has a shoulder at ~575 nm. Energy-transfer rate constants of ~10^9 M^{-1} s^{-1} have been measured for ions with this amount of spectral overlap.[11]

In conclusion, the present study shows the utility of using thermal electron-transfer reactions to help elucidate the quenching reactions of excited-state molecules. We have shown that reactions involving the oxidation of Ti^{3+}(aq) and $TiOH^{2+}$ are normal in a Marcus sense and that their reactions with the ruthenium(II) excited state leading to production of Ti^{2+}(aq) are slow. In order to drive the $Ti^{3+,2+}$(aq) reaction, a couple with a considerably lower reduction potential is needed.

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Registry No. TiO^{2+}, 12192-25-5; Ti^{3+}(aq), 17524-20-8; $TiOH^{3+}$, 23335-62-8; $TiOH^{2+}$, 21029-47-0; $Ru(5\text{-}Cl(phen))_3^{2+}$, 47860-47-9; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(phen)_3^{2+}$, 22873-66-1; $Ru(4,7\text{-}(CH_3)_2phen)_3^{2+}$, 24414-00-4; $Ru(3,4,7,8\text{-}(CH_3)_4phen)_3^{2+}$, 64894-64-0; $Os(4,4'\text{-}(CH_3)_2bpy)_3^{3+}$, 47838-06-2; $Os(bpy)_3^{3+}$, 23648-06-8; $Os(5\text{-}Cl(phen))_3^{3+}$, 70101-70-1.

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(41) Figure 5 was constructed by using the following data: $Ru(NH_3)_5py^{3+,2+}$, $k_{11} = 4.3 \times 10^5$ M^{-1} s^{-1}, $E°_{3+,2+} = 305$ mV;[44] $Ru(NH_3)_6^{3+,2+}$, $k_{11} = 4.3 \times 10^3$ M^{-1} s^{-1}, $E°_{3+,2+} = 51$ mV;[44] $Co(phen)_3^{3+,2+}$, $k_{11} = 40$ M^{-1} s^{-1}, $E°_{3+,2+} = 370$ mV;[44] $Co(tpy)_2^{3+,2+}$, $k_{11} = 40$ M^{-1} s^{-1}, $E°_{3+,2+} = 310$ mV.[45]

(42) The rate constants are the average of the logarithms of the exchange rate constants calculated for each OsL_3^{3+} reaction by using the potentials for the $OsL_3^{3+,2+}$ couples listed in Table V and a rate constant of 2×10^9 M^{-1} s^{-1}[24] for the $OsL_3^{3+,2+}$ exchange reaction.

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Multistep Redox Series of the Tris(*o*-semiquinone)chromium(III) Complexes

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Neutral complexes of chromium(III) with tetrachloro-1,2-benzoquinone, 9,10-phenanthrenequinone, and 3,5-di-*tert*-butyl-1,2-benzoquinone chelated as semiquinone ligands have been examined by using cyclic voltammetry. All three complexes show reversible or quasi-reversible redox series corresponding to complexes of form $Cr(quinone)_3^n$, where n ranges from 3+ to 3−. EPR spectra on the 1+ and 1− members of the series show quite similar $\langle g \rangle$ and ^{53}Cr hyperfine values indicating substantial metal character in the ground states of both types of complexes. These results are compared with $V(O_2C_6Cl_4)_3$ where the ground state is principally ligand and explained in terms of VB and MO views of bonding.

Introduction

There is considerable interest in the modification of electrode surfaces with electroactive complexes to serve as electron-transfer agents.[1] Various problems centered about the rapid, reversible reduction of small molecules (i.e., O_2, N_2) require electrocatalysts which are capable of providing the large numbers of electrons involved. Two approaches may be taken in the design of electroactive complexes which are capable of supporting reversible multielectron redox series. The approach used in the development of systems which serve as analogues for various biological electron-transfer agents has been to incorporate two or more electroactive metal centers within a molecular complex unit so they may act in concert.[2] A second approach involves the complexation of electroactive ligands to a single metal center. In systems of this type a multielectron redox series can be supported which involves the oxidation or

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Table I. Cyclic Voltammetric Data for the $Cr(quinone)_3{}^n$ Complexes[a]

	$Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$			$Cr(O_2C_{14}H_8)_3$			$Cr(O_2C_6Cl_4)_3$		
couple	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p	E_{pc}	E_{pa}	ΔE_p
3–/2–	−1.345	−1.226	0.119	−0.972	−0.848	0.124	−0.047	+0.062	0.109
2–/1–	−0.770	−0.672	0.098	−0.513	−0.455	0.058	+0.390	+0.492	0.102
1–/0	−0.255	−0.172	0.083	−0.180	−0.124	0.056	+0.777	+0.858	0.081
0/+1	+0.930	+1.080	0.150	+0.795	+0.843	0.048		*b*	
1+/2+	+1.152	+1.293	0.141	+0.960	+1.055	0.095		*b*	
2+/3+		*b*		+1.118	+1.180	0.062		*b*	

[a] Scan rate 50 mV s^{-1}; 0.10 M TBAP in CH_2Cl_2. Values given in volts vs. SCE. [b] Not observed.

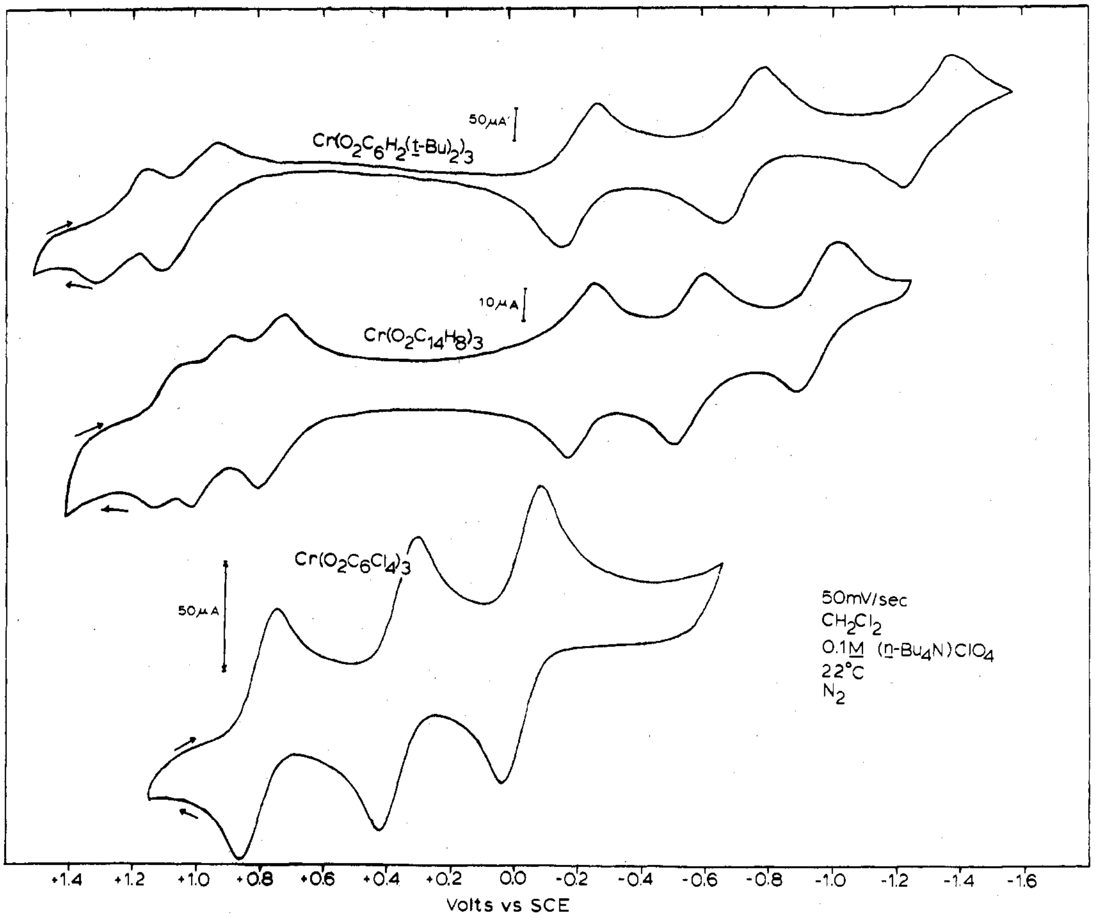


Figure 1. Cyclic voltammograms for $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$, $Cr(O_2C_{14}H_8)_3$, and $Cr(O_2C_6Cl_4)_3$. All solutions were approximately 0.1 mM in complex except for $Cr(O_2C_{14}H_8)_3$ which was approximately 0.05 mM.

reduction of the ligands or potentially both the ligands and the metal ion. In this report we present the results of an electrochemical investigation on three complexes of the general form tris(semiquinone)chromium(III). We have previously described the synthetic routes to these complexes, with their structural and magnetic properties.[3] The semiquinone ligands are capable of oxidation to *o*-quinones or reduction to catecholates. A fully reduced tris(catecholato)chromium(III) trianion would possess six electroactive electrons localized within the ligand π^* levels. The results of this investigation show that the quinone[4] complexes are indeed capable of supporting a multistep electron-transfer series and that the range of potentials within the series can be varied by ligand selection.

Cyclic Voltammetry

The neutral tris(semiquinone)chromium(III) complexes are capable of undergoing both oxidation and reduction reactions without a change in the formal oxidation state of the metal. In a localized valence-bond sense this would correspond to changes in the composition of the ligand π^* levels and can ideally lead to a seven-membered redox series ranging from coordinated oxidized benzoquinone ligands to partially reduced semiquinones and fully reduced catecholate ligands (eq 1).

$$Cr(BQ)_3{}^{3+} \underset{}{\overset{e^-}{\rightleftharpoons}} Cr(BQ)_2(SQ)^{2+} \overset{e^-}{\rightleftharpoons} Cr(BQ)(SQ)_2{}^{+} \overset{e^-}{\rightleftharpoons} Cr(SQ)_3{}^{0} \overset{e^-}{\rightleftharpoons} Cr(SQ)_2(cat)^{-} \underset{e^-}{\rightleftharpoons} Cr(SQ)(cat)_2{}^{2-} \overset{e^-}{\rightleftharpoons} Cr(cat)_3{}^{3-} \quad (1)$$

Unreduced benzoquinones are expected to be poor donors, but the kinetic stability of Cr^{3+} may stabilize the more highly oxidized members of this series relative to related complexes of more labile metal ions. The results of our electrochemical investigation on three complexes prepared with quinone ligands with differing degrees of electrophilic character are presented in Table I and Figure 1.

A. Tris(3,5-di-*tert*-butyl-1,2-semiquinone)chromium(III). The 3,5-di-*tert*-butylbenzoquinone ligand used in the preparation of $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$ is the least electrophilic of the three quinones used in this investigation. This is reflected in the redox series of the complex which occurs at the most negative potential of the three. The voltammogram on $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$ shows five quasi-reversible redox reactions.

The redox couple occurring at −0.21 V represents the first reduction of the neutral complex and is very nearly reversible with ΔE_p of 83 mV. A second couple at −0.73 V corresponds to reduction to the 2− complex and is quasi-reversible with a ΔE_p of 98 mV. A third couple corresponding to complete reduction to the tris(3,5-di-*tert*-butylcatecholato)chromium(III) trianion occurs at −1.32 V and is also quasi-reversible with ΔE_p of 119 mV. The cationic series has proven to be much more difficult to resolve electrochemically. Clear redox couples have only been observed in the absence of oxygen and by careful exclusion of moisture from both solvent and electrolyte. A couple at +0.98 V with ΔE_p of 150 mV corresponds to oxidation of the neutral complex to the 1+ species, and a second oxidation at +1.21 V with ΔE_p of 140 mV corresponds to the 1+/2+ couple. We have been unable to resolve a convincing half-wave for the 2+/3+ couple. No significant changes are observed in peak positions by varying the scan rate from 50 to 200 mV s^{-1}, and, as may be seen from the figure, the ratio of aniodic to cathodic current for each of the couples is approximately unity.

B. Tris(9,10-phenanthrenesemiquinone)chromium(III). The 9,10-phenanthrenequinone ligand is more electrophilic than di-*tert*-butylbenzoquinone by virtue of its polycyclic aromatic structure, and this effect is seen in the redox series of its complex. The three redox couples corresponding to the anionic series of $Cr(O_2C_{14}H_8)_2$ are approximately 0.18 V closer together than they were for $Cr(O_2C_6H_2(t\text{-Bu})_2)_3$ with the first reduction couple occurring at −0.16 V, nearly the same as the first reduction of the previous complex. However, the final reduction to the 3− complex occurs at a value which is approximately 0.42 V more positive than the value for the di-*tert*-butylquinone complex. While the potentials in the anionic series of $Cr(O_2C_{14}H_8)_3$ are shifted positively relative to the previous complex, the potentials in the cationic series are shifted slightly in the negative direction. So the entire series is a bit more compressed than that of $Cr(O_2C_6H_2(t\text{-Bu})_2)_3$. Once again reasonable waves for the cationic series were only observed after careful exclusion of moisture and oxygen. For this particular complex low solubility is also a problem due to strong intermolecular interactions in solid. Couples corresponding to the three reductions of the neutral complex are observed at −0.16, −0.49, and −0.90 V. The first two correspond to the 0/1− and 1−/2− reductions and are reversible while the 2−/3− reduction is quasi-reversible. An oxidation corresponding to the 0/1+ couple is observed at +0.82 V and is reversible. Additional oxidations which are quasi-reversible are observed at +1.00 V for 1+/2+ and +1.14 V. This last oxidation likely corresponds to the 2+/3+ couple not observed for the previous complex. Delocalization within the 9,10-phenanthrenequinone ligand contributes to stronger donor activity for the oxygens relative to 3,5-di-*tert*-butylquinone. The trication tris(9,10-phenanthrenequinone)iron(III), $Fe(O_2C_{14}H_5)_3^{3+}$, can be prepared under anhydrous conditions.[5]

Table II. EPR Data for the $Cr(quinone)_3^n$ Complexes with n = 1+ and 1−

	$Cr(O_2C_6H_2(t\text{-Bu})_2)_3^n$		$Cr(O_2C_{14}H_8)_3^n$		$Cr(O_2C_6Cl_4)_3^n$	
	1+[a]	1−	1+	1−	1+	1−
g	1.9709	1.9698	1.9686	1.9676	1.9689	1.9701
$A_{^{53}Cr}$[b]	27.3	24.5	28.2	27.9	27.2	22.2

[a] Line width at half-height for the 1+ complexes is approximately 3 G and for the 1− complexes 10 G. [b] $I(^{53}Cr) = ^3/_2$; isotopic abundance 9.54%.

C. Tris(tetrachloro-1,2-semiquinone)chromium(III). This complex has been prepared with the most electrophilic ligand of the series, tetrachloro-1,2-benzoquinone(*o*-chloranil). Consequently its redox series is at more positive potentials than the other three. Three redox couples are observed voltammetrically at +0.81, +0.41, and −0.03 V and are all quasi-reversible. These had been assigned as oxidations of the neutral complex in an earlier report due to the ease with which the neutral complex undergoes chemical oxidation and because of the unusually positive potentials at which the redox complex occurs compared with the reductions of related 1,2-dithiolene and diimine complexes.[6] Nevertheless, coulometric generation of the various members of the series has conclusively shown that they correspond to 1−/0, 2−/1−, and 3−/2− reductions. The cationic series which can be prepared by chemical oxidation of the neutral complex lies to still more positive potentials and has not yet been observed voltammetrically.

EPR Spectra of the 1+ and 1− Complexes

For further examination of the various members of the redox series (1), 1+ and 1− complexes have been prepared and examined by EPR. Addition of silver ion to dichloromethane solutions of the neutral complex results in oxidation of the complex and precipitation of Ag metal. One equivalent of Ag^+ produces an $S = {}^1/_2$ complex as observed by the appearance of an EPR signal; additional Ag^+ results in further oxidation and disappearance of the EPR signal. The 1+ complexes prepared by Ag^+ oxidation are lighter red than the neutral complexes, and their spectral parameters are given in Table II. So far, only isotropic spectra have been observed for these complexes, even in dichloromethane–ethylene glycol and dichloromethane–1-propanol glasses at 100 K. We have commented on the EPR spectrum of $Cr(O_2C_6Cl_4)_3^+$ previously; the spectra of the other two cations $Cr(O_2C_{14}H_8)_3^+$ and $Cr(O_2C_6H_2(t\text{-Bu})_2)_3^+$ are similar but unique among chromium complexes.[7] Simple $S = {}^1/_2$ chromium complexes are relatively rare but the $\langle g \rangle$ values in Table II are among the lowest observed for chromium and the stronger hyperfine values higher than values found in any other Cr complex to our knowledge. These spectral results strongly suggest a ground state localized on the metal.

The monoanionic complexes of the series have been prepared by using controlled-potential coulometry. They are violet and are also $S = {}^1/_2$ molecules. EPR spectral parameters for these complexes are also presented in Table II. Band widths are greater for the 1− complexes, but the $\langle g \rangle$ values are also in the 1.97 range observed for the 1+ complexes. Metal hyperfine splitting is a little smaller than observed for the 1+ complexes but is still extremely large among chromium compounds. Therefore, the ground states of both the 1− and 1+ complexes are quite similar in their strong metal compositions. This can be understood in terms of the simple localized valence-bond description of the members of the redox series presented in eq 1. In a previous publication we presented evidence suggesting that the neutral tris(quinone) complexes are best formulated as tris(semiquinone) complexes of high spin, trivalent metal ions.[3] Central to this formulation is their observed temperature-dependent paramagnetism consistent with weak antiferromagnetic exchange between the paramagnetic metal ions and the paramagnetic ligands. The ferric complexes therefore have S = 1 ground states, and the neutral Cr^{3+} complexes examined in this investigation have the S = 0 ground states observed at low temperature. As illustrated in eq 1, *either formal oxidation or reduction of one ligand of the neutral Cr complex would serve to decouple one metal-based electron.* This would account for the similarities in the EPR spectra of 1+ and 1− complexes and the strong metal contribution observed in the $\langle g \rangle$ values and hyperfine splitting.

It is interesting to compare these results with the spectrum obtained on $V(O_2C_6Cl_4)_3$, isoelectronic with the cationic chromium complexes.[8] The $\langle g \rangle$ value of 2.0079 and the very low ^{51}V hyperfine splitting of 4.1 G show convincingly that the unpaired spin in this case is localized in a *ligand* π^* orbital. This is in complete accord with the localized $M(SQ)_3$ formulation for the neutral Cr and Fe complexes since the V^{3+} ion is d^2 and can couple antiferromagnetically with only two of the paramagnetic ligands but is quite different from the metal-based ground state of $Cr(O_2C_6Cl_4)_3^+$. This result is not entirely unexpected (vide infra).

We have recently observed that this, essentially ligand, spectrum of $V(O_2C_6Cl_4)_3$ persists in solution only at very high concentrations of complex (0.02 M) in diethyl ether. Over time and in dilute solutions a second spectrum is observed with a $\langle g \rangle$ value of 1.9668 and ^{51}V coupling of 91 G[9] suggesting a change to a metal-based ground state. This can arise by a ground-state change of the tris complex to the metal-based ground state of $Cr(O_2C_6Cl_4)_3^+$, but there is a more plausible explanation. Sawyer and co-workers have recently reported the synthesis of bis(3,5-di-*tert*-butylcatecholato)vanadium(IV) which appears to give an EPR spectrum similar to the spectrum above.[10] It seems reasonable that the tris(semiquinone)vanadium(III) would undergo dissociation in solution giving free benzoquinone and $V(O_2C_6Cl_4)_2$. This tetrahedral V(IV) complex is likely to be responsible for the new spectrum.

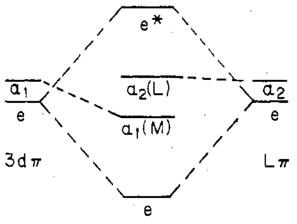
Structural Changes within the Redox Series

Structural work has been carried out on two members of the redox series, the 3– complex $Cr(O_2C_6H_4)_3^{3-}$ and the neutral complex $Cr(O_2C_6Cl_4)_3$.[7,11] Gross changes in molecular structure upon oxidation or reduction generally result in irreversible half-waves. The reversibility or quasi-reversibility of the redox reactions in Table I suggests that only minor structural changes occur through the series and the structural work on these two complexes serves to illustrate these changes. Oxidation of the tris(catecholato)chromium(III) complex would result in a decrease in ligand C–O length, from a value of 1.35 Å which appears typical of chelated catecholate ligands to 1.28 Å typical of chelated semiquinones[3] and a final value of approximately 1.23 Å for $Cr(BQ)_3^{3+}$. The other major change in ligand structure within the chelate ring would occur for the C–C bond. This would increase as the benzoquinone character of the ligand increases, from a value of 1.41 for the catecholate to 1.44 for the semiquinone and 1.53 for the fully oxidized ligand.[12] Of particular interest are the changes in M–O length within the chelate ring, for destabilization of the complex upon ligand oxidation to the weak donor benzoquinone form may result in ligand dissociation and irreversible redox behavior. This is, in fact, observed for the iron complexes. A slight increase in Fe–O length is observed for $Fe(O_2C_{14}H_8)_3$ (2.027 (4) Å)[3] compared with $Fe(O_2C_6H_4)_3^{3-}$ (2.015 (6) Å).[3] While redox behavior has been reported for the anionic series,[13] we have seen no evidence for reversible or quasi-reversible reduction or oxidation of the neutral iron complexes prepared with any of the three ligands included in this investigation in CH_2Cl_2 solution. The chromium complexes, by contrast, show a marked *decrease* in Cr–O length upon oxidation, with a value of 1.986 (4) Å reported for $Cr(O_2C_6H_4)_3^{3-}$ and a value of 1.986 (4) Å reported for $Cr(O_2C_6H_4)_3^{3-}$ and values of 1.949 (5) and 1.94 (1) Å found for $Cr(O_2C_6Cl_4)_3$ and $Cr(O_2C_{14}H_8)_3$,[14] respectively. This may be due, in part, to the decrease in oxygen atom radius as hybridization approaches sp^2, but these results indicate, quite significantly, that complex oxidation does not destabilize the chelated structure of the quinone ligands. Additional structural work on the cationic members of the redox series will be required to determine whether the Cr–O length decreases further with oxidation.

Discussion

It is quite pertinent to compare the tris(quinone)chromium complexes with related complexes prepared with 1,2-dithiolene and diimine ligands. The neutral tris(1,2-dithiolene)chromium complexes have trigonal-prismatic geometries similar to those of their V and Mo analogues,[15] while the neutral tris(semiquinone)chromium(III) complexes are octahedral. Delocalization within the dithiolene chelate ring results in greater ligand contribution to the ground state of the 1– complexes, $Cr(S_2C_2R_2)_3^-$. This is shown in their EPR parameters with $\langle g \rangle$ values of 1.995 and ^{53}Cr hyperfine values in the 16–19-G range.[16] The tris(1,2-dithiolene)chromium complexes do exhibit electrochemical activity, although to a much more limited extent than the quinone complexes. They have been observed with charges ranging from 0 to 3–.

The class of chromium complexes which seems to compare most favorably with the quinones are those prepared with diimine ligands. Tris(bipyridyl)chromium exhibits a five-membered redox series with species ranging in charge from 1– to 3+.[7] The potentials of this series are considerably more negative than those of the quinone complexes, consistent with the lower electrophilic character of the bipyridyl ligand. Spectroscopic studies on the more reduced members of the $Cr(bpy)_3^n$ series have been interpreted in terms of radical-anion coordination to Cr^{3+}.[18] A theoretical study on $M(bpy)_3$ complexes has pointed out that the important MO's for this class of complexes are of π character and consist of doubly degenerate levels of e symmetry (in D_3) corresponding to a ligand π combination with metal $d_{x^2-y^2}$ and d_{xy} levels, a metal level of a_1 symmetry (d_{z^2}) which has no corresponding ligand combination, and a ligand π combination of a_2 symmetry which has no corresponding metal orbital.[19]



The $Cr(quinone)_3^+$ complex, described earlier in VB terms as $Cr(SQ)_2(BQ)^+$, and $Cr(bpy)_3^+$ would each place five electrons in this scheme giving a $^2A_1$ ground state. This is consistent with the properties of $Cr(bpy)_3^+$ for reasons outlined previously. It is also consistent with the EPR spectra of the $Cr(quinone)_3^+$ complexes since this is a metal-localized ground-state orbital, which can mix with the metal 4s level to give large metal hyperfine interactions and a substantial orbital effect. The results of these calculations on $V(bpy)_3$, however, indicate an inversion in order of the a_1 and a_2 levels and a $^2A_2$ ground state. This ligand-based ground state is not entirely in accord with the EPR spectrum of $V(bpy)_3$ ($\langle g \rangle$ = 1.9831, $A_{^{51}V}$ = 84 G) but agrees quite well with our result on $V(O_2C_6Cl_4)_3$.

Characterization of the 1,2-dithiolene complexes showed a drop in energy of ligand π^* levels in the MO scheme as they fill.[20] The inversion of the a_1 and a_2 levels in going from the cationic chromium to the neutral vanadium complex also seems to occur in proceeding from the cationic to anionic chromium complex, $Cr(quinone)_3^-$. This corresponds to further reduction of the ligand but gives, as before, a $^2A_1$ ground state for the complex in agreement with the strong metal contribution also apparent in the EPR spectrum of the 1– complex. An interesting situation is created for the neutral complexes $Cr(quinone)_3$ and $Cr(bpy)_3$, for the a_1 and a_2 levels should be quite close in energy. This would certainly account for the ease with which both complexes undergo both oxidation and reduction, but it also accounts for another interesting property of both classes of complexes, their temperature-dependent paramagnetism. Both the $Cr(quinone)_3$ and $Cr(diimine)_3$ complexes have been found to be weakly paramagnetic at room temperature, showing diamagnetism at low temperature.[3,21] This can be understood in VB terms as metal–ligand antiferromagnetic exchange in the $Cr(SQ)_3$ systems. It is also consistent with the MO diagram above with a thermally accessible $^3A_2$ state, populated at room temperature, giving rise to residual paramagnetism.

While the use of the calculations carried out for the $M(bpy)_3{}^n$ complexes will not be the final word on the electronic structure of the quinone complexes, it is interesting that the quinone complexes seem to conform to the results of these calculations better than the bipyridyl complexes. Also, the MO description of the $Cr(quinone)_3{}^n$ systems adds little to the conventional VB view of bonding contained in eq 1. In fact, it is easier to rationalize the diverse electrochemical behavior of these systems in terms of three noninteracting, essentially parallel ligand π^* levels consistent with the localized view of ligand bonding expressed in this equation.

Experimental Section

Preparative routes to $Cr(O_2C_6Cl_4)_3$, $Cr(O_2C_{14}H_8)_3$, and $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$ have appeared.[3,22] Cyclic voltammetric measurements were performed with a PAR Model 174A polarographic analyzer with platinum working and auxiliary electrodes. Potentials reported in Table I are referenced to a saturated calomel electrode. All runs were examined at scan rates ranging from 50 to 200 mV/s. Coulometry experiments were carried out with a PAR Model 179 digital coulometer positioned to potentials which were slightly more negative than the first reduction wave of the neutral complex.

Electron spin resonance spectra were recorded on a Varian V-4500 and on a Varian E-9 in the laboratory of Dr. Gareth Eaton, University of Denver. Spectra in Table II were recorded in dichloromethane solution at room temperature and referenced to DPPH.

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Registry No. $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3{}^{3-}$, 70130-58-4; $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3{}^{2-}$, 68317-87-3; $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3{}^{-}$, 68317-86-2; $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$, 64020-84-4; $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3{}^{+}$, 70130-59-5; $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3{}^{2+}$, 70145-51-6; $Cr(O_2C_{14}H_8)_3{}^{3-}$, 70130-60-8; $Cr(O_2C_{14}H_8)_3{}^{2-}$, 70130-61-9; $Cr(O_2C_{14}H_8)_3{}^{-}$, 70130-62-0; $Cr(O_2C_{14}H_8)_3$, 68846-34-4; $Cr(O_2C_{14}H_8)_3{}^{+}$, 70130-63-1; $Cr(O_2C_{14}H_8)_3{}^{2+}$, 70130-64-2; $Cr(O_2C_{14}H_8)_3{}^{3+}$, 70145-49-2; $Cr(O_2C_6Cl_4)_3{}^{3-}$, 70130-65-3; $Cr(O_2C_6Cl_4)_3{}^{2-}$, 70130-66-4; $Cr(O_2C_6Cl_4)_3{}^{-}$, 70130-65-3; $Cr(O_2C_6Cl_4)_3$, 60635-34-9; $Cr(O_2C_6Cl_4)_3{}^{+}$, 70130-67-5.

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Intermolecular Energy Transfer between Lanthanide Complexes in Aqueous Solution. 4. Stereoselectivity in the Transfer from Terbium(III) to Europium(III) Complexes of Aspartic Acid

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Intermolecular energy transfer from Tb^{3+} to Eu^{3+}, emission intensity and lifetime measurements, potentiometric titrations, and differential absorption spectroscopy were all used to study the bonding between Tb^{3+} and aspartic acid as a function of pH. At low pH (3.0 – 5.0), the Tb^{3+}/Asp complexes are mononuclear, but once the pH is raised above 6.0, polynuclear association of complexes becomes important. Potentiometric, emission, and differential absorption titration curves were all superimposable for lanthanide complexes of L-Asp, D-Asp, and DL-Asp, but it was found that energy could be transferred from Tb^{3+} to Eu^{3+} more efficiently in associated complexes containing a racemic ligand than in polynuclear complexes containing resolved ligands. This effect represents the first observation of energy transfer characterized by stereoselectivity. All other types of measurement appear to be too insensitive to allow the detection of this effect.

Introduction

The stereoselective binding of metal ions by optically active α-amino acids is an area that has received attention lately and still is a matter of active research.[1] Stereoselectivity was not found in the formation constants for the transition-metal complexes of asparagine, glutamine, aspartic acid, alanine, valine, and proline[2,3] but has been detected in the Co^{2+}, Ni^{2+}, and Zn^{2+} complexes of histidine.[4,5] While the stereoselective effect is largely lacking in the simple amino acid complexes of transition metals, it has been found in the metal complexes of a wide variety of substituted amino acid derivatives.[6–10]

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