

# Properties of ruthenium bipyridyl dimers bridged by disubstituted anthraquinones

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## Abstract

$\text{Ru}(\text{bpy})_2\text{Cl}_2$  reacts with 1,4-DHAQ, 1,5-DHAQ and 1,4-AHAQ to form dinuclear complexes. Its reaction with 1,8-DHAQ produces a monomer. Both 1,4-DHAQ and 1,4-AHAQ produce stable mixed valence complexes when oxidized, and show greater separation of ruthenium oxidation potentials than the 1,5-DHAQ complex.  $K_c$  has been calculated to be  $3.7 \times 10^4$  for the 1,4-DHAQ complex,  $1.3 \times 10^8$  for the 1,4-AHAQ complex, and  $3.4 \times 10^2$  for the 1,5-DHAQ complex. In all cases  $E_{1/2}(1)$  for the dimers is less positive than  $E_{1/2}(1)$  for the monomeric 1,8-DHAQ complex. Spectral studies of the mixed valence states showed IT bands at approximately 2000 nm in acetonitrile for the 1,4-DHAQ complex and at 1368 nm in acetonitrile for the 1,4-AHAQ complex. Solvent dependence was observed for the IT band for the latter complex. The experimental evidence indicates that the three dinuclear complexes may be class II mixed valence dimers.

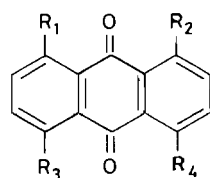
## Introduction

Adriamycin and other related anthraquinone drugs are used as antitumor agents for treatment of over half of the known tumor types, even though prolonged treatment causes damage to heart muscle [1–3]. The cardiotoxic side effects may involve metal ion complexation by these drugs *in vivo* and subsequent redox chemistry involving oxygen [1, 4, 5]. The anthraquinone portion of these drug molecules has been found to complex both copper and iron under physiological conditions [4–9]. Metal complexation destroys the hydrogen bonding between the quinone oxygen and hydroxyl hydrogen in the hydroxyanthraquinones. This hydrogen bonding has been found to stabilize the reduced form of hydroxyanthraquinones relative to the parent anthraquinone, and consequently, their reduction potential should be affected by complexation [10]. Not only will the hydrogen bonding be disrupted by metal complexation, but the bonding properties of the metal ions will differ from the hydrogen ion and may further affect the redox behavior of the anthraquinones.

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Consequently, we have synthesized a number of ruthenium(II) complexes containing substituted anthraquinones (AQ) to study the effect of complexation on redox potentials of selected anthraquinones (Scheme 1).

When *cis*- $\text{Ru}(\text{bpy})_2\text{Cl}_2$  (bpy = 2,2'-bipyridine) reacts with the first four of these ligands (L), complexes of the general formula,  $[(\text{bpy})_2\text{Ru}^{\text{II}}\text{-LRu}^{\text{II}}(\text{bpy})_2]^{2+}$ , are formed except with 1,8-DHAQ where a monomer is formed. These complexes are interesting as well, because the dinuclear complexes can be oxidized to form mixed valence dimers. Ruthenium mixed valence dimer studies have made important contributions toward the understanding of electron transfer reactions [11–14]. The series of bridging ligands in this work examines the importance of the ring position of the metals, the effect of changing a ligation atom, and allows comparison of the bridging anthraquinones with bridging naphthaquinones, quinones and semiquinones [15, 16]. We report here the electrochemical and spectral study of the compounds:  $[\text{Ru}(\text{bpy})_2\text{1,8-DHAQ}](\text{PF}_6)$  (I);  $\text{Ru}_2(\text{bpy})_4\text{1,4-DHAQ}(\text{PF}_6)_2$  (II);  $[\text{Ru}_2(\text{bpy})_4\text{1,5-DHAQ}](\text{PF}_6)_2$  (III);  $\text{Ru}_2(\text{bpy})_4\text{1,4-AHAQ}(\text{PF}_6)_2$  (IV).



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>
1,4-Dihydroxyanthraquinone (1,4-DHAQ)	H	OH	H	OH
1,5-Dihydroxyanthraquinone (1,5-DHAQ)	H	OH	OH	H
1,8-Dihydroxyanthraquinone (1,8-DHAQ)	OH	OH	H	H
1-Amino-4-hydroxyanthraquinone (1,4-AHAQ)	H	NH <sub>2</sub>	H	OH
Anthraquinone component of adriamycin	H	OH	CH <sub>3</sub> O	OH
Anthraquinone component of aclacinomycin	OH	OH	H	H
Mitoxantrone	OH	NHX	OH	NHX

(X = CH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>OH)

Scheme 1.

## Experimental

HPLC grade acetonitrile (CH<sub>3</sub>CN) and Gold label spectrophotometric dimethylformamide (DMF) dried over 3 Å molecular sieves were used as solvents. The RuCl<sub>3</sub>·H<sub>2</sub>O, substituted anthraquinones, 2,2'-bipyridine, and other chemicals were reagent grade and used without further purification.

### Synthesis

The ruthenium starting material for all syntheses of ruthenium-bipyridyl anthraquinone complexes was *cis*-Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O which was prepared by the method of Sullivan *et al.* [17].

[Ru<sub>2</sub>(bpy)<sub>4</sub>1,4-DHAQ](PF<sub>6</sub>)<sub>2</sub> (II) was synthesized by a method that has been described previously [18]. The other complexes were synthesized based on this same method but substituting stoichiometric amounts of the particular anthraquinone and Ru(bpy)<sub>2</sub>Cl<sub>2</sub>·H<sub>2</sub>O. All complexes were recrystallized from acetone as described previously, and analyzed for C, H, and N.

### Electrochemistry

Cyclic voltammetry studies were done on an IBM EC/225 voltammetric analyzer in DMF which was 0.1 M in tetrabutylammonium perchlorate as supporting electrolyte using a glassy carbon working electrode, saturated calomel electrode (SCE) as a reference electrode and platinum wire as the counter electrode.  $E_{1/2}$  values are the average of the peak potentials for the reversible oxidation and reduction waves and are measured versus the SCE. Solutions of the substituted anthraquinones and their corresponding complexes were measured under the same conditions with ferrocene as an internal standard in selected solutions.

### Spectra

IR spectra of the complexed and the uncomplexed bridging substituted anthraquinones were recorded in KBr disks on a Perkin-Elmer 397 spectrophotometer. UV-Vis spectra were recorded in acetonitrile solutions when possible, although H<sub>2</sub>O and DMSO (dimethyl sulfoxide) were also used, on either a Varian DMS-90 UV-Vis spectrophotometer, HP8452A diode array spectrophotometer or a Cary 2390 UV-Vis spectrophotometer. Near infrared spectra were recorded in either CH<sub>3</sub>CN, DMF, DMSO or acetone on a Cary 2390 spectrophotometer. Mixed valence complexes were produced from the fully reduced ([2,2]) form of the complex by either electrolysis at potentials slightly higher than the first electron oxidation wave or by oxidation with stoichiometric amounts of ceric ammonium nitrate. <sup>1</sup>H NMR spectra were recorded on solutions of the complexes in the fully reduced form in CD<sub>3</sub>COCD<sub>3</sub> on either a Bruker WP-80 spectrometer or a Varian XL300 spectrometer.

## Results and discussion

### Analysis results

The analysis results for all of the complexes synthesized in this study showed results that seem to be typical for carbon and hydrogen analyses on quinone and semiquinone complexes [18, 19]. The results for II agree with those found previously [18]. The electrochemical results did not show any electroactive impurities in these complexes. All of the complexes except the one with 1,8-DHAQ are dinuclear. The inability to form a dimer with 1,8-DHAQ is probably due to the large size of the -Ru(bpy)<sub>2</sub> unit as Cu<sub>2</sub>(1,8-DHAQ)<sub>2</sub> is known [20].

### IR spectra

IR spectra of the totally reduced form of each complex help to confirm that the ligands are bidentate. The IR spectra of 1,4-DHAQ and  $\text{Ru}_2(\text{bpy})_41,4\text{-DHAQ}^{2+}$  agree with previously reported spectra [18]. For all the uncomplexed anthraquinones used, the carbonyl stretching frequency occurs between 1615 and 1670  $\text{cm}^{-1}$  and in all complexes this frequency is shifted to longer wavelengths by at least 20  $\text{cm}^{-1}$ . This shift to lower frequencies is typical of complexed quinones which act as electron acceptors [21]. Similar results have been found in substituted anthraquinone complexes with other metals [8, 21–23].

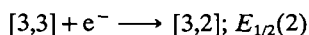
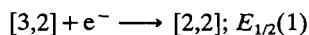
### $^1\text{H}$ NMR spectra

At both 80 and 300 MHz the bipyridine and anthraquinone resonances in the complexes overlap with many complex multiplets in the aromatic region from  $\delta=9.0\text{--}7.0$  ppm. Even though the  $^1\text{H}$  NMR spectrum of  $\text{Ru}_2(\text{bpy})_41,4\text{-DHAQ}^{2+}$  at 300 MHz was better resolved and showed six distinct multiplets in this region, the six 1,4-DHAQ protons were buried in the multiplets from the bipyridines which have chemical shifts from 32 protons in this same region. In the spectrum of the uncomplexed 1,4-DHAQ the 2,3 hydrogens produce a singlet at 7.4 ppm, but no singlet in the aromatic region is apparent in the spectrum of **II** at either 80 or 300 MHz. For the 1,4-DHAQ ruthenium dimer (as well as all the other complexes) a mixture of stereo and optical isomers could be formed. The diastereomers should show distinct singlets in the aromatic region so the one singlet in the free ligand could have become several when complexed [24]. But, because of the bipyridine peaks,  $^1\text{H}$  NMR may not be useful for the identification of diastereomers. What the NMR spectra did show was that no paramagnetic species were present in the fully reduced form. However, a 300 MHz  $^1\text{H}$  NMR spectrum of the fully oxidized form of **II** in  $\text{D}_2\text{O}$  showed peaks from +11 to -16 ppm which is characteristic of paramagnetic ruthenium(III) complexes [21].

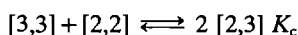
### Electrochemistry

Cyclic voltammograms of the free anthraquinones showed two reduction waves with potentials that agreed with previously reported values (quinone/semiquinone and semiquinone/catechol) [10] (see Table 1). Cyclic voltammograms of the dimers showed two oxidation peaks ( $E_{1/2}$ ) and three reduction peaks ( $E'_{1/2}$ ) while the monomer showed only one oxidation peak and three reduction peaks (Table 1). The two oxidation waves displayed by the dinuclear complexes were reversible ( $\Delta E=60\text{--}90$  mV,  $i_{pa}/i_{pc}\sim 1$ , and the

peak positions were independent of scan rate), as was the one observed for the mononuclear complex. Due to the absence of these peaks in the free ligands and the different number for the two types of complexes, these oxidations are assigned to the metal and not the ligand [16, 21, 24]. In studies of other Ru–quinone complexes the number of peaks did not change from free to complexed ligand which made the redox processes more difficult to assign [16]. The oxidation waves of **II**, **III** and **IV** are typical of dinuclear ruthenium(II) complexes with weakly interacting metal sites, and can be represented by [25, 26]



The difference between these potentials for **II** and **III** is 0.27 and 0.15 V, respectively, which agrees with previous results under similar conditions for the latter complex [27], and is used to calculate the conproportionation constants,  $K_c$ , for each compound [28] (see Table 1).



A recent article on the 1,4-dihydroxynaphthaquinone complex which is analogous to **II**, reported that the second oxidation for that complex was the oxidation of the ligand which caused the ligand to be further oxidized by the ruthenium(III) which returned to ruthenium(II) producing a diamagnetic product [15]. Since no fully oxidized product was isolated in this work, no magnetic measurements on the solid form of **II** were made, and our assignment of the [3,3] form with oxidized ruthenium is based on similarities with other ruthenium dimers, lack of an oxidation potential for the free ligand in the +1.0 to 0.0 V range, and  $^1\text{H}$  NMR solution data.

Electrolysis gave  $n$  values of  $\sim 1$  for the first oxidation wave for **II**. In **II** the oxygen atoms are bonded to the ruthenium on two of the three  $\text{C}_6$  rings of the anthraquinone while in **III** all of the rings are involved, thereby, decreasing the direct electronic interaction. (Both anthraquinones are complexed as -2 anions). In **III**, the increased distance between the metal centers leads to a decrease in the electrostatic interaction, and as the repulsion between the metal centers decreases, the difference between the potentials should be less. The difference in the  $K_c$  values for the two complexes is then due to the difference in both the electronic and electrostatic interactions between the ruthenium centers [24, 29]. Since **IV** is an asymmetric complex, we can calculate a value for  $K_c$  based on the difference in potential between  $E_{1/2}(1)$  and  $E_{1/2}(2)$ , but we cannot assign the position of the electron in the

TABLE 1. Redox potentials in DMF<sup>a, b</sup>

Compound	$E_{1/2}(2)$ (V)	$E_{1/2}(1)$ (V)	$E'_{1/2}(1)$ (V)	$E'_{1/2}(2)$ (V)	$E'_{1/2}(3)$ (V)
<b>I</b>		0.73	-0.65(-0.53) <sup>f</sup>	-1.25	-1.65
<b>II<sup>c</sup></b>	0.86	0.59	-0.95(-0.54) <sup>f</sup>	-1.38	-1.73
<b>III<sup>d</sup></b>	0.86	0.71	-0.71(-0.49) <sup>f</sup>	-1.12	-1.69
<b>IV<sup>e</sup></b>	0.77	0.29	-1.18(-0.83) <sup>f</sup>		

<sup>a</sup>Potentials are in V vs. saturated calomel electrode and are uncorrected; 0.38 V was obtained for the Fc<sup>+</sup>/Fc couple (Fc=ferrocene). <sup>b</sup> $T=24 \pm 1$  °C,  $E_{1/2} = \pm 0.01$  V. <sup>c</sup> $K_c = 3.7 \times 10^4$ . <sup>d</sup> $K_c = 3.4 \times 10^2$ . <sup>e</sup> $K_c = 1.8 \times 10^8$ . <sup>f</sup>Value for free ligand given in parentheses; this work and ref. 10 agree within 0.02 V.

mixed valence form without the appropriate monomer data or 1,4-DAAQ dimer data [12, 26].

The positive potentials for  $E_{1/2}(1)$  in Table 1 show that the [2,2] form of the complex is favored in solution. This stability can be accounted for from the donation of electron density from the metal  $d\pi$  to ligand  $\pi^*$  orbitals. However,  $\pi^*$  acceptance by the anthraquinone is not as great as it is in bipyridine, as shown by  $E_{1/2}(1)$  of 1.27 V in Ru(bpy)<sub>3</sub><sup>2+</sup> compared to 0.73 V in **I** [30].  $E_{1/2}(1)$  is different for all the dinuclear complexes and less than that for the mononuclear complex possibly because of electron donation by the first Ru(II), but could also be a charge effect, although this is unlikely as the increased charge of the dimers should increase  $E_{1/2}(1)$  instead of decreasing it [31]. When a ligating atom is changed from O to N (**II** to **IV**),  $E_{1/2}(1)$  goes from 0.59 to 0.29 V. Because this value is so different from  $E_{1/2}(1)$  for **I**, it implies the reduction of the Ru-N side of the dimer, but further data is needed to confirm this [12, 26].

The reduction peaks are ligand based with the anthraquinone reductions ( $E'_{1/2}(1)$  and (2)) occurring before the bipyridine reduction, as is observed with similar complexes [32]. The electrolysis results of the first reduction potential in **II** gave  $n \sim 1$ . Based on the first reduction potential of the free ligands (Table 1), it would appear that the lowest  $\pi^*$  orbital of all the free dihydroxyanthraquinone ligands should be of about the same energy. Because of the different metal  $d\pi$  to ligand  $\pi^*$  interaction for each complex, its energy is raised to different degrees in the complexes. The replacement of the protons by -Ru(bpy)<sub>2</sub> moieties on the DHAQs results in an increase of the charge on the molecule, as well as a change in the bonding. However, the change in reduction potentials is opposite from what would be expected for the increased charge and it appears that the change in bonding has the greater effect. These results may be relevant for the complexed anthraquinone drugs and their analogues [4, 5].

Although the complexes in this work should have stereo and optical isomers, the potentials of all isomers must be similar enough to show only one potential for each oxidation state change at the ruthenium centers or our synthetic methods produce only one stereoisomer. Similar behavior has been found for other bidentate bridging ligands where there is a possibility of optical and stereoisomerism [24, 25, 31].

#### UV-Vis spectra

The absorption maxima of all the complexes can be divided into two regions: 245–379 and 425–625 nm. Spectral results are shown in Table 2. Each complex in the [2,2] form shows three transitions in the higher energy region and these are independent of the ligand. In fact, the  $\lambda_{\max}$  for each transition is within a 3 nm range for the four complexes. These are assigned to ligand  $\pi$  to  $\pi^*$  transitions (possibly due to bipyridine transitions or a mixture from the two ligands) [17]. Compared to the free anthraquinone ligands the middle transition is shifted approximately 10 nm lower in energy in the complex. In the second region, the higher energy transition ranges from 425 to 472 nm depending on the complex and probably involves MLCT to the bipyridyl ligands as the electronic transitions in other complexes containing the -Ru(bpy)<sub>2</sub> unit have maxima around 450 nm [25]. For Ru(bipy)<sub>3</sub><sup>2+</sup>, there are two  $d\pi$  to  $\pi^*$  transitions due to the degeneracy of the  $d\pi$  energy levels [30]. The lower energy transitions ( $\lambda_{\max} > 550$  nm) vary in energy and could reasonably be assigned to  $d\pi$  to  $\pi^*$  MLCT transitions for the anthraquinone ligand. However, band positions do not agree with predictions of band position from electrochemical potentials, and we should expect the spectra of the mixed ligand complexes to be complicated [32]. Although three or less bands are observed in this region, they are broad with many shoulders and could be due to overlap of a number of states (MLCT, LLCT and some with strongly coupled vibrations) [33]. Spectral transitions in complexes with similar ligands have been thoroughly discussed [32].

TABLE 2. UV-Vis spectra in acetonitrile

Compound	Absorption maxima (nm) (log $\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ ))					
[2,2] form						
I·2H <sub>2</sub> O	245 (4.52)	292 (4.60)	365 (3.91)	461 (4.00)	553 (3.94)	
II	248 (4.89)	292 (4.99)	368 (4.20)	435 (4.18)	602 (4.45)	
III·C <sub>3</sub> H <sub>6</sub> O	245 (4.90)	294 (4.97)	367 (4.27)	472 (4.26)	597 (4.34)	643 (4.34)
IV·H <sub>2</sub> O	245 (4.93)	293 (5.00)	365 (4.15)	425 (4.26)	568 (4.48)	
[3,3] form						
I·2H <sub>2</sub> O		417 (4.03)				
II	370sh (4.20)	562 (4.28)	1120 (4.08)			
III·C <sub>3</sub> H <sub>6</sub> O	362 (4.23)	492 (4.23)	696 (4.11)			
IV·H <sub>2</sub> O		450 (4.20)	1233 (4.00)			

#### Near IR spectra

We were only able to observe IT bands for the mixed valence complexes containing the 1,4-DHAQ and 1,4-AHAQ ligands which supports the finding of a large  $K_c$  value for the former and a larger pseudo  $K_c$  for the latter. For II the solution obtained from electrolysis at a potential slightly higher than  $E_{1/2}(1)$  had the same spectral properties as the solution obtained by adding one equivalent of ceric ammonium nitrate. The band widths calculated from the equation  $\nu_{1/2} = (2310 \nu_{\max})^{1/2} \text{ cm}^{-1}$  (where  $\nu_{1/2}$  is the band width at half-height and  $\nu_{\max}$  is the position of the band maximum in  $\text{cm}^{-1}$ ) for II is similar to the actual measured value of  $3.4 \times 10^3 \text{ cm}^{-1}$  [11]. When this equation was used for IV the calculated value of  $\nu_{1/2}$  was greater than the experimental value, implying class III behavior, but because IV is asymmetric this calculation is not valid and should be replaced by  $\nu_{1/2} = ((\nu_{\max} - \nu_0)2310)^{1/2} \text{ cm}^{-1}$ . We have no value for  $\nu_0$  and therefore, cannot use  $\nu_{1/2}$  as a test for class II behavior [12, 26]. The solvent dependence of the IT band was examined for the 1,4-DHAQ dimer and 1,4-AHAQ dimer. The noise in the spectra did not allow accurate assignment of the  $\lambda_{\max}$  when it occurred in the 2000 nm region as it did for the 1,4-DHAQ complex. The 1,4-AHAQ complex has a maximum at 1368 nm ( $\epsilon = 2965 \text{ M}^{-1} \text{ cm}^{-1}$ ) in  $\text{CH}_3\text{CN}$ , 1385 nm ( $\epsilon = 3080 \text{ M}^{-1} \text{ cm}^{-1}$ ) in acetone, 1404 nm ( $\epsilon = 2609 \text{ M}^{-1} \text{ cm}^{-1}$ ) in DMF and 1428 nm ( $\epsilon = 2920 \text{ M}^{-1} \text{ cm}^{-1}$ ) in DMSO. The plot of  $1/D_{\text{op}} - 1/D_s$  versus  $\nu_{\max}$  is linear as predicted for class II mixed valence complexes [28]. However,

correction for  $\nu_0$  in each of these solvents was not made. The oxidation state changes for the 1,4-DHAQ complex were the easiest to see as the [2,2] state was blue, the [2,3] state green and the [3,3] state red.

The lowest energy transitions in II and IV in the [3,3] state (which was produced by adding 2 equivalents of ceric ammonium nitrate) may reflect the difference in energy between the [2,3] and [3,3] states (similar to the IT band for the [2,3] state) plus the electron pairing energy as well as some differences in energies due to changed bond lengths. The HOMO in the [2,3] state may become the LUMO in the [3,3] state, but both are important for spectral transitions [16].

#### Conclusions

The reversible peaks in the cyclic voltammograms suggest that electron transfer is facile in all the complexes prepared with the anthraquinone ligand stabilizing the fully reduced form of the metal and the metal stabilizing the dihydroxyanthraquinone form of the ligand. Our results indicate that all of the mixed valence dimers may be class II where electronic interaction between the two metal centers is weak.

#### Supplementary material

A table of elemental analyses for reported compounds (1 page) and a table of infrared absorption

frequencies for reported compounds (1 page) are available from the authors on request.

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