# METAL–LIGAND ELECTRONIC INTERACTIONS IN MONONUCLEAR AND DINUCLEAR TRIETHYLENETETRAMINECOBALT(III) COMPLEXES CONTAINING THE ANION OF QUINIZARIN (1,4-DIHYDROXY-9,10-ANTHRAQUINONE)

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*Dedicated to Professor Václav Horák on the occasion of his 70th birthday.*

1,4-Dihydroxy-9,10-anthraquinonatotriethylenetetraminecobalt(III) cation and its conjugate acid and the tetrapositive dinuclear μ-1,4-dihydroxy-9,10-anthraquinonatobistriethylenetetraminedicobalt(III) cation have been prepared in aqueous solution and characterized by spectroscopy and cyclical voltammetry. Both spectra and electrochemistry indicate that there is significant interaction between ligand-centered orbitals and metal-centered orbitals in all three species.

Václav Horák and his co-workers have made many important contributions to the study of the chemistry of the quinones. Recently, there has been considerable interest in quinones as ligands for transition-metal ions[1].

Transition-metal *d*-orbital energies are similar to the energies of quinone $\pi$-orbitals[2] and quinones are readily reducible, so that the possibility of diverse electronic forms of ligands gives rise to interesting spectroscopic, electrochemical, and magnetic[3] behavior – but also complicates characterization of complexes.

We have used dihydroxyquinolate ions as bridging ligands for inner-sphere redox reactions in which Ti(III) reduces Co(III) or Ru(III) complexes[4]. In the former reaction, sluggish through-bridge electron-transfer (hereafter, ET) was observed; in the latter case, ET from Ti(III) to the quinolate is rapid but ET from the ligand to Co(III) is much slower. Rates of electron-transfer reactions involving quinones as bridging ligands evidently depends on the details of metal–ligand electronic interaction. This property may eventually be useful in molecular electronics[5].

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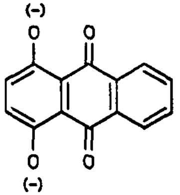
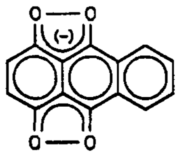
Stable mixed-valence dimetallic compounds are often used as models for transition states of inner-sphere ET processes. A number of complexes of quinones containing two transition-metal centers have been prepared and studied[6]. One of the most interesting features of these complexes is the intervalence charge-transfer (IVCT) absorption that occurs in the near-IR spectrum of these species. Most of these dimetallic complexes have bipyridine or its derivatives as nonbridging ligand[7]. Electronic transitions between metal- and quinone-centered orbitals and also transitions between bipyridyl-centered and quinone-centered orbitals are observed in UV-VIS spectra of these complexes. Aromatic ligands are not innocent in their effects on electronic structure of transition-metal complexes. Interaction between metal and bipyridine orbitals would be expected greatly to influence the details of the quinone–metal interaction. This is a complication in the assignment and interpretation of the spectra, particularly the IVCT bands.

In order to minimize such complications, we prepared mononuclear and dinuclear cobalt(III) complexes of the anion of 1,4-dihydroxy-9,10-anthraquinone (hereafter referred to as quinizarin) with triethylenetetramine(trien) as nonbridging ligand. Trien has no π system to interact with the metal–ion *d*–π orbitals and therefore it should be possible to understand the electronic structure of dimetallic complexes involving trien non-bridging ligands more readily than that of complexes containing aromatic non-bridging ligands.

Normally, dihydroxyquinones coordinate through the conjugate base of the quinone, the form shown at *a* for the ligand of present interest. Although several cases in which extensive delocalization is evident have been described[8], the fully-delocalized ligand structure shown at *b* has not been established for any complex. Since quinones are readily reducible to semiquinones and then to alcohols (by electrodes, external reagents or by metal ions to which they are coordinated) the two additional structures shown at *c* and *d* might also be important.



a



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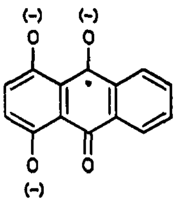

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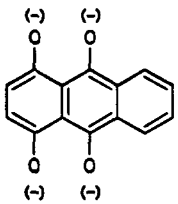

d

## EXPERIMENTAL

UV-VIS spectra were recorded on a Hewlett–Packard HP8451A diode-array spectrophotometer. To determine extinction coefficients of dissolved species, cobalt concentrations were estimated as the 1-nitroso-2-naphthol-3,6-disulfonic acid complex at 520 nm. Infrared spectra were recorded (4 000 – 250 $cm^{-1}$) on a Perkin–Elmer 457 grating infrared spectrophotometer using KBr disks.

Voltammetric measurements were made using a Bioanalytical Systems CV-1 instrument and a glassy carbon working electrode. Potentials are reported as peak potentials vs SCE. (6 mM $K_3Fe(CN)_6$ in 1 M $KNO_3$ gave $E = -0.225$ mV, peak separation 60 mV.) Ethylene glycol and water were used as solvents, with 0.5 M $NaClO_4$ /$10^{-2}$ M $HClO_4$ as supporting electrolyte in both cases.

Reagents were "reagent grade" and were used as received. Nitrogen was dried by $SiO_2$ and Drierite. $[Co(trien)Cl_2]Cl$ was prepared according to a procedure of Basolo[10].

*$[Co(trien)(CF_3SO_3)_2](CF_3SO_3)$* was synthesized by using a modification of a procedure of Bernhardt and Lawrance[11]. Anhydrous $CF_3SO_3H$ (17 ml) was added to purple $[Co(trien)Cl_2]Cl$ (1.0 g) in a three-necked round bottom flask. Dry nitrogen was bubbled through the solution as it was heated at 100 °C for 2 h. When evolution of HCl had ceased, the solution was cooled in an ice bath. Diethyl ether (60 ml) was added dropwise with vigorous stirring. The pink solid that formed was filtered on a medium porosity glass frit, washed with diethyl ether, and air dried. To remove traces of $CF_3SO_3H$, the pink powder was ground in a mortar and then boiled in chloroform for 10 min. The pink solid was filtered again, washed with diethyl ether, and dried in a vacuum dessicator over Drierite. (Yield 1.6 g, 98%). Wavelengths (nm) of maximum absorption in acetone (extinction coefficients, log ε, $cm^{-1}$ $mol^{-1}$ l) are : 512 (2.05); 364 (1.94). Infrared spectra (KBr disk) confirm the presence of bound triflate through the presence of C–F and S=O stretching bands at 1 000 – 1 400 $cm^{-1}$ and the absence of absorbance at 1 280 $cm^{-1}$ (ionic $CF_3SO_3$).

Quinizarin was ligated to Co(trien) fragments by two procedures. In the first method, 0.5 g (1.6 mmol) of $[Co(trien)Cl_2]Cl$ was dissolved in 150 – 200 ml of distilled water and adjusted to pH 8 with KOH. An excess of quinizarin (0.58 g, 2.4 mmol) was then added and the solution heated to 90 °C. A peak at 620 nm slowly appeared in the spectrum of the reaction mixture. After 40 min, the solution was cooled and filtered to removed unreacted ligand. An aliquot of the solution was loaded onto a Bio-Rad AG50W-X2 cation exchange column and eluted with 2 – 5 M HCl. A blue band eluted from the column. The spectrum of that fraction had absorbances at 358, 534, 572, and 620 nm. Absorbance-intensities indicated a low yield of product.

A second method of preparation was used to increase yield. $[Co(trien)(CF_3SO_3)_2](CF_3SO_3)$ (0.1500 g) and quinizarin (0.243 g) were added to ethylene glycol (100 ml). The orange solution was stirred vigorously at 80 °C until the color changed to purple (2 h). The solution was filtered to remove unreacted quinizarin. An aliquot was loaded onto an SP-Sephadex CP25 cation-exchange column. Elution from this column with 10 mM $NaClO_4$ containing varying amounts of $NaClO_4$ yielded first a purple fraction at concentrations as low as 0.1 M $NaClO_4$ and then a blue fraction starting at 0.5 M $NaClO_4$. The observed elution pattern is consistent with a larger positive charge on the species in the blue fraction than on the species in the purple fraction.

Another aliquot of the reaction mixture was loaded onto a Sephadex G25 molecular-weight column. With distilled water as eluent, the blue fraction was eluted from the column followed by the purple fraction. This pattern of elution is consistent with the blue fraction containing the solute with the higher molecular weight.

The complexes were also eluted from a Sephadex G-25 molecular weight column using ethylene glycol containing 10 mM $HClO_4$ and 0.5 M $NaClO_4$. These solutions were used for electrochemical measurements.

Crystalline solids separated slowly from some fractions eluted from chromatographic columns. The complexes displayed some tendency to decompose, particularly under basic conditions[12].

## RESULTS AND DISCUSSION

Results of column chromatography provide strong evidence for characterization of the blue solute as $[Co_2(trien)_2(quinizarinate)]^{4+}$ and the purple solute as $[Co(trien)(quinizarinateH)]^{2+}$. The binuclear species is expected to have a molecular weight approximately 1.5 times as great as that for the mononuclear complex and to elute more quickly from a Sephadex G-25 column. The more highly charged binuclear species is expected to elute more slowly from a cation-exchange column. Both complexes exhibit UV-VIS spectra (Table I, Figs 1 – 3) that resemble those reported for other transition-metal complexes of quinizarin and of anthraquinones[13].

Deprotonation of quinizarin is accompanied by large changes in spectrum which have previously been used to evaluate acidity constants for quinizarin as $pK_1 = 9.92 \pm 0.01$ and $pK_2 = 13.7 \pm 0.1$ (ref.[14]). Reaction of Co(III) with quinizarin to form a mononuclear complex would be expected to lower $pK_a$ by stabilizing negative charge on the anion, if there is interaction of ligand-based and metal-based orbitals. The purple complex exhibits a shift in the position and intensity of low-energy transitions with increasing pH (Fig. 3). This behavior is consistent with formulation of the purple complex as a mononuclear species (which would lose a proton from the uncomplexed hydroxyl). Analysis of six measurements between pH 5.45 and pH 8.08 at 542 nm and 618 nm yields $pK_a = 6.53 \pm 0.14$ (Table II). (Higher values of pH were not used because the mononuclear complex decomposes in basic solution.) Such a large decrease in $pK_a$ on coordination indicates that the difference in delocalization of electrons is significantly greater between the deprotonated form of the mononuclear complex and its

TABLE I
UV-VIS spectra of quinizarin complexes and related species

| Species | λ (nm) / log ε | | | | | | |
|---|---|---|---|---|---|---|---|
| Quinizarin[a] | 252 | 284 | 330 | 484 | | | |
| | 4.3 | 3.9 | 3.2 | 3.8 | | | |
| Quinizarinate dianion[a] | 252 | 290 | | | 554 | | |
| | 4.5 | 4.0 | | | 4.1 | | |
| $[Co_2(trien)_2(quinizarinate)]^{4+,b}$ | 258 | | 362 | | 530 | 572 | 620 |
| | 4.2 | | 4.5 | | 4.0 | 4.3 | 4.5 |
| $[Co(trien)(quinizarinate)]^{+,c}$ | 254 | | 342 | | | 576 | 616 |
| | 4.4 | | 3.6 | | | 4.4 | 4.4 |
| $[Co(trien)(quinizarinateH)]^{2+,b}$ | 248 | 290 | 346 | 508 | 542 | 584 | |
| | 4.5 | sh | 3.6 | 3.5 | 3.7 | 3.8 | |

[a] Ethylene glycol, 25 °C; [b] aqueous 0.5 M $NaClO_4$, 10 mM $HClO_4$, 25 °C; [c] aqueous 0.5 M $NaClO_4$, pH 8.0, 25 °C.

conjugate acid than between quinizarinate anion and quinazarine itself. As expected for a complex with no acidic protons, the spectrum of the blue complex does not change with change in pH.

$[Co(trien)CO_3]^+$ exhibits peaks at 360 nm and 506 nm which are assigned as ${}^1A_{1g}\backslash{}^1T_{1g}$ and ${}^1A_{1g}\backslash{}^1T_{2g}$ transitions. In aqueous solution, the visible-region spectrum of quinizarin dianion exhibits a broad band composed of at least three transitions (515, 548, and 580 nm). This system of bands has previously been assigned as the HOMO–LUMO transition of the quinazarin $\pi$-electron system. MNDO calculations indicate that this transition corresponds to transfer of charge from the oxygens and central ring of the ligand to the ring that is not involved in coordination[15]. The multiplicity of closely-spaced bands in this system is attributed to transitions involving several vibrational energy states of the HOMO and LUMO. This vibronic structure is quite characteristic of this transition for this particular ligand and enables unambiguous identification of this transition. Quinizarin itself exhibits a similar broad band at higher energy (480 nm) with somewhat poorer resolution of vibronic structure. A series of three intense bands appears in 508 – 620 nm region for both monocobalt and dicobalt complexes, with the transitions for the dinuclear species appearing at lower energy and higher intensity than the corresponding transitions for the mononuclear species. Coordination of a second metal fragment such as Co(trien) is known to perturb the $\pi$-system of ambidentate ligands, shifting transitions to lower energy[16]. The variation of these bands between the two complexes is consistent with the formulation given for these complexes. The red shift on addition of a second Co(trien) fragment indicates that mixing of ligand-based and metal-based orbitals occurs. This band structure is at higher energies for both of the complexes of present interest than for corresponding Zn(II), Cu(II), Ni(II) or Co(II)

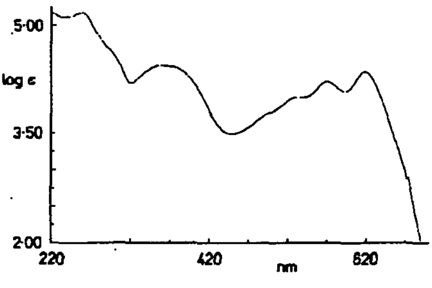

FIG. 1
Spectrum of $[Co_2(trien)_2(quinizarinate)]^{4+}$ in aqueous 0.5 M $NaClO_4$, 10 mM $HClO_4$; 25 °C: log ε vs wavelength in nm

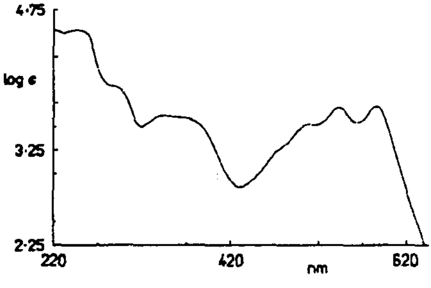

FIG. 2
Spectrum of $[Co(trien)(quinizarinateH)]^{2+}$ in aqueous 0.5 M $NaClO_4$, 10 mM $HClO_4$; 25 °C: log ε vs wavelength in nm

complexes. This also indicates stabilization of the ligand HOMO by interaction with the $d$–$\pi$ orbitals of Co(III).

A single band appears at 330 nm for the free ligand. This band is red-shifted on formation of the dianion, appearing as a shoulder at 364 nm. In the dinuclear complex, a band appears at 362 nm with essentially the same intensity as the corresponding band for the dianion. The mononuclear complex exhibits a composite band around 350 nm. The second derivative shows a pair of transitions at 340 and 365 nm. The transitions in this region have previously been attributed to intraligand quinoid $n$ to $\pi^*$ transitions[17]. These transitions are evidently not much affected by coordination of Co(III).

Quinizarin exhibits intense absorption at 252 and 284 nm. On deprotonation to form the dianion, the lower-energy transition of these two is red-shifted, and there is an increase in intensity of both bands. These two high-energy bands can be attributed to intraligand $\pi$–$\pi^*$ ($^1A_{1g}$ to $^1B_{1u}$) transitions[18]. These transitions remain essentially unchanged on coordination to form the monocobalt species (Fig. 1). The dicobalt species in acidic solution (Fig. 2) exhibits only a band at 258 nm. Delocalization (form

TABLE II
Spectrophotometric titration data[a] at 542 nm and 618 nm

| pH | $A_{542}$ | $A_{618}$ | p$K_a$ |
|---|---|---|---|
| 5.45 | 0.063 | 0.015 | 6.56 |
| 6.70 | 0.050 | 0.054 | 6.28 |
| 7.37 | 0.044 | 0.060 | 6.49 |
| 7.63 | 0.044 | 0.065 | 6.58 |
| 7.82 | 0.048 | 0.072 | 6.62 |
| 8.08 | 0.047 | 0.074 | 6.68 |

[a] 0.029 mM Co, 0.5 M $NaClO_4$, 25 °C.

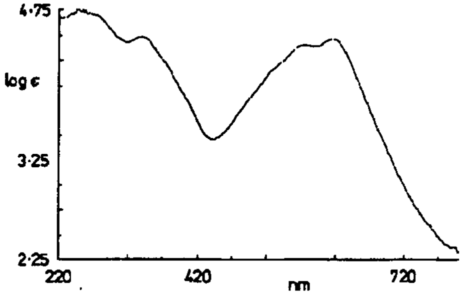

FIG. 3
Spectrum of [Co(trien)(quinizarinate)]$^+$ in aqueous 0.5 M $NaClO_4$, pH 8.0; 25 °C: log ε vs wavelength in nm

*b* above) should be increased by coordination, especially for the dinuclear species. The loss of the 290 nm transition on protonation and in going from the mono- to the dinuclear species supports suggestions[19] that this band derives from transitions based on quinone-like ground states.

Cyclical voltammograms in aqueous solutions ($NaClO_4/HClO_4$ supporting electrolyte) show at least four cathodic waves and three anodic waves. The shapes of the waves suggest that chemical reactions are coupled to the electrode processes. Hydroquinones undergo substitution during anodic oxidation in the presence of nucleophiles[20]. It seems probable that this reaction occurs during reduction of the complexes in aqueous solution and complicates the voltammograms.

In ethylene glycol (with $NaClO_4/HClO_4$ as supporting electrolyte) cyclical voltammograms are less complicated (Table III). The mononuclear and dinuclear complexes exhibit similar electrochemical behavior. Two reduction waves and two oxidation waves appear but the waves are separated by six times the 59 mV that would be expected for reversible one-electron processes. None of these waves is observed for $[Co(trien)Cl_2]Cl$ or $[Co(trien)(CF_3SO_2)_2](CF_3SO_2)$ and no Co(III) reduction-wave is observed at ca 0.3 V for the complex. The lack of the Co(III) reduction wave for the complexes indicates interaction of metal and ligand-based $\pi$ orbitals. The observation that, for both complexes, the reduction peaks appear at nearly the same potentials as the reversible waves for the two one-electron reductions of quinizarin suggests that the reductions of the complexes primarily involve reducing the ligand from the quinone to the semiquinone and then to the alcoholate forms. The peaks of the binuclear complex are slightly shifted in the cathodic direction, relative to the mononuclear complex. This is consistent with stabilization of the ligand against reduction by coordination to the two metal ions.

TABLE III

Cyclical voltammetry of quinizarin complexes (peak potentials, V vs SCE)

| Compound | $E_o$ | $E_r$ | $E_o'$ | $E_r'$ |
|---|---|---|---|---|
| Quinizarin[a] | -0.53 | -0.59<br>-0.58[b] | -1.16 | -1.22 |
| $[Co(trien)CF_3SO_2)_2]^{+}$[c] | | -0.35 | | |
| $[Co(trien)Cl_2]^{+}$[c] | | -0.20 | | |
| $[Co(trien)(quinizarinateH)]^{2+}$[c,e] | -0.13 | -0.55 | -0.58 | -1.13 |
| $[Co(trien)_2(quinizarinate)]^{4+}$[c,e] | -0.18 | -0.57 | -0.59 | -1.13 |

[a] In dimethylformamide[21]; [b] in acetonitrile, this work; [c] in ethylene glycol, this work; 0.20 mM complex; [d] in ethylene glycol, this work; 10 mM complex; [e] 500 mV $s^{-1}$, 10 mM $HClO_4$, 0.5 M $NaClO_4$, 25 °C.

The irreversible nature of the waves indicates that reoxidation at the electrode is slow. Evidently, both reduction products rearrange to forms with somewhat different geometry. The odd electron from the first reduction might be stabilized on the ring that is not involved with coordination or by interaction with the Co(III) to yield some contribution of Co(II) quinizarinate character. Involvement of the metal ion could thus avoid the formation of relatively less stable radical species. After the second reduction, the most stable form of the electrode product should be a tetroxoCo(III) complex (form *d* above). The difference in cyclical voltammograms for the quinizarin complexes and those for $[Co(trien)Cl_2]Cl$ and $[Co(trien)(CF_3SO_2)_2](CF_3SO_2)$ (for which no anodic peaks are observed) indicates that both reduction products (in contrast with usual Co(II) species) are non-labile with respect to ligand dissociation. This also suggests relatively strong π interactions between ligand- and metal-based orbitals.

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