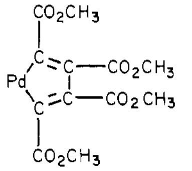
a metal-metal bond whereas molecules such as $Pd_2(dpm)_2(\mu\text{-}C_2\{COCH_3\}_2)Cl_2$ and $(Ph_3P)_2Au(\mu\text{-}C_2\{CF_3\}_2)$, which contain d^8 and d^{10} metal atoms, respectively, lack formal metal-metal bonds.

A number of different palladium compounds are known to catalyze the cyclotrimerization of acetylenes, and at least two distinct mechanisms have been demonstrated to be involved.[27] Catalysis by Pd(0) in the form of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) proceeds via the formation of a metallocycle (**8**).[13] On the other hand catalysis by palladium(II)-chloro complexes, particularily $(PhCN)_2PdCl_2$, proceeds via initial insertion of the acetylenes into the Pd-Cl bond. This is followed by successive insertions of acetylenes into the vinylic Pd-C bonds. The mechanism of catalysis in the presence of $Pd_2(dpm)_2X_2$ appears to proceed by a different route involving initial insertion into the Pd-Pd bond to give the acetylene adduct **3**. Since we have demonstrated that this inserted acetylene may be incorporated into the final product of catalysis, it is possible that catalysis proceeds via successive insertions into the Pd-C bonds to give **9** and **10** as intermediates. A mechanism of this type would be akin to the acetylene addition products obtained from $(\eta^5\text{-}C_5H_5)_2M_2(CO)_4$ (M = Cr, Mo) where stepwise addition of three acetylenes across the metal-metal bond has been demonstrated.[28]



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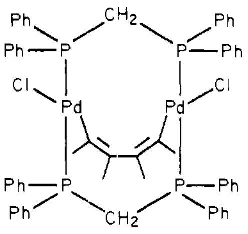

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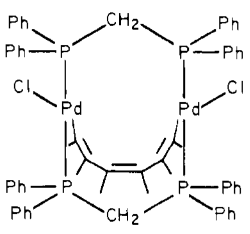

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Registry No. **1**, X = Cl, 64345-29-5; **1**, X = Br, 60482-68-0; **1**, X = I, 67477-87-6; **2**, Y = S, X = Cl, 71171-39-6; **3**, R = CO_2CH_3, 71957-42-1; **3**, R = $CO_2CH_2CH_3$, 77590-21-7; **3**, R = CF_3, 71957-44-3; **4**, R = CO_2CH_3, PF_6 salt, 77590-23-9; **5**, 68228-56-8; **6**, R = CH_3, 64345-34-2; **6**, R = C_6H_5, 64345-38-6; **7**, BPh_4 salt, 77590-25-1; **7**, PF_6 salt, 77590-26-2; $Pd_2(dam)_2(\mu\text{-}C_2\{CF_3\}_2)Cl_2$, 77590-27-3; $Pd_2(dpm)_2(\mu\text{-}C_2\{CO_2CH_3\}_2)Br_2$, 77590-28-4; $Pd_2(dpm)_2(\mu\text{-}C_2\{CO_2CH_3\}_2)I_2$, 77590-29-5; $Pd_2(dam)_2(\mu\text{-}C_2\{CO_2CH_3\}_2)Cl_2$, 71957-43-2; $Pd_2(dam)_2(\mu\text{-}C_2\{CO_2CH_2CH_3\}_2)Cl_2$, 77590-30-8; $Pd_2(dpm)_2(\mu\text{-}HC_2\{CO_2CH_3\})Cl_2$, 77590-31-9; $Pd_2(dpm)_2(\mu\text{-}HC_2\{CO_2H\})Cl_2$, 77590-32-0; $Pd_2(dam)_2Cl_2$, 67415-28-5; $Pd(dpm)I_2$, 77462-40-9; $Pd_2(dpm)_3$, 37266-95-8; dimethyl acetylenedicarboxylate, 762-42-5; hexamethyl mellitate, 6237-59-8; maleic anhydride, 108-31-6.

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Ruthenium(II) Azophenol and Azonaphthol Complexes

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Bis(2,2′-bipyridine)(azophenol)- and bis(2,2′-bipyridine)(azonaphthol)ruthenium(II) complexes have been synthesized and characterized by their chromatographic behavior, conductivity, and visible-ultraviolet spectra. These Ru(II) azo ligand derivatives are of particular interest for the characterization of metal-azo protein complexes currently under investigation. A ligand-localized, bathochromically shifted absorption band at 18 000 cm^{-1} (550 nm) is observed upon Ru(II) complexation of the azo ligands. Analogous behavior has been observed on complexation of azo dyes and azo proteins by Co(III), Co(II), and Zn(II).

Introduction

Methods for incorporating substitution-inert metal ions into proteins and peptides through azotyrosine and azohistidine derivatives are currently under investigation.[2-5] Of primary interest have been metal ions with the low-spin d^6 configuration, in particular cobalt(III). Ruthenium(II) offers several potential advantages over cobalt(III) for the biological studies. Because Ru(II) forms particularly stable complexes with π-acid ligands, it is anticipated that Ru(II) will be more specific than Co(III) for the azotyrosines and azohistidines present in the modified proteins. Ruthenium(II) complexes also offer the advantage of having significantly higher molar absorptivities than cobalt(III) complexes and thus should be detected more readily at the low concentrations generally encountered in biological studies. Finally, isomorphous replacement with heavy metals to establish the sign of real structure factors has been extensively applied in protein crystallography.[6] The method that we have developed offers the possibility of systematizing the approach to isomorphous replacement, and Ru(II) has a distinct advantage over Co(III) due to its greater atomic number.

Model cobalt(III) azophenol complexes have provided essential information[3-5] for the synthesis and characterization of the corresponding protein complexes.[2] This study reports

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(1) To whom correspondence should be addressed.

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Table I. Analyses of Bis(2,2'-pyridine)azoruthenium(II) Complexes

	% C		% H		% N	
compd	calcd	found	calcd	found	calcd	found
$[Ru(bpy)_2(PhAC)]ClO_4$	54.74	54.39	3.76	3.80	11.61	11.41
$[Ru(bpy)_2(DAC)]ClO_4$	55.89	55.25	4.15	4.49	11.07	10.86
$[Ru(bpy)_2(\text{Sudan I})]ClO_4$	56.89	56.62	3.58	3.42	11.06	10.96
$[Ru(bpy)_2(\text{Para Red})]ClO_4$	53.71	53.29	3.26	3.41	12.18	11.94
$[Ru(bpy)_2(PAN)]ClO_4$	55.24	55.18	3.44	3.34	12.88	12.30
$[Ru(bpy)_2(OD\text{-}II)]\cdot 3H_2O$	54.48	54.50	4.06	4.18	10.59	10.60

Table II. Physical Properties of Bis(2,2'-bipyridine)azoruthenium(II) Complexes

	R_f		molar conductivities,[a] Ω^{-1} m^2 mol^{-1} × 10^4	
complex	complex	ligand	complex	ligand
$[Ru(bpy)_2(PhAC)]ClO_4$	0.06	0.79	1.87	0.0667
$[Ru(bpy)_2(DAC)]ClO_4$	0.06	0.81	1.85	0.138
$[Ru(bpy)_2(\text{Sudan I})]ClO_4$	0.06	0.77	1.91	0.124
$[Ru(bpy)_2(\text{Para Red})]ClO_4$	0.07	0.87	2.03	0
$[Ru(bpy)_2(PAN)]ClO_4$	0.07	0.81	2.10	0.245
$[Ru(bpy)_2(OD\text{-}II)]\cdot 3H_2O$	0.43	0.93	0.330	2.34

[a] In methanol.

the synthesis and characterization of ruthenium(II) azophenol and azonaphthol complexes. As in the case of the Co(III) complexes[4,5] the Ru(II) complexes will provide the necessary spectral data for the characterization of ruthenium(II) azo protein derivatives. Although the conditions employed to synthesize the Ru(II) complexes in this study are too harsh for the protein studies, the information gained is being used to establish the mild conditions required for protein incorporation of Ru(II).

Experimental Section

Reagents. Common organic chemicals required were reagent grade and were used without further purification. 1-(Phenylazo)-2-naphthol (Sudan I), 1-((*p*-nitrophenyl)azo)-2-naphthol (Para Red), and 2-((4-carboxyphenyl)azo)-4,5-dimethylphenol (CDP) were purchased from the Aldrich Chemical Co., while 1-(2-pyridylazo)-2-naphthol (PAN) was obtained from the J. T. Baker Chemical Co. The azophenols 2-(phenylazo)-*p*-cresol (PhAC) and 2-((2,6-dimethylphenyl)azo)-*p*-cresol (DAC) and the azonaphthol sodium *p*-((2-hydroxy-1-naphthyl)azo)benzenesulfonate (Orange II, OD-II) were prepared by a standard method.[7] Bis(2,2'-bipyridine)(oxalato)ruthenium(II) tetrahydrate was prepared from potassium hexachlororuthenate(IV) by the method of Liu et al.[8] as modified by Demas et al.[9] Reagent grade tris(bipyridine)ruthenium(II) chloride hexahydrate was purchased from the G. Frederick Smith Chemical Co.

Preparation of Bis(2,2'-bipyridine)(azophenol)ruthenium(II) and the Corresponding Azonaphthol Complexes. A 0.17-g (0.30-mmol) sample of $[Ru(bpy)_2(ox)]\cdot 4H_2O$ was dissolved in 25 mL of absolute methanol in a 50-mL Erlenmeyer flask having a ground-glass neck, and 1.2 mL of 1.0 M hydrochloric acid was added. The flask was then mounted in an oil bath on a stirrer-hot plate and fitted with a reflux condenser. The dark red solution was heated at reflux for a minimum of 12 h to displace the coordinated oxalate. To this solution were added 0.15 g (0.60 mmol) of Sudan I and 2.0 mL of 0.90 M sodium hydroxide. After being refluxed, for a minimum of 6 h more, the hot solution was filtered into a 30-mL beaker, and 0.5 mL of a 1.0 M solution of sodium perchlorate in methanol was added. When the volume was reduced to about 6–7 mL by drawing air over the surface of the dark brown-black solution, a precipitate could be observed on the bottom of the beaker. The dark brown precipitate was filtered and washed with several portions of water and then with ether until the washings were clear. The fine, black crystals were dried under vacuum in a drying pistol at the temperature of boiling water, giving a yield of 75%. The corresponding complexes with PhAC, DAC, OD-II, and CDP were prepared in similar fashion with yields ranging from 50% to 75% in replicate preparations. The bis(2,2'-bipyridine) complexes of PAN and Para Red were prepared in an analogous manner except that the complexes were washed with benzene until the washings were clear before the final washing with ether. Chemical analyses are summarized in Table I. Satisfactory analyses for $[Ru(bpy)_2(CDP)]$ could not be obtained on repeated preparations. However, the absorption spectrum of this complex was very similar to the spectra obtained for the corresponding PhAC and DAC complexes and is included in Table IV along with the spectral data for the other complexes.

Chromatography. The reactions and purity of complexes were monitored by thin-layer chromatography utilizing commercially prepared sheets having silica gel (0.2-mm thickness) supported on aluminum (Silica Gel 60 F-254, EM Laboratories, Inc.). Ascending tank development was performed with use of a solvent mixture of methanol–water (95:5). All components were colored; thus, no visualization technique was necessary.

Physical Measurements. Visible and ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer using methanol solutions in 1-cm cells. Conductivity measurements were made with an Industrial Instruments Model RC 16B2 conductivity bridge using methanol as the solvent. Analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Synthesis and Characterization of Complexes. The conditions that gave optimum yields of product were determined by monitoring the reactions with thin-layer chromatography. Table II lists the chromatographic properties of the complexes prepared. The starting material, $Ru(bpy)_2(ox)$, produced a red spot with an R_f value of 0.29–0.34 in comparison to the brown spots observed for the products with R_f values less than 0.1. Neutral $[Ru(bpy)_2(OD\text{-}II)]\cdot 3H_2O$, as expected, was an exception with an R_f value of 0.43. When a methanolic solution of $Ru(bpy)_2(ox)$ with hydrochloric acid was heated, a dark spot indicative of a charged complex (presumably some solvated species[10]) was observed near the origin. Preliminary studies showed that a 4:1 mole ratio of acid to complex gave maximal conversion to the solvated intermediate when the solution was refluxed for 12 h.

When the azo ligand was added to this mixture, the spot due to the solvated intermediate remained and a tail leading a spot near the top of the chromatograph now appeared. This spot had a color and R_f value indicative of the azo dye added. Upon the addition of sodium hydroxide a new darker spot characteristic of the product complex formed near the origin. In most cases a faint spot due to $Ru(bpy)_2(ox)$ would also be observed since the anation reaction with the oxalate present in solution would compete with the reaction between the azo ligand and the solvated intermediate. In most cases a 2:1 mole ratio of azo ligand to starting complex was used since when lower ratios were used, more $Ru(bpy)_2(ox)$ re-formed. In like manner, high mole ratios of sodium hydroxide favored the

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Table III. Absorption Spectra of Azophenol and Azonaphthol Ligands[a]

azophenol			azonaphthol			
DAC	PhAC	CDP	PAN	Para Red	Sudan I	Orange II
			44.2 (37.6)	44.2 (37.9)	43.5 (36.3)	43.9 (32.0)
40.7 (10.6)	40.8 (8.40)	40.0 (7.56)	39.5 (10.3)	38.5 (5.27) sh[b]	39.2 (11.8) sh	39.2 (11.3) sh
					38.2 (10.8) sh	37.9 (10.0) sh
			33.8 (9.38) sh		35.8 (5.87) sh	
31.2 (14.8)	30.8 (20.4)	29.4 (15.8)	32.8 (9.59)	33.8 (7.36)	32.1 (7.25)	32.3 (7.90)
26.5 (7.28)	25.6 (8.45)	25.1 (7.78)	24.1 (12.2) sh	23.5 (14.1) sh	23.8 (10.6) sh	24.1 (10.0) sh
			21.7 (17.0)	20.6 (26.9)	20.9 (14.5)	20.8 (18.0)
			21.0 (16.1)	19.9 (24.7) sh	19.6 (13.0) sh	19.8 (15.7) sh

[a] $cm^{-1} \times 10^3$; ϵ values, $\times 10^3$, in parentheses. [b] sh = shoulder.

Table IV. Absorption Spectra of the Bis(2,2'-bipyridine)azoruthenium(II) Complexes[a]

		azophenol			azonaphthol			
ox	en	DAC	PhAC	CDP	PAN	Para Red	Sudan I	Orange II
					45.9 (54.7)	45.7 (59.6)	45.2 (61.2)	45.4 (67.8)
40.8 (20.8)	41.3 (24.5)	41.0 (29.5)	40.7 (32.7)	41.0 (30.6)	41.7 (40.6) sh[b]	40.8 (35.2) sh	41.7 (37.9) sh	41.2 (38) sh
	39.5 (13) sh							
34.0 (57.7)	35.0 (63)	34.1 (43.1)	34.1 (50.1)	34.0 (44.1)	34.6 (49.8)	34.4 (57.0)	34.1 (55.1)	34.1 (58.8)
27.4 (9.55)	28.7 (8.7)		29.1 (8.70)	28.2 (10.4) sh	29.4 (11.6)	28.9 (12.4)	28.7 (13.8)	28.7 (14.4)
		24.1 (9.24) sh	25.4 (7.79)	25.4 (8.53)	26.0 (8.84) sh	26.0 (10.4) sh	26.3 (10.3) sh	26.0 (10.3) sh
	22.8 (5.0) sh							
19.2 (9.21)	20.3 (10.9)	20.9 (11.8)	21.1 (14.1)	21.1 (12.3)	20.4 (15.0)	20.5 (13.6)	20.9 (16.9)	20.8 (17.4)
		17.8 (3.77) sh	18.2 (6.03) sh	18.2 (5.38) sh	17.5 (4.62) sh	17.6 (5.85) sh	18.1 (6.91)	18.2 (6.77)

[a] $cm^{-1} \times 10^3$; ϵ values, $\times 10^3$, in parentheses. [b] sh = shoulder.

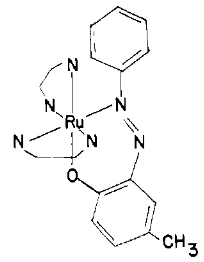

Figure 1. Structure of bis(2,2'-bipyridine)(azophenol)- and -(azonaphthol)ruthenium(II) complexes as exemplified by $[Ru(bpy)_2(PhAC)]^+$; bridged N's = bpy.

formation of starting complex. The best results were obtained when the mole ratio of $Ru(bpy)_2(ox)$:HCl:azo ligand:NaOH was 1:4:2:6.

The molar conductivities measured for the azo ligands and the corresponding ruthenium(II) complexes are also reported in Table II. The azo ligands were found to be nonelectrolytes in methanol as would be expected. The molar conductivities obtained for the bis(2,2'-bipyridine)azoruthenium(II) perchlorate complexes indicated that they exist as 1:1 electrolytes in solution. The conductivity data are consistent with the structure shown in Figure 1 in which the azo ligands are coordinated as bidentates through an azo nitrogen and the phenolate or naphtholate oxygen to give a complex with a net 1+ charge. However, Orange II, due to the presence of the sulfonate on the ligand, gave results that were the opposite to this general observation; the dye itself is a 1:1 electrolyte while the complex in which it is incorporated is a nonelectrolyte. For comparison, $Ru(bpy)_2(ox)$ was a nonelectrolyte in methanol while a solution of $[Ru(bpy)_2]Cl_2$ gave a molar conductivity of $3.80 \times 10^{-4}\ \Omega^{-1}\ m^2\ mol^{-1}$, which is in the range expected for a 2:1 electrolyte.

The complexes are of the type $M(AA)_2(BC)$ where only one geometric isomer is possible as shown in Figure 1. Azophenols and azonaphthols could exhibit linkage isomerism through the azo group to give a five- or six-membered ring. In the case where a five-membered ring is formed, there is the possibility of isomerism about the diazo bond. Isomerism inherent to the mode of coordination of the azo ligand has been discussed in detail previously.[5] We have shown that the relative position of the azo nitrogen and phenolate or naphtholate oxygen to the remainder of the ligands on cobalt(III) chelates has little effect on the absorption spectrum.[11] Thus, the more subtle modes of isomerism inherent to azo ligand chelation are not expected to have an effect on the absorption spectra of these complexes discussed below.

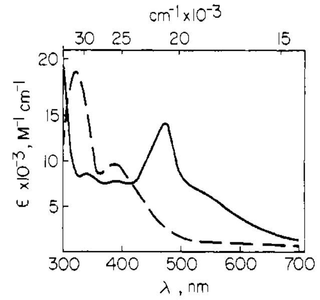

Figure 2. UV-visible spectra in methanol of $[Ru(bpy)_2(PhAC)]ClO_4$ (—) and PhAC (- - -).

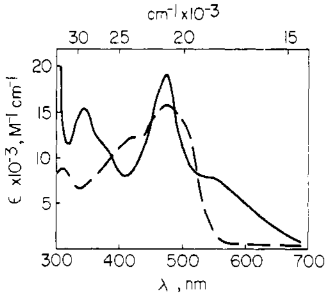

Figure 3. UV-visible spectra in methanol of $[Ru(bpy)_2(Sudan\ I)]ClO_4$ (—) and Sudan (- - -).

Absorption Spectra. The absorption spectra of the azophenol and azonaphthol ligands and their bis(2,2'-bipyridine)ruthenium(II) complexes are summarized in Tables III and IV. Table IV also summarizes the spectra of $Ru(bpy)_2(ox)$ and

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[11] K. Igi, M. S. Urdea, and J. I. Legg, *Inorg. Chem.*, in press.

$Ru(bpy)_2(en)^{2+}$ for comparative purposes. Representative spectra are shown in Figures 2 and 3. As expected, the presence of both strongly absorbing azo dyes and bipyridine on ruthenium(II) leads to rather complex spectra. However, a number of comparisons and useful observations can be made. A survey of Tables III and IV reveals a greater similarity between the spectra of the complexes than between the spectra of the free ligands. In fact, with the exception of the band at 45 000 cm^{-1} in the naphthol complexes, the spectra of the two sets of complexes are quite similar with respect to both band position and intensity. The band at 45 000 cm^{-1}, which is also present in the free naphthols, most likely is a ligand-localized transition. The only other transition which stands out as primarily a ligand–ligand transition in the complexes is the band between 23 500 and 26 500 cm^{-1} found in both the azophenols and the azonaphthols, which does not appear in $Ru(bpy)_2(ox)$ or $Ru(bpy)_2(en)^{2+}$. The absorption band at about 40 000 cm^{-1} in the azo complexes appears to be an overlay of absorption bands found in the free azo ligands and the complexes, $Ru(bpy)_2(ox)$ and $Ru(bpy)_2(en)^{2+}$. Some interaction apparently occurs between the transitions since the combined intensity, particularly in the case of the naphthols, is greater than that obtained by simply adding the separate molar absorptivities.

The band at 34 700 cm^{-1} (ϵ = 76 000) has been assigned to the $\pi \rightarrow \pi^*$ transition in 2,2′-bipyridine in $Ru(bpy)_3^{2+}$.[12] This band is clearly evident in the spectra obtained for the $Ru(bpy)_2(azophenol)^+$ (Table IV) and corresponding naphthol complexes (Table IV) between 34 000 and 35 000 cm^{-1} with ϵ's of about 50 000, two-thirds of the ϵ found for $Ru(bpy)_3^{2+}$ as expected.

Of particular interest in this study were spectral changes associated with Ru(II) complexation of azophenols since this information could be used to determine when Ru(II) complexes of azophenols in proteins are formed. As with the Co(III) complexes, spectral changes occurring in the visible region of the spectrum, which are displaced from the protein absorption in the UV, are most useful. The anionic forms of the azophenols investigated have similar spectra, with one peak in the near-ultraviolet and another at approximately 21 000 cm^{-1} (480 nm). The azonaphtholates are similar except that the band at 21 000 cm^{-1} exhibits low- and high-energy shoulders. Complexation of the azophenolates to Co(III) induces a shift of the visible absorption maximum to lower energy.[3-5] This again would appear to be the case for the Ru(II) complexes. However, since a charge-transfer transition from ruthenium to 2,2′-bipyridine is also expected around 20 000 cm^{-1} (500 nm), a somewhat more complex situation is anticipated.[12,13]

A reasonable explanation for the visible spectrum obtained for the $Ru(bpy)_2(azophenol)^+$ complexes can be obtained by comparing the spectra of $Ru(bpy)_2(ox)$ and of $Ru(bpy)_2(en)^{2+}$, where only the Ru(II) to bpy charge transfer is expected around 20 000 cm^{-1},[13] with the spectra obtained for the $Co(EDDA)(azophenol)^-$ complexes (EDDA = ethylenediamine-*N,N′*-diacetate), where only an azophenol-localized transition is expected in the same region.[5,11] The $Ru(bpy)_2(azophenol)^+$ spectrum might then be thought of as a composite of the spectra obtained for the parent complexes, $Ru(bpy)_2(en)^{2+}$ (and oxalate) and $Co(EDDA)(azophenol)^-$. However, a zeroth-order interaction would be anticipated between the charge-transfer and ligand transitions, which would cause the two transitions to split apart, ideally by an equal amount. Thus, the charge-transfer transition at 20 000 cm^{-1} in the parent complex $Ru(bpy)_2(en)^{2+}$ (and oxalate) should shift to higher energy, and the azophenol transition at 19 500 cm^{-1} in the parent complex $Co(EDDA)(azophenol)^-$ should shift to lower energy. The spectra obtained for the $Ru(bpy)_2(azophenol)^+$ and $Ru(bpy)_2(azonaphthol)^+$ complexes are consistent with this analysis as shown in Table IV and Figures 2 and 3. The spectra show maxima at about 21 000 cm^{-1} with a poorly defined shoulder at about 18 000 cm^{-1}. The transition at 18 000 cm^{-1} (550 nm) is then the bathochromically shifted azophenol-localized transition that has been previously observed for the Co(III), Co(II), and Zn(II) model and protein azophenol complexes and is diagnostic of metal chelation to the azophenol.[2-5,11,14]

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Registry No. $[Ru(bpy)_2(PhAc)]ClO_4$, 77590-03-5; $[Ru(bpy)_2(DAC)]ClO_4$, 77590-05-7; $[Ru(bpy)_2(Sudan\ I)]ClO_4$, 77590-07-9; $[Ru(bpy)_2(Para\ Red)]ClO_4$, 77590-09-1; $[Ru(bpy)_2(PAN)]ClO_4$, 77590-11-5; $[Ru(bpy)_2(OD\text{-}II)]$, 77611-45-1; $Ru(bpy)_2(CDP)$, 77590-12-6; DAC, 77590-51-3; PhAc, 952-47-6; CDP, 3810-51-3; PAN, 10335-31-6; Para Red, 607-27-2; Sudan I, 3375-23-3; OD-II, 573-89-7; $Ru(bpy)_2(en)^{2+}$, 47597-15-9; $Ru(bpy)_2(ox)$, 19418-69-0.

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