Linkage Isomers of Ruthenium Alizarin Complexes

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For molecular switch and/or information storage systems, molecules are required which can exist in two stable forms and be conveniently interconverted. Most systems reported to date involve complex organic systems and cis/trans isomerism or cyclization.[1-7] We report here an inorganic system involving linkage isomers of an alizarin–bis(bipyridine)ruthenium(II) complex[8,9] [isomers **QCat²⁻(Ru-1,2)** and **QCat²⁻(Ru-1,9)** as shown in Figure 1], with significantly different electronic spectra (Figure 2). Comparison with the 1-hydroxyanthraquinone **(QOH)** bis(bipyridine)ruthenium complex **[QO⁻(Ru-1,9)]**[11] aids in the elucidation of the bonding of these isomers.

Alizarin (1,2-dihydroxy-9,10-anthraquinone) contains two redox-active quinonoid fragments, the 9,10-dioxo unit labeled here as *p*-Q, *p*-Sq, or *p*-HQ^{2-} in its neutral quinone, one electron reduced (−1), and two electron reduced (−2) redox levels, and the 1,2-catechol-like fragment labeled *o*-Q, *o*-Sq, and *o*-Cat in its quinone, semiquinone, and catechol forms. Alizarin will be abbreviated as **$QCatH_2$**, Q referring to the 9,10-dioxo unit and $CatH_2$ referring to the doubly protonated 1,2-catechol unit. The abbreviations used include (Ru-1,2) or (Ru-1,9) to indicate the site of ruthenium coordination.

Protonation of **QCat²⁻(Ru-1,2)** gives **QCatH⁻(Ru-1,9)**, as followed by electronic spectroscopy (Figure 1). Deprotonation of **QCatH⁻(Ru-1,9)** gives **QCat²⁻(Ru-1,9)**, which is reversibly interconverted to **QCatH⁻(Ru-1,9)** by addition of acid.[13] Most importantly, complex **QCat²⁻(Ru-1,9)** converts back to complex

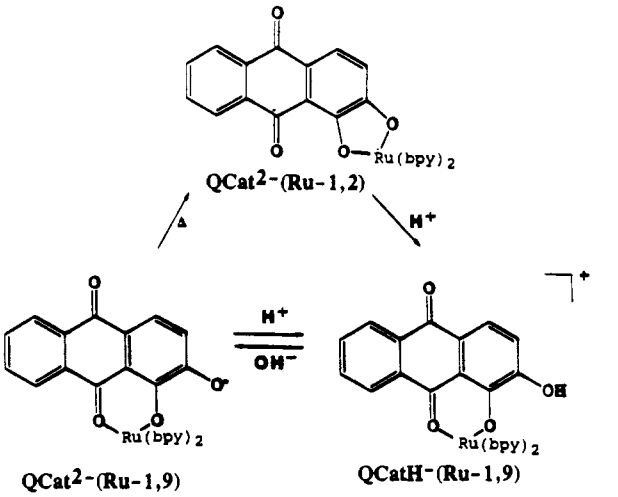

Figure 1. Interconversion of ruthenium alizarin isomers.

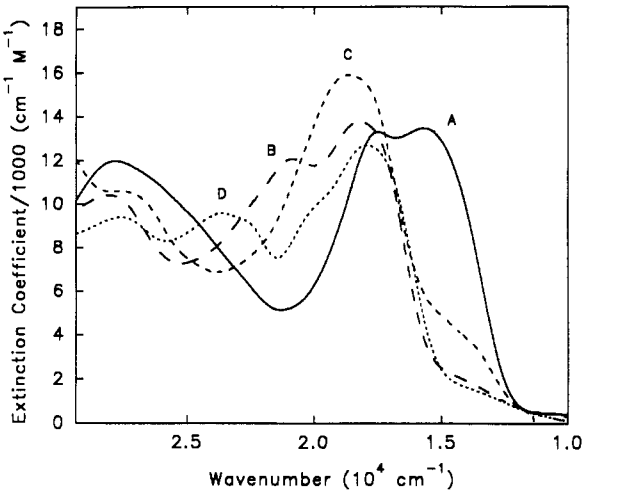

Figure 2. Electronic spectra of bis(bipyridine)ruthenium ligand complexes: (A) **QCat²⁻(Ru-1,2)**, (B) **QCatH⁻(Ru-1,9)**, (C) **QCat²⁻(Ru-1,9)**, and (D) **QO⁻(Ru-1,9)**, in methanol. The electronic spectrum of **QCat²⁻(Ru-1,9)** was obtained by adding triethylamine to a methanolic solution of **QCatH⁻(Ru-1,9)**.

QCat²⁻(Ru-1,2) when refluxed in 1-butanol (bp 117 °C) for 30 min, as confirmed by electronic and infrared spectroscopy.

The similarity in cyclic voltammograms between **QCatH⁻(Ru-1,9)** and **QO⁻(Ru-1,9)** (Figure 3) indicates that they have similar bonding. The complexes **QCatH⁻(Ru-1,9)** and **QO⁻(Ru-1,9)** show

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(8) **QCat²⁻(Ru-1,2)** synthesis: To dichlorobis(bipyridine)ruthenium(II) (0.45 g, 0.87 mmol) in methanol was added dropwise silver nitrate (0.26 g, 1.55 mmol) in methanol (10 mL). The stirred mixture, under nitrogen, was filtered 24 h later through Celite. The solvent was evaporated and replaced with a 1:1 mixture of methanol and absolute ethanol (30 mL). To **$QCatH_2$** (0.20 g, 0.83 mmol) in the same solvent mixture (10 mL) was added sodium methoxide (0.09 g, 1.57 mmol). This mixture was added to the ruthenium solution slowly and stirred over a hot plate under nitrogen for 15 min. The solution was filtered to isolate deep blue microcrystals of **QCat²⁻(Ru-1,2)**. The product was washed with absolute ethanol, cold methanol, and diethyl ether (0.33 g, 59% yield). Anal. Calcd for $C_{34}H_{30}N_4O_8Ru$: C, 56.43; H, 4.18; N, 7.74. Found: C, 56.68; H, 4.00; N, 7.67.

(9) **QCatH⁻(Ru-1,9)** synthesis: To dichlorobis(bipyridine)ruthenium(II) (0.28 g, 0.58 mmol) in methanol (20 mL) was added **$QCatH_2$** (0.15 g, 0.62 mmol) in methanol (20 mL) followed by a potassium hydroxide pellet (0.03 g, 0.58 mmol) in double distilled water. The mixture was refluxed for 30 h under nitrogen and then filtered to obtain **QCat²⁻(Ru-1,2)**.[10] To the purple filtrate acetic acid (2 mL) and trichloroacetic acid (0.5 mL) were added to ensure acidic conditions (pH 3.5). Ammonium hexafluorophosphate (0.15 g, 0.62 mmol) was added to the stirred mixture, which was then filtered to collect dark purple microcrystals of **QCatH⁻(Ru-1,9)**. This product was washed with a 1:1 mixture of acetic acid and double distilled water and air dried (0.36 g, 77% yield). **QCatH⁻(Ru-1,9)** was purified by using a Bio-Beads SX1 column with a 1:1 mixture of acetone and dichloromethane as the eluant. Anal. Calcd for $C_{34}H_{25}F_6N_4O_5PRu$: C, 50.07; H, 3.09; N, 6.87. Found: C, 49.67; H, 2.82; N, 6.50.

(10) **QCat²⁻(Ru-1,2)** from this preparation was impure, probably because it slowly decomposes in solution.

(11) **QO⁻(Ru-1,9)** synthesis (a modified procedure of Merrel[12]): To dichlorobis(bipyridine)ruthenium(II) (0.15 g, 0.31 mmol) in methanol (25 mL) was added **QOH** (0.07 g, 0.31 mmol) in methylene chloride (25 mL) slowly followed by solid sodium methoxide (0.02 g, 0.31 mmol). The red solution was refluxed for 3 h under nitrogen. Potassium hexafluorophosphate (0.30 g, 1.63 mmol) was added to the stirred mixture, which was left in the freezer to allow precipitation. A purple compound was filtered out, from solution, recrystallized from 2-propanol, and dried *in vacuo* at 100 °C (0.18 g, 75% yield). Anal. Calcd for $C_{34}H_{23}F_6N_4O_3PRu$: C, 52.25; H, 2.97; N, 7.17. Found: C, 52.12; H, 3.15; N, 7.02.

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(13) The acid and base used to carry out these reactions in methanol were trifluoroacetic acid and triethylamine, respectively.

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Table 1. Electrochemical Potentials of Ligands and Complexes[a]

	$E_{1/2}$ (V vs SCE)[b]			
ligand	*o*-Q/*o*-Sq	*o*-Sq/*o*-Cat	*p*-Q/*p*-Sq	*p*-Sq/*p*-HQ^{2-}
$QCatH_2$[c]	+1.55 (irr)[f]		−0.70 (0.09)	−1.24 (0.08)
QOH[c]			−0.73 (0.08)	−1.24 (0.11)
$QCatH^-$[d,h]		+0.06 (irr)[f]	−1.40 (0.13)	−1.90 (0.23)
$QCat^{2-}$[d,i]		−0.54 (0.12)	−1.59 (0.33)	

	$E_{1/2}$ (V vs SCE)[b]						
complex	Ru^{IV}/Ru^{III}	*o*-Q/*o*-Sq	*o*-Sq/*o*-Cat	Ru^{III}/Ru^{II}	*p*-Q/*p*-Sq	*p*-Sq/*p*-HQ^{2-}	bpy[j]/bpy^-
$QCat^{2-}$(Ru-1,2)[e]		+0.88 (0.08)[k]	+0.06 (0.07)		−1.58 (irr)[g]	−1.70 (irr)[g]	
$QCatH^-$(Ru-1,9)[c]			+1.5 (irr)[f]	+0.73 (0.06)	−0.87 (0.07)	−1.37 (0.08)	−1.68 (0.07)
QO^-(Ru-1,9)[c]	+1.93 (irr)[f]			+0.69 (0.06)	−0.84 (0.06)	−1.31 (0.06)	−1.69 (0.08)
							−1.99 (0.12)

[a] Note: The potentials are the average anodic and cathodic peak potentials in a cyclic voltammogram recorded at 100 $mV \cdot s^{-1}$. All potentials were recorded in the presence of 0.2 M tetrabutylammonium hexafluorophosphate ($(TBA)PF_6$), and the reference electrode is AgCl/Ag, with internal reference ferrocenium/ferrocene, which is assumed to lie at +0.425 V vs SCE.[26] [b] Peak to peak separation in parentheses. [c] In acetonitrile. [d] In dichlorobenzene. [e] In dichloroethane. [f] E_{pa}. [g] E_{pc}. [h] This couple may be Ru^{III}/Ru^{II} or *o*-Q/*o*-Sq, experimental work is in progress. [h] Tetraethylammonium alizarinate.[27] [i] Obtained by adding an excess of tetraethylammonium hydroxide to tetraethylammonium alizarinate. [j] bpy = bipyridine.

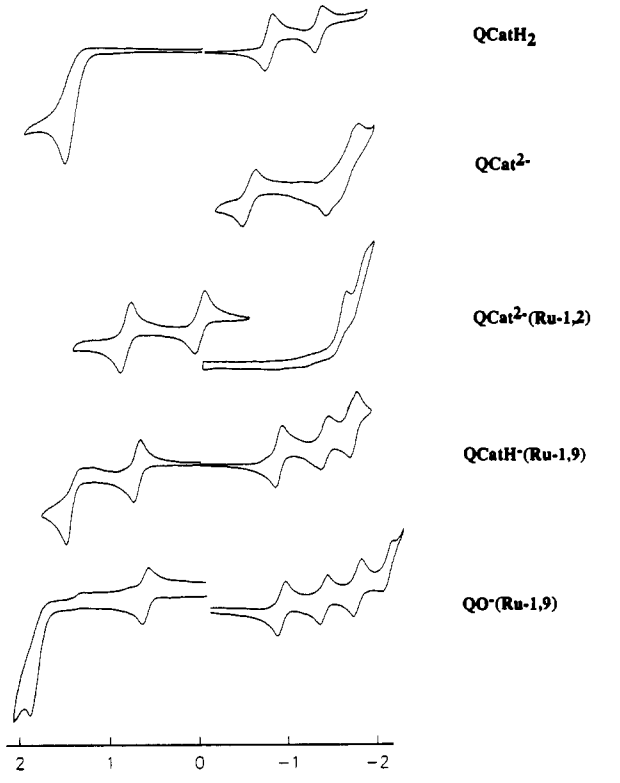

Figure 3. Cyclic voltammograms of **$QCatH_2$** in acetonitrile, **$QCat^{2-}$** in dichlorobenzene, **$QCat^{2-}$(Ru-1,2)** in dichloroethane, **$QCatH^-$(Ru-1,9)** in acetonitrile, and **QO^-(Ru-1,9)** in acetonitrile. All cyclic voltammograms were taken with 0.2 M $(TBA)PF_6$ solutions and a scan rate of 100 $mV \cdot s^{-1}$.

reversible Ru^{III}/Ru^{II} couples and *p*-quinonoid reductions (separated by 0.5 V as in **$QCatH_2$** and **QOH**) at approximately the same potential (Table 1). The redox couple in **$QCatH^-$(Ru-1,9)** at −1.68 V is assigned to bipyridine reduction, on the basis of similar potentials in other $[Ru(bpy)_2]^{2+}$ complexes of the same charge.[14,15]

The electrochemical behavior of **$QCat^{2-}$(Ru-1,2)**, very different from that of **$QCatH^-$(Ru-1,9)** (Figure 3), itself is an indication of a different mode of coordination. This behavior is readily explained by consideration of the electrochemistry of the dianion, **$QCat^{2-}$**. There is a large separation (1.05 V) between the *o*-Sq/*o*-Cat and *p*-Q/*p*-Sq processes (Table 1) in the alizarin dianion, **$QCat^{2-}$**. In the complex **$QCat^{2-}$(Ru-1,2)**, the separation is even greater (0.6 V greater) because the *o*-Sq/*o*-Cat process is shifted positively by +0.6 V, through binding to ruthenium, while the *p*-Q/*p*-Sq process is apparently unaffected.

Infrared data, obtained experimentally, and by AM1 computation, agree with the conclusions reached here and will be described in full later.

Thus the linkage isomers **$QCat^{2-}$(Ru-1,9)** and **$QCat^{2-}$(Ru-1,2)** are established by electrochemical and spectroscopic data and may be interconverted by a combination of proton-transfer and thermal methods.

The most common bonding found in alizarin complexes is (1,9) coordination.[16-21] To date, little evidence has indicated that alizarin complexes may be (1,2)-coordinated.[22-25]

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