly negative of E_{pc} for the bromide complexes in the PF_6^- medium proved n values of 0.5 in each case at 20 °C (Table II). Polarographic and CV monitoring of the reduced SALEN solution showed the absence of any oxidation wave at potentials where reduction had been observed prior to the electrolysis. A low oxidative response (<20% of the current anticipated for a stoichiometric reverse oxidation) was seen for the SALPN and SALOPHEN cases. Importantly, an apparent increase in the free Br^- concentration was detected in reduced SALPN and SALEN solutions by examination of the bromide oxidation waves before and after exhaustive electrolysis.

For [MoO(SALPN)Cl], n values of 0.82 and 0.63 ± 0.05 were observed in the Et_4NPF_6 and Et_4NCl media, respectively.

Discussion

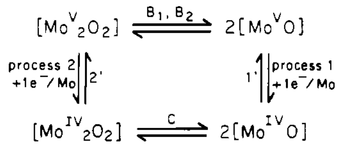
There are considerable uncertainties in the interpretation of the results furnished by the present solution equilibrium and electrochemical studies of *trans*-[MoOL(MeOH)]Br and [MoO(SALPN)Cl] in DMF. The problems are linked to the various equilibria present that are modulated by features such as (a) the possibility of various cis and trans mononuclear species in solution, (b) ligand exchange of halide, MeOH, and solvent (assuming the ligands L remain quadridentate in the present conditions), (c) the relative bridging tendencies of the halides Cl^- and Br^- and of the oxo ligand, in the formation of condensed species, and (d) how points a, b, and c are affected by change of oxidation state. Mononuclear oxomolybdenum(V) species ($4d^1$) tend to associate in solution to form binuclear or polynuclear products that are stabilized by

Scheme I. Proposed Equilibria for [Mo^{V}O] Species[a]



[a] For simplicity, polynuclear species are assumed to be binuclear (X = Cl, Br).

Scheme II. Simplified Redox Scheme for [Mo^{V}O] Species



spin–spin interactions, whereas the oxomolybdenum(IV) analogues tend to thermodynamically favor mononuclear (low-spin $4d^2$) forms (see, for example, ref 18). The existing data are inadequate to canvass all these points but serve to demonstrate that the solution behavior of the four compounds examined in this study and, most probably, that of the complexes [MoOLCl] isolated by other groups,[3-6] is more complex than expected and certainly not consistent with a simple equilibrium between halide-bound and -free mononuclear species. Furthermore, the electrochemistry cannot be explained by simple one-electron reversible or quasi-reversible steps, although under some conditions a restricted data set can appear to be deceptively simple.

Equilibria. *trans*-[MoO(SALOPHEN)(MeOH)]Br is mononuclear in the solid state[2] and a 1:1 conductor in DMF ($\Lambda_M = 68\ \Omega^{-1}\ cm^2\ mol^{-1}$; 1 mM).[19] Solutions in DMF (4 mM, 0.1 M Et_4NPF_6) exhibit a single ESR-active species at 100 mol % spin concentration and an equivalent free Br^- concentration. The mononuclear cation present is almost certainly *trans*-[MoO(SALOPHEN)(DMF)]$^+$ with this rather rigid ligand bound in an essentially planar conformation. The situation is consistent with equilibrium A (Scheme I) being displaced completely to the left, or nearly so. For equivalent solutions of *trans*-[MoOL(MeOH)]Br (L = SALEN, SALPN), the free Br^- and spin concentrations are less than 100 mol % (Table I) and the free Br^- concentration increases after exhaustive electrolysis. The data suggest the presence of low concentrations of ESR-silent polynuclear species containing bound bromide. For simplicity, these are assumed to be binuclear in equilibria B_1 and B_2 (Scheme I).

The concentration of polynuclear species in equivalent solutions of [MoO(SALPN)Cl] is much greater as the spin concentration drops to 49 mol % and to less than 15 mol % when Cl^- replaces PF_6^- in the medium. The free Cl^- concentration is <10 mol % in the PF_6^- medium, and so the dominant ESR-active monomer must be [MoO(SALPN)Cl]. Scheme I again broadly describes the situation with equilibrium A displaced to the right. However, the observed ESR parameters (Table I) would suggest the presence of [MoO(SALPN)(DMF)]$^+$ in solutions of *both* [MoO(SALPN)(MeOH)]Br and [MoO(SALPN)Cl]. But, the average *g* and *A* values for [Mo^{V}O] species are no indicator of structure,[20] and such a conclusion is not consistent with the free halide concentrations determined polarographically.

Polarography and Cyclic Voltammetry. [MoO(SALPN)Cl]. The complex electrochemical data for [MoO(SALPN)Cl] (Tables II and IV; Figures 2, 4, and 5) can be most straightforwardly, but not unequivocally, rationalized in terms of Scheme II, which incorporates equations B_1 and B_2 and the observations that two reduction processes, 1 and 2, are present and that they each involve one electron per molybdenum atom. Processes 1 and 2 are assigned to reduction of chloride-bound mononuclear [MoO(SALPN)Cl] and polynuclear (binuclear?) species, respectively.

The scan rate dependence of the CV peak currents and potentials (Table IV) show that processes 1 and 2 are under the kinetic control of preceding chemical reactions A, B_1, and B_2. There is clear evidence of concentration-dependent kinetic control as well. As the total concentration of molybdenum increases, the ratio of polynuclear to mononuclear species at equilibrium will increase. Thus, although process 1 is resolved at 1 mM concentrations (Figure 4a), it is not resolved at 4 mM (Figure 4b). However, peak shape analysis suggests that this process is still present and contributing to the current response, but at lower level due to the reduced relative concentration of mononuclear species. The equilibrium spin concentrations show that increased chloride concentrations favor the polynuclear Mo^V species. The simpler behavior at 1 mM Mo in the chloride medium is consistent with the presence of a redox couple (2 and 2′ of Figure 4c; Scheme II), nearly chemically reversible on the CV times scale and involving the *polynuclear* species. Kinetic control is also exercised on the reduced species, as indicated by the current ratios being less than 1 and by the concentration dependence of the oxidative peak potentials (e.g., Figure 4c,d). Note particularly the appearance of process 1 as a *secondary* process at faster scan rates for 5 mM solutions in the Cl^- medium at −48 °C (Figure 5b). In terms of Scheme II, the reduced polynuclear species [$Mo^{IV}{}_2O_2$] is dissociating via equilibrium C and the resultant mononuclear Mo^{IV} species becomes available for oxidation via process 1′. In addition, the dissociation C competes favorably at −48 °C with association of oxidized mononuclear species via equilibria B_1 and B_2. In summary, while the behavior at 1 mM concentration in DMF (0.1 M Et_4NCl) is consistent with the presence of a chemically reversible couple (2 and 2′ of Figure 4c) involving polynuclear species (Figure 4c; Scheme II), the behavior at 5 mM concentration appears to involve a large contribution from the reduction of the oxidized *polynuclear* species (process 2) and oxidation of the reduced *mononuclear* species (process 1′) linked by eq B_1, B_2, and C (Figure 4d; Scheme II).

[MoOL(MeOH)]Br. The electrochemical behavior of [MoO(SALOPHEN)(MeOH)]Br in PF_6^- or Br^- media is superficially that of simple, one-electron, chemically reversible couple involving electron transfer between structurally simple species. The equilibrium data suggest that equilibrium A (Scheme I) is displaced almost completely to the left and that equilibria B_1 and B_2 are unimportant. It is therefore tempting to suggest the presence of the simple couple

$$[Mo^VO(SALOPHEN)(DMF)]^+ + e^- \rightarrow [Mo^{IV}O(SALOPHEN)(DMF)] \quad (D)$$

However, the behavior of the closely related systems [MoOL(MeOH)]Br (L = SALPN, SALEN) is more complex and shows substantial evidence of kinetic control of the reduction process:

(i) The reduced relative concentrations of mononuclear species due to the presence of polynuclear species via equations B_1 and B_2 should lead to lowered current response. The lower limiting current i_{lim} for the SALPN, compared to that of the SALOPHEN, system (Table II) and the lowering of the reductive peak current, $I_{pc}C^{-1}$, on changing the concentration from 1 to 4 mM (Table III) might be interpreted in this way.

(ii) The very low limiting current for the SALEN system (Table II) is not consistent with the high concentration of

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mononuclear species (Table I) and is apparently under the kinetic control of eq A (Scheme I). In addition, the reduction behavior of the bromide systems is simpler, on the whole, in the bromide media where equilibrium A will be displaced to the right and the concentration of bromide-bound species enhanced.

The above points suggest that the redox-active *mononuclear* species in all *three* bromide systems (*including [MoO(SALOPHEN)(MeOH)]Br*) is halide-bound $[Mo^VOLBr]$, as postulated for the [MoO(SALPN)Cl] system:

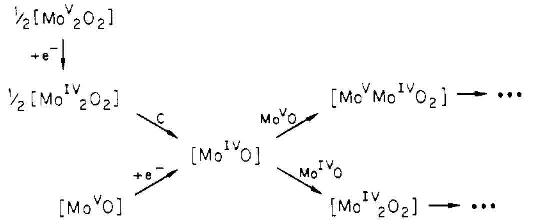
$$[Mo^VOLX] + e^- \rightarrow [Mo^{IV}OLX] \qquad (E)$$

It must also be mentioned that the postulated kinetic control could be exercised by reactions B_1 and B_2 and not by reaction A. In that case, reduction of the *polynuclear* species is involved as observed in the [MoO(SALPN)Cl] system (Figure 4; Scheme II). In any case, the main possibilities appear to be covered by Schemes I and II.

Reactions subsequent to electron transfer also occur in the bromide systems. For example, the reduction peak current, $I_{pc}C^{-1}$, for 1 mM [MoO(SALEN)(MeOH]Br in the Br^- medium is similar to that for the other two compounds (Table III), but the oxidative component $I_{pa}C^{-1}$ is much lower, leading to $I_{pa}I_{pc}^{-1} = 0.3$–0.5. Reactions involving the *reduced* species may well be involved (Scheme II), or alternatively the reduced species are unstable to further chemical reaction on the cv time scale.

In summary, it appears that the halide-bound complexes are electroactive and the halide-free species electroinactive at the potentials being considered.

Coulometry. Despite the complexity of the polarographic and CV results for the present systems, the evidence strongly suggests that the redox processes involve one electron per molybdenum atom (Scheme II). Coulometric *n* values of between 0.5 and 1 (Table II) suggest that additional reactions are occurring on the longer time scale of controlled-potential electrolysis. Presumably, reactions of reduced species with the oxidized starting materials are occurring, leading to *n* values less than 1.0.



Conclusions. It can be seen that dissolution of the four compounds examined in this study in DMF leads to equilibria between mononuclear and binuclear or more highly condensed species (Scheme I). The behavior in other solvents such as CH_2Cl_2 and MeCN is even more complex, and it is not surprising that synthetic aspects of these systems can also be complex.[4] The electrochemistry of the DMF solutions are complicated by the equilibria, and a totally convincing interpretation is not possible from the present (quite extensive) data. In fact, deceptively simple behavior can be inferred from a preliminary data set. However, the major features are consistent with Scheme II; in particular, while the electrochemistry of the bromo compounds *trans*-[MoOL(MeOH)]Br in DMF are essentially that of mononuclear species, the corresponding properties of [MoO(SALPN)Cl] are dominated by polynuclear species. Very similar behavior characterizes the redox chemistry of oxomolybdenum(V) thiolate species,[18] where spin-paired binuclear forms for Mo^V are favored thermodynamically while for Mo^{IV}, low-spin, mononuclear forms are favored.

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Registry No. *trans*-[MoO(SALOPHEN)(MeOH)]Br, 78891-61-9; *trans*-[MoO(SALPN)(MeOH)]Br, 78891-62-0; *trans*-[MoO(SALEN)(MeOH)]Br, 78891-63-1; [MoO(SALPN)Cl], 64085-33-2; Et_4NPF_6, 429-07-2; Et_4NBr, 71-91-0; Et_4NCl, 56-34-8; NaBr, 7647-15-6; Hg, 7439-97-6.

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Effects of Substituted Polar Groups on Ionic Association of Bis(β-diketonato)(ethylenediamine)cobalt(III) Perchlorate Complexes in Nitrobenzene

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The conductances of $[Co(\beta\text{-dik})_2(en)]ClO_4$, where β-dik is 2,4-pentanedionato (acac), 3-bromo-2,4-pentanedionato (acacBr), and 3-nitro-2,4-pentanedionato ($acacNO_2$), were studied in nitrobenzene at 25 °C. It was found that the degree of ionic association increases in the order $[Co(acac)_2(en)]^+ < [Co(acacBr)_2(en)]^+ < [Co(acacNO_2)_2(en)]^+$, whereas the order of the ionic mobility of the chelate cations is of opposite trend. The relative acidity of the N–H protons of the ligand ethylenediamine, determined from the rate of H–D exchange, increases in the same order as for the ionic association. These effects of the substituents were electronic and the Hammett relationship was found to hold true for the ionic association and the rate of H–D exchange. The increasing association was explained in terms of enhanced polarity of the cations and hydrogen-bond interactions between N–H protons and the perchlorate ion.

Introduction

The ligand X in the fragment $H-N-M^{n+}-X$ of octahedral complexes involving amine, where X is Cl^-, Br^-, etc. and M^{n+} are metal ions, polarizes the complexes and affects labilization of the N–H protons via the central metal ions.[1,2] Hydrogen-bonding interactions between the N–H protons in the metal complexes and the associating anions are important in the ionic association.[2,3] We previously reported that, for the

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