

Synthesis and Solvent-Dependent Properties of Ru(acac)₂dppz

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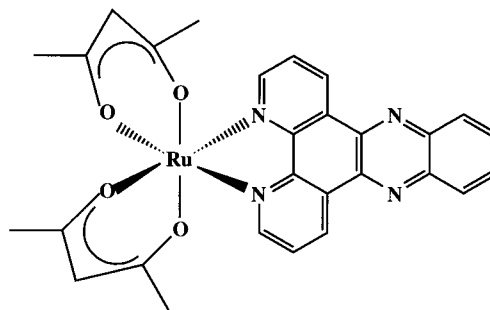
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Introduction

Polypyridyl complexes of ruthenium(II) have attracted wide interest due to their ability to function as optical sensors and probes.^{1,2} Among them dipyrldophenazine complexes of ruthenium(II) have shown interesting properties that could be used for the development of sensors of high sensitivity and selectivity. The complexes [Ru(bpy)₂dppz]²⁺ and [Ru(phen)₂dppz]²⁺ have been found to be nonemissive in water but emit brightly in nonaqueous solvent or in aquated polymers such as DNA by intercalative binding.^{3–5} This quenching of luminescence in aqueous media is possibly due to the interaction of the phenazine nitrogens of the dipyrldophenazine ligand with the water via hydrogen-bonding or excited-state proton transfer;^{5,6} a low-lying (800 nm) state with a short (~200 ps) lifetime has been observed in water, but in other solvents the lowest excited state is the “normal” metal-to-ligand charge transfer (MLCT) at ~600 nm.⁷ Upon intercalation between the base pairs of DNA, the phenazine nitrogens are protected from water, and hence luminescence is observed. [Ru(phen)₂dppz]²⁺ also exhibits solvent-dependent changes in rates of nonradiative decay that are correlated with solvent polarity and, to lesser extent, hydrogen bond donation ability of the solvent.⁸

An understanding of the photophysical processes in dipyrldophenazine complexes of ruthenium(II) is necessary to further develop similar complexes as biological probes and chemical sensors. The effect of the ancillary ligands on the photophysical properties of monodipyrldophenazine complexes of ruthenium(II) could assist in explaining the photophysical properties of these complexes and could also provide us more insight into the “light switch” effect for [Ru(bpy)₂dppz]²⁺ and [Ru(phen)₂dppz]²⁺. We have been exploring the effect of strong-field ligands such as NH₃ and CN[−] on the Ru–dppz fragment.^{9,10} In this Note we report the synthesis and characterization

of Ru(acac)₂dppz, (below), the first neutral Ru–dppz complex to our knowledge, and solvatochromism in its charge-transfer transitions.



Experimental Section

Instrumentation and Materials. All reagents were obtained from Aldrich and were of the highest purity available. ¹H NMR spectra were obtained on a Bruker AM-300 instrument. Absorption spectra of the complex in various solvents were obtained on a Perkin-Elmer Lambda 14 UV–visible spectrophotometer at room temperature. Cyclic voltammograms were obtained on a BAS CV-50W in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. An Ag/AgCl electrode was used as a reference electrode with a 2 mm inlaid Pt disk working electrode. All scans were obtained at a rate of 500 mV/s. The concentration of the ruthenium complex in the electrolyte was ~1–2 mM.

Synthesis and Characterization. Dipyrldophenazine (dppz) was synthesized according to a literature method.^{11,12}

[Ru(dppz)Cl₄]. The complex [Ru(dppz)Cl₄] was synthesized via a modification of the literature method for [Ru(bpy)Cl₄].¹³ A 0.5572 g amount of RuCl₃·xH₂O and a 0.7583 g amount of dipyrldophenazine were added to 50 mL of 1 M HCl and stirred for about 30 min under nitrogen and then allowed to sit under nitrogen for 10 days. The rather insoluble product [Ru(dppz)Cl₄] (0.943 g, 66% yield) was filtered, washed with water, and dried in air.

Ru(acac)₂dppz. Ru(acac)₂dppz was synthesized via a modification of the literature method for Ru(acac)₂phen.¹⁴ A 0.2021 g amount of [Ru(dppz)Cl₄] was added to 50 mL of a 1:1 mixture of ethanol/water and stirred for 15 min. To this were added 1.0 g of Na₂CO₃ and 2 mL of 2,4-pentanedione, and the resulting mixture was refluxed at 80 °C for 1 h. The resulting solution was filtered, and 0.5 g of Na₂S₂O₇ was added to the filtrate and stirred for 20 min. The ethanol from the solution was then removed by evaporation, resulting in the precipitation of small amounts of purple solid that were filtered and air-dried. The crude Ru(acac)₂dppz was purified using a neutral activated alumina column, eluting with acetonitrile. Overall yields were typically less than 10%. Due to the instability of the complex to heat (even drying down on a rotary evaporator at ~40 °C resulted in decomposition), solvent removal was accomplished by vacuum pumping at room temperature. Anal. Calcd: 57.83 C, 4.13 H, 9.64 N. Found (Galbraith Laboratories, Knoxville, TN): 55.17 C, 4.36 H, 8.14 N. ¹H NMR (C₆D₆): δ 9.48 (2H, d), 8.78 (2H, dd), 8.29 (2H, dd), 7.41 (2H, dd), 6.84 (2H, dd), 5.48 (1H, s), 2.32 (3H, s), and 1.66 (H, s). IR: 1640 cm^{−1} (C–O). EI direct probe mass spectrometry of the complex showed the parent ion [Ru(acac)₂dppz][−] at m/z = 581.

Results and Discussion

The UV–visible absorption spectrum of Ru(acac)₂dppz in benzene (Figure 1) exhibits bands at 365–375 nm which are

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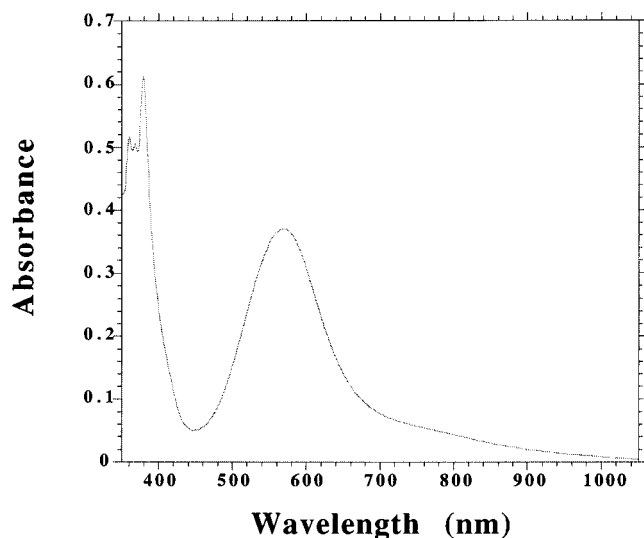


Figure 1. UV-visible absorption spectrum of Ru(acac)₂ dppz in benzene.

similar in shape and energy to the bands of the free dppz ligand and other monosubstituted dipyrrophenazine ruthenium(II) complexes;^{3–5} these bands are assigned as dppz(π) \rightarrow dppz(π^*) transitions. The low-energy band at 569 nm is assigned as an MLCT Ru(d π) \rightarrow dppz(π^*) transition on the basis of intensity and energy. For comparison, [Ru(NH₃)₄dppz]²⁺ has a similar MLCT band at 544 nm in water.⁹ The bipyridine analogue of our complex, Ru(acac)₂bpy, has absorption bands at 416 nm ($\epsilon = 9400 \text{ M}^{-1} \text{ cm}^{-1}$) and 621 nm ($\epsilon = 4980 \text{ M}^{-1} \text{ cm}^{-1}$) in dichloromethane, which have been assigned as bpy-based MLCT transitions; the multiple MLCT transitions reflect the lower symmetry of the complex compared to tris-diimine Ru(II) complexes.¹⁵ The lower energy of the MLCT transition in Ru(acac)₂dppz (557 nm in dichloromethane, compared to the bpy 416 nm transition) is likely due to the stronger electron-withdrawing character of the dppz ligand compared to the bipyridine ligand of Ru(acac)₂bpy (if the 621 nm band in the bpy complex was shifted in the dppz complex by a similar amount, the lower-energy band in the dppz complex would occur at >1000 nm). Also, the MLCT transition of Ru(acac)₂dppz is of lower energy compared to [Ru(bpy)₂dppz]²⁺, [Ru(phen)₂dppz]²⁺, and [Ru(NH₃)₄dppz]²⁺, which is consistent with the weak-field ligand character of acac compared to bpy, phen, and ammonia. Ru(acac)₂dppz does not show any photoluminescence at room temperature in any solvent examined, or in ethanol glass at 77 K, over the wavelength range of 500–750 nm.

Cyclic voltammetry of Ru(acac)₂dppz in various solvents shows two reversible waves, at ~ 30 and ~ -1100 mV vs Ag/AgCl (Table 1). Depending on the solvent window, more waves can be seen. For comparison, we find [Ru(phen)₂dppz]²⁺ has a Ru(II/III) wave at 1300 mV and a dppz(0/–1) wave at –1000 mV under the same conditions, similar to the potentials reported by others.¹⁶

The MLCT transition of Ru(acac)₂dppz has been reported, without details, to be sensitive to solvent.¹⁵ The MLCT transition maximum of Ru(acac)₂dppz is also solvatochromic (Table 1), shifting to higher energy with an increase in solvent polarity as judged by the polarity scale E_T (Figure 2). The dppz transitions

Table 1. Spectroscopic and Electrochemical Characteristics of Ru(acac)₂dppz in Various Nonaqueous Solvents^a

solvent	E_T (kcal/ mol)	α	MLCT absorption maximum: λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$)	$E_{1/2}$, mV vs Ag/AgCl
carbon tetrachloride	32.5	0.00	576 (11000)	
benzene	34.3	0.00	569 (7200)	
trichloroethylene	35.9	0.00	566 (9400)	
tetrahydrofuran	37.0	0.00	566 (9200)	56, –1149
chlorobenzene	37.5	0.00	567 (10860)	
chloroform	39.1	0.34	557 (10200)	
dichloromethane	40.7	0.22	557 (12800)	1688, 62, –1118
acetone	42.2	0.07	555 (7400)	
dimethyl formamide	43.2	0.00	560 (7600)	–7, –1118
dimethyl sulfoxide	45.1	0.00	556 (7000)	
acetonitrile	45.6	0.15	554 (9100)	1539, 15, –1118, –1756
ethanol	52.0	0.86	547 (6400)	35, –1000*
methanol	55.4	0.98	538 (6500)	41, –888*

^a Ru(acac)₂dppz is not soluble in water. E_T , an empirical solvent polarity scale, and α , empirical hydrogen bond donation ability values, are taken from: Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. *Prog. Phys. Org. Chem.* **1981**, *13*, 485. Electrochemical data are reported as the average of cathodic and anodic peak positions; peak separations were ~ 60 mV except for the alcohols (*). In methanol and ethanol (*), only cathodic peak potentials are reported because reduction is irreversible. Solubility difficulties precluded electrochemical measurements in all solvents.

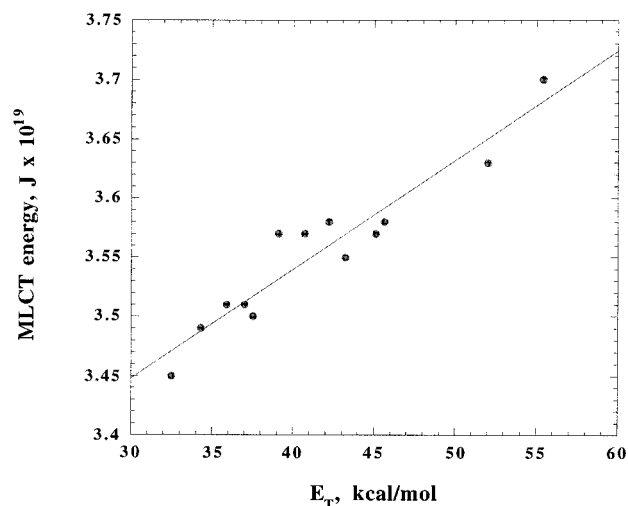


Figure 2. Dependence of MLCT absorption maximum of Ru(acac)₂dppz in different solvents on solvent polarity (E_T scale).

are relatively unaffected by solvent. It appears that nonpolar solvents stabilize the MLCT state compared to polar solvents, consistent with the notion that the MLCT is centered on the dppz ligand: in the ground state, negative charge is weighted toward the anionic acac ligands to give a nonzero dipole moment, but in the excited state, negative charge is pushed onto the dppz ligand, reducing the overall dipole moment. Thus in the excited state, the complex has a smaller dipole moment than in the ground state and is stabilized by nonpolar solvents. These

- (16) Oxidation potential of [Ru(phen)₂dppz]²⁺: (a) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. *Science* **1993**, *262*, 1025. Oxidation and reduction potentials of [Ru(bpy)₂dppz]²⁺, which are nearly identical to that of the phen analogue: (b) Chambron, J.-C.; Sauvage, J.-P.; Amouyal, E.; Koffi, P. *New J. Chem.* **1985**, *9*, 527. (c) Fees, J.; Kaim, W.; Moscherosch, M.; Matheis, W.; Klima, J.; Krejci, M.; Zalis, S. *Inorg. Chem.* **1993**, *32*, 166. In (c), multiple reductions are observed and assigned to the dppz ligand. [Ru(dppz)₃]²⁺ has redox potentials similar to both [Ru(phen)₂dppz]²⁺ and [Ru(bpy)₂dppz]²⁺: (d) Ackermann, M. N.; Interrante, L. V. *Inorg. Chem.* **1984**, *23*, 3904.

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results may be contrasted with the behavior of $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_4\text{dppz}]^{2+}$, in which the MLCT transition energy is not correlated with solvent polarity.^{8,9} Other workers have noted the stabilization of the Ru(III)/diimine L(-1) MLCT state by the electron-donating ability of the acac ligand.¹⁷

Correlations of $\text{Ru}(\text{acac})_2\text{dppz}$ absorption energies with other solvent scales such as hydrogen bond donation ability and appropriate function of refractive index (for polarizability) were also examined. For example, it might have been anticipated that hydrogen bonding of the solvent to the phenazine nitrogens of the dppz ligand, or even to the oxygens of the acac ligands, would influence the photoinduced charge-transfer transition energy. Inspection of Table 1 reveals that hydrogen bond donor ability of the solvent does not correlate with the MLCT transition energy. No correlations of MLCT energy with solvent polarizability (as given by $(n^2 - 1)/(2n^2 + 1)$, where n is the refractive index) or with dielectric constant itself were found either. Taken together, the results suggest that the primary solvent effect is a reorientation of the solvent dipoles to the change in dipole moment of photoexcited $\text{Ru}(\text{acac})_2\text{dppz}$ compared to its ground state.

The electrochemical behavior of $\text{Ru}(\text{acac})_2\text{dppz}$ is not that sensitive to solvent (Table 1) except in the case of alcohols; in methanol and ethanol, the redox waves at negative potential are not reversible. *cis*- $\text{Ru}(\text{acac})_2(\text{pyrazine})_2$ and *cis*- $\text{Ru}(\text{acac})_2(\text{CH}_3\text{CN})_2$ have been reported to have redox potentials at +260 mV vs NHE (= 40 mV vs Ag/AgCl), which have been assigned as the Ru(II/III) couple.¹⁸ Recently, complexes of the type $\text{Ru}(\text{acac})_2(\text{olefin chelate})$ have been prepared and have Ru(II/III) potentials of ~400 mV vs Ag/AgCl, depending on olefin ligand.¹⁹ Compared to diimine complexes, it seems that the acac ligand greatly decreases the Ru(II/III) potential.

We assign the redox waves as follows: ~-1100 mV corresponds to dppz(0/-1) reduction, based on its similarity to free ligand; ~30 mV corresponds to Ru(II/III) oxidation, based on its similarity to that of *cis*- $\text{Ru}(\text{acac})_2(\text{pyrazine})_2$ and *cis*- $\text{Ru}(\text{acac})_2(\text{CH}_3\text{CN})_2$. $\text{Ru}(\text{acac})_2\text{bpy}$ and $\text{Ru}(\text{acac})_2\text{phen}$ made by us according to literature methods also exhibit a redox couple at similar potentials. The ~1500 mV oxidation observed in two of the solvents may correspond to a Ru(III/IV) event.²⁰ The only Ru-acac-diimine complex precedent we know of for this

last assignment is $[\text{Ru}(\text{tpy})(\text{acac})(\text{H}_2\text{O})]^+$, which exhibits two metal-based oxidations at 190 mV (Ru(II/III)) and 560 mV (Ru(III)/(IV)) vs SCE, but proton transfer is coupled into the second metal oxidation.¹⁷ Tris(β -diketonate) complexes of Ru(III) show Ru(III/IV) oxidation potentials at approximately 1100 mV vs Ag/AgClO₄, depending on ligand.^{21,22}

The work of Barton and Barbara has suggested that $[\text{Ru}(\text{phen})_2\text{dppz}]^{2+}$ has two MLCT states closely spaced in energy, and one of these, which has a rapid radiationless decay pathway, corresponds to a species in which the dppz has more negative charge on the phenazine nitrogens and thus can more readily accept hydrogen bonds from the solvent.⁷ In water, then, the light switch effect would be due to this state being lower in energy than the "regular" red-emitting MLCT state.⁷ The solvation of these two MLCT states is likely different as well. If these results are applicable to $\text{Ru}(\text{acac})_2\text{dppz}$, the anionic acac ligands, strong electron donors, may push electron density onto the dppz ligand in $\text{Ru}(\text{acac})_2\text{dppz}$ and permanently "turn off the light", as we observe here. However, the acac ligands do impart to the MLCT transition a sensitivity to environmental polarity that is not observed in the visible absorption spectra of the phen analogue.⁸

Crystal structure analysis of transition metal acac complexes (used as hydrogenation catalysts; refs 23–26) show that the complexes are highly solvated;²⁷ in one case the solvent penetrates into the hydrophobic "hollows" provided by the acac ligands and is somewhat close to the metal center.²⁷ For optically interesting Ru(II) complexes, such intimate solvation may be used to advantage in the future design of sensor molecules.

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