2552 *Inorg. Chem.* **1983**, *22*, 2552–2556

Iron-57 Mössbauer spectra were collected on a constant-acceleration spectrometer. Computer fitting of ^{57}Fe Mössbauer data to Lorentzian lines was carried out with a modified version of a previously reported program.[35]

Elemental analyses were carried out at the School of Chemical Sciences Microanalytical Laboratory, University of Illinois.

Acknowledgment. We are grateful for support from National Institutes of Health Grant HL 13652. J.-P.M.T. is grateful for support from a NATO postdoctoral fellowship. Mark Timken is to be thanked for help in fitting the magnetic susceptibility data and obtaining the Mössbauer spectra.

Registry No. Fe^{II}(salpren), 55095-98-2; Fe^{II}(saloph), 16828-80-1; Fe^{II}(salprenOH), 86471-94-5; Fe^{II}(saldien), 86471-95-6; [Fe^{III}(salpren)]$_2$(*p*-BHQ), 86471-96-7; Fe^{III}(salpren)(9,10-phenSQ), 86471-97-8; Fe^{III}(salpren)(3,5-DtBSQ), 86471-98-9; [Fe^{III}(saloph)]$_2$(*p*-BHQ), 86471-99-0; Fe^{III}(saloph)(2,6-DtBSQ), 86472-00-6; Fe^{III}(saloph)(9,10-phenSQ), 86472-01-7; Fe^{III}(saloph)(3,5-DtBSQ), 86472-02-8; [Fe^{III}(salprenO)]$_2$, 86480-34-4; Fe^{II}(salprenOH)(Hacac), 86472-03-9; Fe^{II}(salprenOC(O)NHPh), 86472-04-0; [Fe^{III}(saldien)]$_2$(*p*-BHQ), 86472-05-1; Fe(saloph)(CatH), 80041-63-0; Fe(saloph)(2,6-DtBHQ), 86507-79-1; 2,6-DtBHQ, 2444-28-2.

Supplementary Material Available: Tables IV–XVI, experimental and calculated magnetic susceptibility data (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Colorado, Boulder, Colorado 80309

Studies on Complexes Containing Mixed-Valence Semiquinone–Catecholate Ligands. Synthesis and Characterization of Bis(*o*-quinone)(bipyridine)chromium(III) Complexes

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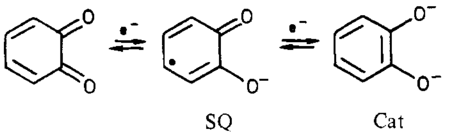
The synthesis of bis(*o*-quinone)(bipyridine)chromium complexes has been carried out by treating Cr(bpy)(CO)$_4$ with 3,5-di-*tert*-butyl-1,2-benzoquinone, tetrachloro-1,2-benzoquinone, or 9,10-phenanthrenequinone. The neutral complexes have two unpaired electrons and undergo one-electron oxidations and reductions by either chemical or electrochemical means. EPR studies on the $S = {}^1/_2$ cationic complexes indicate electronic ground states with spin density concentrated on the metal ions. The anionic complexes appear to be normal complexes of Cr^{3+}. Formulations for the members of the redox series based on their physical properties are Cr(SQ)$_2$(bpy)$^+$,Cr(SQ)(Cat)(bpy), and Cr(Cat)$_2$(bpy)$^-$. In each form the metal ion is trivalent, and redox activity involves changes in charge of the quinone ligands rather than the chromium ion.

Introduction

The coordination chemistry of *o*-quinone ligands, primarily catechols, has been a subject of interest since the beginning of the century, but only within the past decade have detailed studies been carried out on the composition and properties of quinone complexes.[1] One particularly interesting feature of these compounds is their redox chemistry. This interest has led to the development of compounds that show multielectron redox series facilitated by the electrochemical activity of ligands rather than the metal ion.[2] Problems with complex decomposition due to metal ion lability or reactivity are avoided in such a system.

Free *o*-quinones exist as catecholates, *o*-semiquinones, and *o*-benzoquinones, related by the addition or removal of charge (eq 1). Electrochemical interconversion of these forms can



(1)

occur by either one- or two-electron processes.[3] In principle, a complex containing quinone ligands can undergo two electron-transfer steps per quinone. The neutral tris(*o*-semiquinone)chromium(III), Cr(SQ)$_3$, complexes undergo both oxidation and reduction reactions through a sequence of species (eq 2) containing mixed-charge ligands bonded to Cr(III).[2]

$$\mathrm{Cr(BQ)_3}^{3+} \overset{3e^-}{\rightleftarrows} \mathrm{Cr(SQ)_3} \overset{3e^-}{\rightleftarrows} \mathrm{Cr(Cat)^{3-}} \qquad (2)$$

The metal ion is kinetically stable and not directly involved in the redox activity, and not until the ligands are in a fully oxidized BQ form does dissociation become a factor. In contrast, the M$_4$(3,5-DBSQ)$_8$ (M = Mn, Co, Ni) molecules,[4,5] which have potential for showing a large number of redox steps, show only one or two reversible couples due to dissociation of the complex in solution. Members of the chromium series with mixed-charge ligands are related in an inverse sense to the class of complexes with mixed-valent metal ions joined by a ligand bridge. As such, there are metal ion bridges between mixed-charge ligands supporting interaction between ligands. When interligand coupling is strong, a delocalized ground state or class III behavior in the Robin and Day[6] sense results. Examples of this are found among the neutral bis and tris 1,2-dithiolene and diimine complexes.[7] A compound that shows localized mixed-charge ligands similar to the intermediate members of the chromium series is the cobalt complex Co(3,5-DBCat)(3,5-DBSQ)(bpy).[8] This compound has a localized electronic structure in solid state but in solution exists in equilibrium with a Co(II) form related by ligand-to-metal electron transfer (eq 3). Closely related is the P(V) compound

$$\underset{\mathrm{I}}{\mathrm{Co^{III}(3,5\text{-}DBCat)(3,5\text{-}DBSQ)(bpy)}} \rightleftarrows \mathrm{Co^{II}(3,5\text{-}DBSQ)_2(bpy)} \qquad (3)$$

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(1) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *38*, 45.

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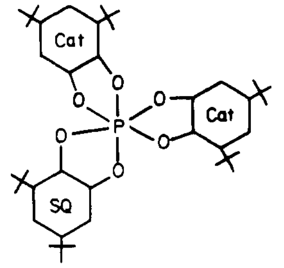
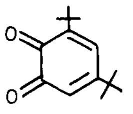
$P(3,5\text{-}DBCat)_2(3,5\text{-}DBSQ)$ (II) which shows interligand electron transfer over the temperature range from −100 to −40 °C. This is characteristic of weak interaction between mixed-charge sites or class II behavior, a property that is often difficult to identify.[9]

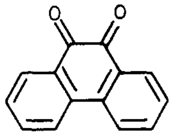


II

We wish to report in this publication the synthesis and characterization of a series of chromium complexes that are related to the cobalt complex above and also related to the $M(Q)_2(N\text{-donor})_2$ series reported previously with Mn, Co, and Ni.[4,5] Quinone ligands used in this investigation are 3,5-di-*tert*-butyl-1,2-benzoquinone (III), 9,10-phenanthrenequinone (IV), and tetrachloro-1,2-benzoquinone (V) bonded in their various electronic forms.[10]



III



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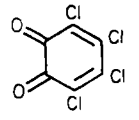


V

Experimental Section

Compound Synthesis. $\mathbf{Cr(O_2C_6H_2(\textit{t}\text{-}Bu)_2)_2(bpy)}$. A solution containing 3,5-di-*tert*-butyl-1,2-benzoquinone (0.072 g, 0.33 mmol) in 50 mL of toluene was added to 0.05 g (0.16 mmol) of $Cr(CO)_4(bpy)$ in 50 mL of toluene under an atmosphere of dry nitrogen. The mixture was heated at reflux for a period of 1 h and allowed to cool at room temperature. The solvent was removed under vacuum, giving 0.10 g of dark red complex, which was then recrystallized from hexane and vacuum dried.

Anal. Calcd for $Cr(O_2C_6H_2(C_4H_9)_2)_2(N_2C_{10}H_8)$: C, 70.37; H, 7.41; N, 4.32; Cr, 8.02. Found: C, 69.27; H, 7.64; N, 4.02; Cr, 7.69.

$\mathbf{Cr(O_2C_6Cl_4)_2(bpy)}$. Tetrachloro-1,2-benzoquinone (0.080 g, 0.33 mmol) and $Cr(CO)_4(bpy)$ (0.05 g, 0.16 mmol) were combined in 100 mL of toluene under dry nitrogen. The dark red product was recrystallized from THF and dried under vacuum.

Anal. Calcd for $Cr(O_2C_6Cl_4)_2(N_2C_{10}H_8)$: C, 37.71; H, 1.14; Cl, 40.51; N, 4.00; Cr, 7.43. Found: C, 38.06; H, 1.36; Cl, 41.28; N, 3.89; Cr, 8.04.

$\mathbf{Cr(O_2C_{14}H_8)_2(bpy)}$. 9,10-Phenanthrenequinone (0.067 g, 0.33 mmol) and $Cr(CO)_4(bpy)$ (0.05 g, 0.16 mmol) were combined in 100 mL of toluene under dry nitrogen. The product was recrystallized from THF to give a dark red powder.

Anal. Calcd for $Cr(O_2C_{14}H_8)_2(N_2C_{10}H_8)$: C, 73.08; H, 3.85; N, 4.49; Cr, 8.33. Found: C, 72.36; H, 4.06; N, 4.52; Cr, 8.04.

Cationic complexes were formed by the addition of 1 equiv of $AgPF_6$ to the neutral complex dissolved in dichloromethane. A gray silver metal precipitated from solution and was separated from the complex by filtration.

Anionic complexes were generated either by coulometry or by reduction of the neutral complex with 1 equiv of sodium naphthalide. Neither the cations nor anionic complexes were isolated as solid products.

Physical Measurements. Optical spectra were recorded on Cary 14 and 17 spectrophotometers with use of dried toluene and dichloromethane solutions. Electron paramagnetic resonance spectra were recorded on a Varian E-109 spectrometer with DPPH used as the *g*-value standard. Electrochemical experiments were performed under argon by using a three-electrode arrangement in dry dichloromethane. Cyclic voltammograms were obtained by using a PAR Model 174A potentiostat with a Houston 2000 X-Y recorder. A platinum-wire working electrode and a platinum-coil auxiliary electrode were used. The reference was a saturated calomel electrode (SCE). Tetra-*n*-butylammonium perchlorate (TBAP) was the supporting electrolyte. Magnetic susceptibility measurements were made on a standard Faraday balance.

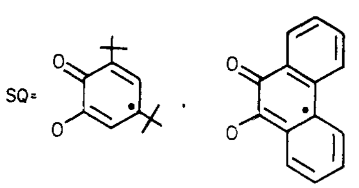
Experimental Results

Pyridine and bipyridine adducts of the tetrameric bis(*o*-semiquinone) complexes prepared with Mn, Co, and Ni have been reported (eq 4).[5,8,11] Products obtained with nickel have

$$[M^{II}(SQ)_2]_4 + N\text{–}N \rightarrow M(SQ)_2(N\text{–}N) \qquad (4)$$

$$M = Mn, Co, Ni; \quad N\text{–}N = bpy, 2\ py$$

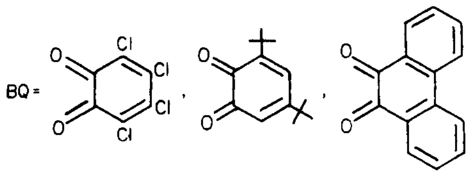
been shown to contain the Ni^{2+} ion, with the charge distribution between metal and quinone ligands remaining unchanged, $Ni^{II}(SQ)_2(N\text{–}N)$. The divalent manganese ion of $[Mn^{II}(3,5\text{-}DBSQ)_2]_4$ undergoes a two-electron oxidation upon adduct formation, giving as a product the Mn(IV) complex $Mn^{IV}(3,5\text{-}DBCat)_2(py)_2$. With cobalt, a subtle dependence upon the nature of the quinone ligand was observed. The 9,10-phenanthrenesemiquinone complex $Co(phenSQ)_2(py)_2$ showed variable-temperature magnetic susceptibility behavior, which fits a model with the metal ion remaining divalent at all temperatures. The related complex (I) prepared with 3,5-di-*tert*-butyl-1,2-benzoquinone and bipyridine has been shown to have a Co(III) metal ion with catecholate and semiquinone ligands in solid state at room temperature and in solution at temperatures below −40 °C. At higher temperatures in solution there is an equilibrium mixture of Co(II) and Co(III) forms. This series of quinone complexes containing aromatic nitrogen-donor ligands illustrates the dependence of charge distribution within the metal–quinone unit upon metal ion, counterligand, and quinone. Changes in charge distribution across the first transition series make the chromium complexes of particular interest. Possible formulations for the neutral complexes formed in this investigation are $Cr(SQ)_2(bpy)$ with Cr(II), $Cr(SQ)(Cat)(bpy)$ with Cr(III), or $Cr(Cat)_2(bpy)$ with Cr(IV).



Synthesis of the $\mathbf{Cr(quinone)_2(bpy)}$ Complexes. The bipyridine–quinone complexes of chromium have been prepared by displacement of carbonyl ligands from $Cr(CO)_4(bpy)$ (eq 5). Attempts have been made to prepare these compounds

$$Cr(CO)_4(bpy) + BQ \rightarrow Cr(Q)_2(bpy) \qquad (5)$$

by ligand displacement from the $Cr(SQ)_3$ complexes. The Cr(III) ions of these compounds are quite inert, and over the period of days only small quantities of bipyridine product could be detected. The cationic complexes formulated as Cr-



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(9) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 1086.

(10) We use "quinone" as a general expression in instances where ligand charge is ambiguous. The abbreviation SQ will be used to refer to ligands in their semiquinone form, and Cat, for catecholates.

(11) Lynch, M. W.; Buchanan, R. M.; Pierpont, C. G.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1028.

Table I. Effective Magnetic Moments of the $Cr(quinone)_2(bpy)^n$ Redox Series

compd	$n = 0^a$	$n = 1-$
$Cr(O_2C_6H_2(t\text{-}Bu)_2)_2(bpy)$	2.65	3.54
$Cr(O_2C_{14}H_8)_2(bpy)$	2.92	3.65
$Cr(O_2C_6Cl_4)_2(bpy)$	2.89	3.72

[a] Magnetic moment in units of Bohr magnetons.

Table II. Electron Spin Resonance Parameters for the $Cr(SQ)_2(bpy)^+$ Complexes

compd	$\langle g\rangle$	$A_{^{53}Cr}$, G	$A_{^{14}N}$, G
$Cr(3,5\text{-}DBSQ)_2(bpy)^+$	1.9757	25.5	3.0
$Cr(phenSQ)_2(bpy)^+$	1.9741	26.1	3.0
$Cr(o\text{-}Cl_4SQ)_2(bpy)^+$	1.9746	25.9	3.0

Table III. Cyclic Voltammetric Data for the Cr(SQ)(Cat)(bpy) Complexes

	$Cr(O_2C_6H_2\text{-}(t\text{-}Bu)_2)_2(bpy)$		$Cr(O_2C_{14}H_8)_2\text{-}(bpy)$		$Cr(O_2C_6Cl_4)_2\text{-}(bpy)$	
couple	$E_{1/2}{}^a$	Δ^b	$E_{1/2}$	Δ	$E_{1/2}$	Δ
−/0	−0.30	0.087	−0.37	0.056	0.46	0.048
0/+	0.20	0.073	0.00	0.065	0.86	0.058

[a] Volts vs. SCE. [b] Separation between E_{ox} and E_{red} (volts).

$(SQ)_2(BQ)^+$ show more rapid ligand replacement by bipyridine due to the weaker donor character of the benzoquinone ligand rather than a change in the kinetic stability of the metal ion. Over the period of 1 day, a solution of $Cr(SQ)_2(BQ)^+$ can be converted completely to $Cr(Q)_2(bpy)^+$ in the presence of excess bipyridine.

Magnetism. The room-temperature magnetic moments of complexes prepared with the three quinone ligands are given in Table I. All three neutral complexes have values that are consistent with two unpaired electrons per molecule. Furthermore, an investigation of the temperature dependence of the paramagnetism of the 9,10-phenanthrenequinone complex has shown that the magnetic moment remains constant at the $S = 1$ value with no evidence of intermolecular spin–spin coupling.[12] This result is consistent with any of the three formulations given above: a d^2 Cr(IV) ion of $Cr(Cat)_2(bpy)$, a d^3 Cr(III) ion of Cr(SQ)(Cat)(bpy) with strong coupling between the semiquinone ligand and one metal ion electron, and a strongly coupled Cr(II) complex, $Cr(SQ)_2(bpy)$, could each potentially have an $S = 1$ ground state.

Electrochemistry. The neutral $Cr(Q)_2(bpy)$ complexes all undergo a one-electron oxidation and a one-electron reduction. Cyclic voltammograms are shown in Figure 1; potentials are given in Table I. Reduction potentials for the complexes prepared with 9,10-phenanthrenequinone and 3,5-di-*tert*-butyl-1,2-benzoquinone occur at negative potentials of approximately −0.37 V, whereas reduction of the tetrachloro-1,2-benzoquinone complex occurs at a positive potential of about 0.47 V. A similar result was observed for the redox series of the $Cr(SQ)_3$ complexes where the reduction potentials of the tetrachloroquinone complex were observed at values that were approximately 1 V more positive than those of the complexes prepared with the other two quinone ligands.[2] The first reductions of the neutral $Cr(SQ)_3$ complexes were found to occur at potentials which are 0.2 V more positive than those of the bipyridine series. Oxidation potentials of the bipyridine complexes are shifted to more negative values relative to the corresponding $Cr(SQ)_3$ complexes by about 0.7 V. An additional redox couple associated with the bipyridine ligand can be observed at −1.5 V for experiments carried out in acetonitrile. Both oxidation and reduction reactions of the neutral complexes can be carried out chemically. Sodium naphthalide is a convenient reducing agent, giving the monoanion cleanly at an equimolar ratio with the neutral complex. Addition of stoichiometric quantities of $AgPF_6$ can be used to reoxidize the monoanion to the neutral complex and also to form the monocation form of the complexes prepared with all three quinone ligands.

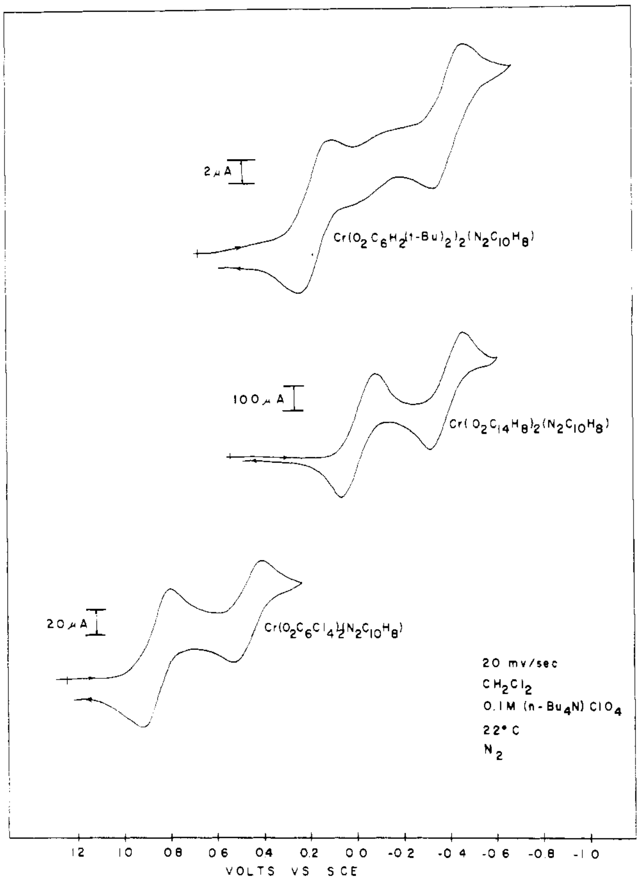

Figure 1. Cyclic voltammograms for $Cr(bpy)(O_2C_6H_2(t\text{-}Bu)_2)_2$, $Cr(bpy)(O_2C_{14}H_8)_2$, and $Cr(bpy)(O_2C_6Cl_4)_2$. An additional couple corresponding to reduction of the bipyridine ligand occurs in the −1.5 to −1.6 V region.

EPR Studies. Attempts have been made to investigate the cationic and anionic complexes by using EPR. The cationic complexes prepared by silver ion oxidation have one unpaired electron. In the case of the isoelectronic tris(quinone) complexes, spin density can be concentrated either on the metal ion as found for the $Cr(SQ)_2(BQ)^+$ series or on the ligands as for the $V(SQ)_3$ complexes.[2,13] The spectra of $Cr(3,5\text{-}DBSQ)_2(3,5\text{-}DBQ)^+$ and the bipyridine complex prepared with 3,5-di-*tert*-butyl-1,2-benzoquinone are shown in Figure 2. Spectra of the other cationic complexes are quite similar. Isotropic *g* values and hyperfine coupling constants for all three bipyridine complexes are given in Table II. As with the $Cr(SQ)_2(BQ)^+$ complexes, *g* values are all around 1.975 and ^{53}Cr coupling is found to be exceptionally strong. Additional coupling of 3 G to two equivalent nitrogen atoms is also observed for all three complexes. Spectra on complexes that have ligand-localized spin density typically show quite weak metal hyperfine coupling, *g* values close to 2.00, and hyperfine coupling to ligand protons.[1] The spectra obtained for the $Cr(Q)_2(bpy)^+$ complexes are clearly indicative of a metal-localized ground state.

The anionic complexes $Cr(Q)_2(bpy)^-$ do not show EPR spectra under the same conditions used to obtain spectra on

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[12] Hendrickson, D. N.; Lynch, M. W., private communication.

[13] Buchanan, R. M.; Downs, H. H.; Shorthill, W. B.; Pierpont, C. G.; Kessel, S. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1978**, *100*, 4318.

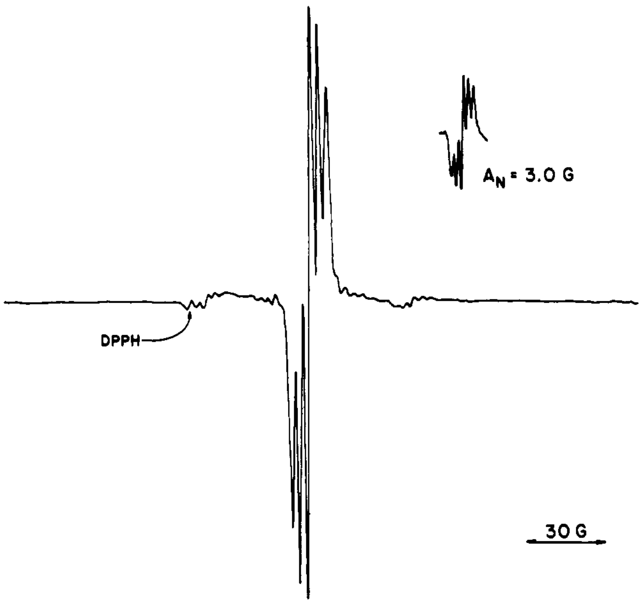

Figure 2. EPR spectrum of the $Cr(bpy)(3,5\text{-}DBSQ)_2^+$ cation. Bipyridine nitrogen superhyperfine coupling to one of the ^{53}Cr hyperfine lines is shown in the insert.

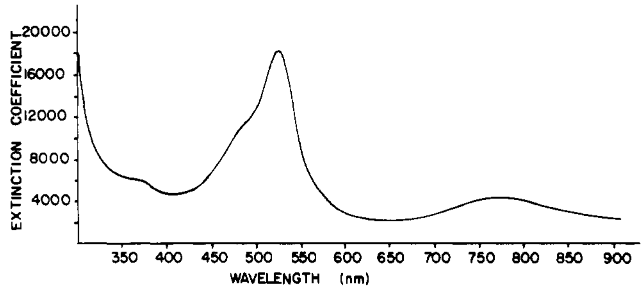

Figure 3. Optical spectrum of $Cr(3,5\text{-}DBSQ)_3$ recorded in dichloromethane solution.

the $Cr(SQ)_2(Cat)^-$ anions. Reasons for this remain to be determined, but this observation points to a difference in electronic structure.

Electronic Spectra. Electronic spectra of complexes of both the $Cr(SQ)_3$ and $Cr(Q)_2(bpy)$ series are dominated by high-intensity charge-transfer bands. Spectra of $Cr(3,5\text{-}DBSQ)_3$, $Cr(3,5\text{-}DBSQ)(3,5\text{-}DBQ)^+$, $Cr(3,5\text{-}DBQ)_2(bpy)$, and $Cr(3,5\text{-}DBQ)_2(bpy)^+$ within the 300–900-nm range are shown in Figures 3–6. Raymond and co-workers have published the spectra of the $Cr(3,5\text{-}DBQ)_3^{0,1-,2-,3-}$ series previously.[14] The most prominent features of the spectra shown in the figures are bands that appear in 500-nm region in each case. Other noteworthy features are the low-energy charge-transfer bands in the visible region, which extend into the near-infrared region. Even though Fenske–Hall calculations have been carried out on the complexes, assignment of these transitions is complicated by the close proximity of electronic levels.[15]

Discussion

Gordon and Fenske have reported the results of a theoretical study on the *o*-quinone complexes of chromium and vanadium.[15] The results of their calculations provide a much clearer view of the charge distribution in the compounds reported in this investigation. In the case of the cationic bipyridine complexes, the energy levels shown in Figure 7 give a ground state with the unpaired electron assigned to a metal-localized orbital of a symmetry (in C_2). The LUMO that is only 0.2 eV higher in energy is delocalized over the entire complex including both the quinone and bipyridine ligands. Isotropic *g* values of the EPR spectra recorded on the cationic complexes and the magnitude of metal hyperfine coupling constants are in accord with the ground-state assignment obtained from the calcula-

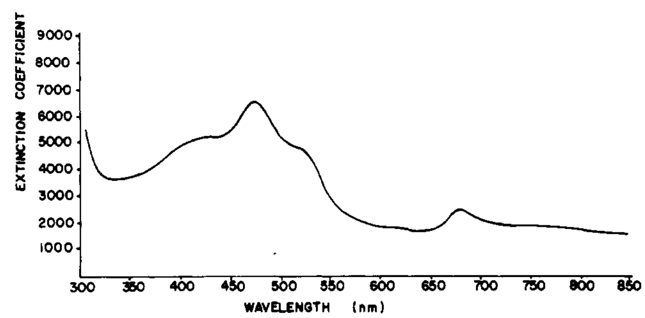

Figure 4. Optical spectrum of the $Cr(3,5\text{-}DBQ)(3,5\text{-}DBSQ)_2^+$ cation recorded in dichloromethane solution.

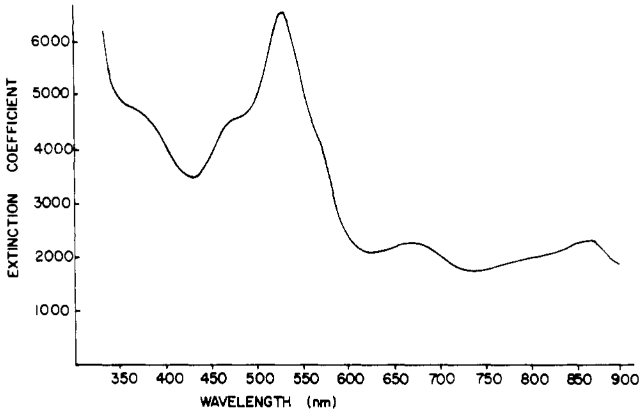

Figure 5. Optical spectrum of $Cr(bpy)(3,5\text{-}DBSQ)(3,5\text{-}DBCat)$ recorded in dichloromethane solution.

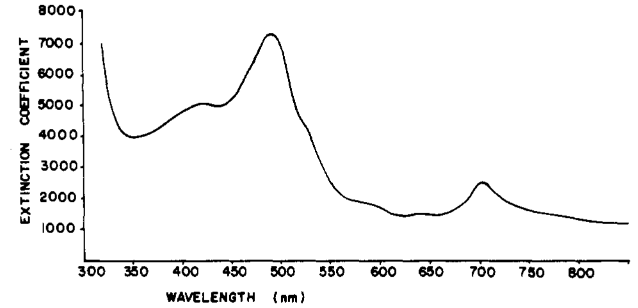

Figure 6. Optical spectrum of the $Cr(bpy)(3,5\text{-}DBSQ)_2^+$ cation recorded in dichloromethane solution.

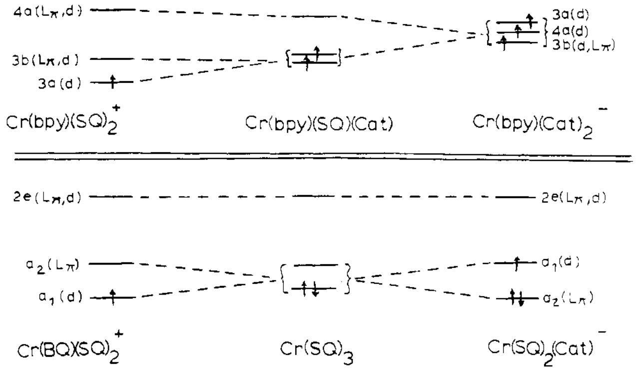

Figure 7. Diagrams showing important molecular orbital levels for the $Cr(Q)_3^n$, n = 1+, 0, 1−, series on the basis of calculations performed by Gordon and Fenske. In a few cases changes in order have been made to agree with magnetic properties of the complexes.

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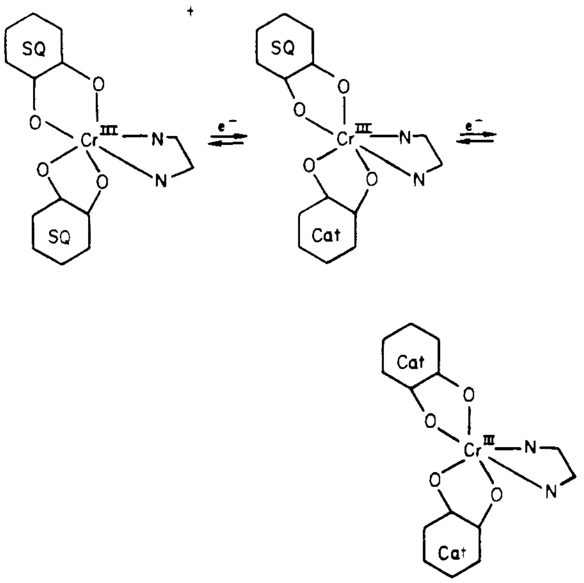
tion. The monocationic complexes obtained from $Cr(SQ)_3$ species were calculated to have a ligand-localized a_2 HOMO. This is in disagreement with the EPR results, which clearly point to a metal-localized ground state. But, as before, the energy separation between the ligand-based HOMO and the metal-localized LUMO is only a few tenths of an electronvolt. In a valence-bond sense the complex can be viewed as having a Cr(III) ion, $Cr(SQ)_2(BQ)^+$, with strong spin–spin coupling between the $S = {}^3/_2$ metal ion and the two $S = {}^1/_2$ semiquinone ligands. Fenske's calculations show that there is little change in metal ion charge through the seven-membered redox series (eq 2). Characterization of the 3– complex by Raymond has shown that it can properly be viewed as a Cr(III) complex of catecholate ligands. The cationic bipyridine complexes conform to this view with $Cr(SQ)_2(bpy)^+$ related to $Cr(SQ)_2(BQ)^+$.

The neutral complexes containing the bipyridine ligand seem to have rather different electronic structures from the neutral $Cr(SQ)_3$ compounds. Spin–spin coupling between the Cr(III) ion and the three semiquinone ligands is relatively strong, and the $Cr(SQ)_3$ compounds are either diamagnetic (3,5-DBSQ) or weakly paramagnetic (9,10-phenSQ, *o*-Cl_4SQ) at room temperature.[16] At 4.2 K all of the $Cr(SQ)_3$ complexes are diamagnetic. In the Fenske formulation, residual paramagnetism at higher temperatures would result from thermal population of the a_1 LUMO, a level of the neutral complex that is slightly greater than 1 eV above the HOMO. In the case of the neutral bipyridine complex, calculations point to a diamagnetic ground state although, as before, there is a separation of only a few tenths of an electronvolt between the HOMO and LUMO. Indeed, this separation must be quite small since the complexes all appear to have $S = 1$ ground states and show no temperature-dependent magnetic behavior. The physical properties of the neutral complexes provide little direct information on charge distribution, but the similarity of the electrochemical behavior to the $Cr(SQ)_3$ series points to redox activity of quinone ligands rather than the metal ion. Reduction of the one quinone ligand of $Cr(SQ)_2(bpy)^+$ would give $Cr^{III}(SQ)(Cat)(bpy)$, a molecule containing quinone ligands with different charges similar to I. (See eq 6.) Coupling of the $S = {}^3/_2$ Cr(III) ion to the semiquinone ligand gives the $S = 1$ spin state for the complex. The second reduction would give the anion with fully reduced catecholate ligands bonded to Cr(III), $Cr^{III}(Cat)_2(bpy)^-$. This species should exhibit normal magnetic behavior for a Cr(III) complex, a result which is quite different from that of the $S = {}^1/_2$ $Cr(SQ)_2(Cat)^-$ anions. Calculations predict $S = {}^1/_2$ states for both types of anions. For $Cr(SQ)_2(Cat)^-$ the low- to high-spin transformation would correspond to a $(a_2)^2(a_1)^1(e)^0 \rightarrow (a_2)^1(a_1)^1(e)^1$ configuration change, and for $Cr(Cat)_2(bpy)^-$ this is $(3b)^2(3a)^1(4a)^0 \rightarrow (3b)^1(3a)^1(4a)^1$. The calculated



(6)

energy separation between the a_2 and e levels of $Cr(SQ)_2(Cat)^-$ is greater than 3 eV, but for the bipyridine complex the 3b–4a separation is roughly 1.2 eV. A higher spin configuration is clearly a more viable option in the latter case. Magnetic susceptibility measurements on $Cr(3,5\text{-DBCat})_2(bpy)^-$ in solution have given values greater than 3.5 μ_B. The close proximity in energy of electronic levels for these compounds is quite interesting, particularly in cases where the HOMO and LUMO are localized in different regions of the molecule. A transition between localized metal and ligand levels can dramatically change the character of a complex.[17] Fenske's calculations suggest that these transitions can be well into the infrared region (0.2 eV, ~1600 cm^{-1}). The temperature-dependent behavior of the cobalt complex discussed above (I) can be viewed as an example of thermally induced ligand-to-metal electron transfer requiring a small energy separation between metal and ligand electronic levels. This opens the possibility of interesting photochemical behavior for the quinone complexes, a subject of considerable current interest.

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Registry No. $Cr(O_2C_6H_2(t\text{-Bu})_2)_2(bpy)$, 86364-86-5; $Cr(O_2C_6H_2(t\text{-Bu})_2)_2(bpy)^+$, 86364-87-6; $Cr(O_2C_6H_2(t\text{-Bu})_2)_2(bpy)^-$, 86364-88-7; $Cr(O_2C_6Cl_4)_2(bpy)$, 86364-89-8; $Cr(O_2C_6Cl_4)_2(bpy)^+$, 86364-92-3; $Cr(O_2C_6Cl_4)_2(bpy)^-$, 86372-60-3; $Cr(O_2C_{14}H_8)_2(bpy)$, 86364-90-1; $Cr(O_2C_{14}H_8)_2(bpy)^+$, 86364-91-2; $Cr(O_2C_{14}H_8)_2(bpy)^-$, 86364-93-4; $Cr(CO)_4(bpy)$, 15668-63-0.

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