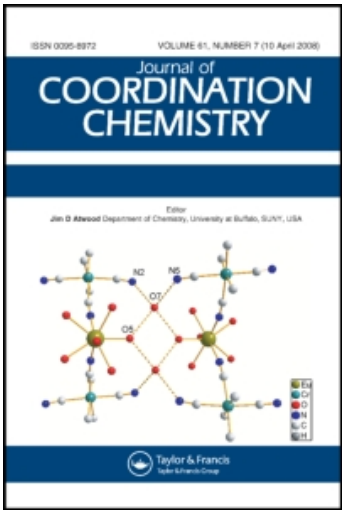

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Synthesis and characterization of ruthenium(II) phenanthroline complexes containing quaternary amine substituents

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A series of mixed-ligand complexes of ruthenium(II) containing 5-methylphenanthroline and trimethylamino-5-methylphenanthroline have been synthesized to investigate the impact of the quaternary amine on the photophysical properties. Thermal stability studies indicate that the quaternary amine is stable with respect to hydrolysis. Mass spectral analysis of the complexes revealed only fragments consistent with homolytic cleavage of the amines and no parent ions were observed. Both electrochemical and photophysical investigations indicate that the quaternary amine has little or no impact on the properties of the complex when compared to complexes lacking the amine.

Keywords: Ruthenium; Phenanthroline; Synthesis; Photophysics; Electrochemistry

1. Introduction

Numerous studies have focused on "tuning" the redox and excited-state properties of ruthenium(II) polypyridine complexes through modification of the ligands and pendant groups [1–6]. A related problem is the determination of which ligand modifications can be made without significantly altering the excited-state and/or redox properties of the parent complex. Many potential applications require attention to this question. For example, a particular complex may have appropriate redox or excited-state properties but may require structural modifications to achieve a different overall charge state or enhanced solubility in water. Our group has made extensive application of ruthenium complexes to initiate electron-transfer reactions between proteins. This approach has provided the ability to study the reactions of cytochrome c with cytochrome c oxidase and the bc_1 complex as well as other metalloprotein reactions [7–10]. In these studies complexes that have a high charge and are water soluble are required.

In the current study, we have focused on a ligand modification, the addition of a quaternary amine to a benzylic position, that can raise the overall charge of a complex and enhance the water solubility. A search of literature reveals only a very small number

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of studies of complexes containing quaternary amines in a benzylic position [11,12]. Despite the scarcity of reports, this moiety has a number of notable features. Perhaps most important is the ease of synthesis of phenanthroline ligands containing quaternary amines, such as trimethylamine, from commercially available starting materials. The choice of the amine substitutent can provide additional flexibility when designing complexes and many suitable amines are commercially available.

In this study, we focus on how well trimethylamine fulfills the initial criteria by investigating the impact of the group on the excited-state and redox properties of a collection of representative complexes. Since the ultimate goal is to prepare compounds that are suitable for investigation of protein-protein electron-transfer reactions in water, we have focused most of the effort on the simplest members, i.e., trimethylamine derivatives of complexes prepared from 5-methyl-1,10-phenanthroline. Given the benzylic location of the amine and the intended application, the question of stability with respect to loss of the amine by hydrolysis was also addressed.

2. Experimental section

2.1. *Materials*

$RuCl_3 \cdot 3H_2O$ and trimethylamine were purchased from Aldrich. 2,2′-bipyridine was purchased from Alfa Aesar. 5-methyl-1,10-phenanthroline (mephen) was purchased from Lancaster. All were used without further purification. $Ru(bpy)_2Cl_2 \cdot 2H_2O$, $Ru(bpy)Cl_4$, and 5-bromomethylphenanthroline were prepared according to literature methods [13–15]. The complex Ru(5-methyl-1,10-phenanthroline)$_3Cl_2$ was prepared by the method described by Walker *et al*. [16] by substituting 5-methyl-1,10-phenantholine for bipyridine.

2.2. *Synthesis*

2.2.1. N,N,N-trimethyl(1,10-phenanthrolin-5-yl)methanammonium bromide, (TMAphen). 5-bromomethyl-1,10-phenanthroline (1.0 g, 3.7 mmol) [15] was added to 100 mL of absolute ethanol and stirred for 1 h in an ice bath. Excess trimethylamine was added (10 mL) and the solution was allowed to stir for 2 h. The product precipitated as an off-white solid and was recovered by vacuum filtration. The yield was 1100 mg, (90%). ^{1}H NMR (CD_3CN): δ 9.22 (m, 2H), 8.88 (dd, 1H), 8.52 (dd, 1H), 8.25 (s, 1H), 7.80 (m, 2H), 5.08 (s, 2H), 3.15 (s, 9H).

Caution: Trimethylamine has a very strong offensive odor that is detectable at extremely low levels.

2.2.2. [Ru(bpy)$_2$(TMAphen)](PF$_6$)$_3$. $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (250 mg, 0.48 mmol) and TMAphen (250 mg, 0.99 mmol) were dissolved in 50 mL H_2O. The solution was refluxed under argon for 4 h with stirring. The solution was cooled to room temperature and filtered. Concentrated aqueous ammonium hexafluorophosphate (5 mL) was added to the filtrate to precipitate the product. The precipitate was collected by vacuum filtration and washed three times with 15 mL of water followed by 50 mL of

diethyl ether. The orange product was dried in a desiccator. The yield was 420 mg (80%). ^{1}H-NMR (MeCN-d_3) δ 8.85 (dd, 1H), 8.69 (dd, 1H), 8.56 (s, 1H), 8.50 (m, 4H), 8.19 (t, 2H), 8.11 (t, 2H), 8.01 (t, 2H), 7.82 (m, 4H), 7.54 (tm, 2H), 7.46 (tm, 2H), 7.24 (tm, 2H), 5.06 (s, 2H), 3.18 (s, 9H). Elemental analysis calculated for $RuC_{36}H_{34}N_7P_3F_{18}$: C, 39.28; H, 3.11; N, 8.90. Found: C, 39.60; H, 3.23; N, 8.90.

2.2.3. [Ru(bpy)(TMAphen)$_2$](PF$_6$)$_4$. Ru(bpy)Cl$_4$ (250 mg, 0.63 mmol) and TMAphen (380 mg, 1.5 mmol) were dissolved in 50 mL of 80/20 ethanol/H_2O. The solution was refluxed for 24 h under argon, cooled to room temperature and filtered. 5 mL concentrated aqueous ammonium hexafluorophosphate was added to the filtrate to precipitate the product. The product was purified by column chromatography on alumina using acetonitrile as an eluant. The first band was collected and added dropwise to diethyl ether to precipitate. The orange-red precipitate was collected by vacuum filtration and placed in a desiccator to dry. The yield was 840 mg (60%). ^{1}H-NMR (MeCN-d$_3$) δ 8.90 (dt, 1H), 8.80 (dd, 1H), 8.73 (dt, 1H), 8.63 (dd, 1H), 8.55 (bs, 1H), 8.52 (bs, 2H), 8.49, (s, 1H), 8.28 (m, 2H), 8.07 (dm, 2H), 7.99 (dm, 2H), 7.88 (m, 2H), 7.65 (m, 4H), 7.31 (tt, 2H), 5.06 (d, 4H), 3.18 (d, 18H). Elemental analysis calculated for $RuC_{42}H_{44}N_8P_4F_{24}$: C, 37.60; H, 3.31; N, 8.35. Found: C, 37.76; H, 3.55; N, 8.62.

2.2.4. [Ru(TMAphen)$_3$](PF$_6$)$_5$. This complex was prepared by modification of the procedure described by Ioachim *et al.* [17]. $RuCl_3 \cdot 3H_2O$ (23 mg, 0.09 mmol), $AgNO_3$ (57 mg, 0.34 mmol), and TMAphen (79 mg, 0.31 mmol) were dissolved in 10 mL of DMF and the solution was heated to reflux for 2 h. The dark red solution was cooled and filtered through celite to remove AgCl. Concentrated aqueous NH_4PF_6 (5 mL) was added to the dark red solution. Addition of 30 mL of deionized water resulted in an orange/brown precipitate. Precipitate was isolated by vacuum filtration, washed with water and diethyl ether, and allowed to dry overnight. Yield was 67 mg (47%). ^{1}H-NMR (MeCN-d$_3$) δ9.17 (m, 6H), 8.70 (dd, 3H), 8.46 (dd, 3H), 8.18 (s, 3H), 7.79 (m, 6H), 4.97 (s, 6H), 3.13 (s, 27H). Elemental analysis, calculated for $RuC_{48}H_{54}N_9P_5F_{30}$: C, 36.42; H, 3.43: N, 7.96. Found: C, 36.22; H, 3.25; N, 5.97.

2.3. *Photochemical measurements*

Anaerobic emission measurements were performed on samples sealed in glass test tubes after 5 cycles of freeze-thaw-pumping. The samples were excited with 355 nm pulses from a DCR-1 QuantaRay Nd:YAG laser. The power was kept at the minimum level ($\sim$1 mJ/pulse) necessary to obtain an adequate signal to noise ratio. The emitted light was focused on a monochromator fitted with a photomultiplier detector. Transients were recorded and averaged using a digital oscilloscope (LeCroy 7200) and finally transferred to a PC for data analysis. Typically, 100 individual transients were recorded and averaged before transfer to the PC. The temperature of the solutions was monitored with a thermocouple mounted inside the cell holder. Control experiments with thermocouple in the sample showed that the temperature of the cell and the solution were identical after 5 minutes of equilibration if the temperature increments were kept under 5°C. Temperature dependent emission measurements were obtained as the temperature was lowered and raised at random increments to avoid systematic

errors caused by the sample temperature lagging behind the temperature of the cell holder.

2.4. *Other measurements*

Cyclic voltammetry was performed with a CH Instruments Electrochemical Analyzer. The working electrode was a 2 mm diameter platinum disk electrode, the auxiliary electrode was platinum wire and the reference electrode was a saturated calomel electrode from CH Instruments. ^{1}H-NMR spectra were recorded using a Bruker 300 MHz spectrometer. Electrospray mass spectral measurements were performed with a Bruker "Esquire" LCMS. Samples, dissolved in acetonitrile, were injected directly with a flow rate of approximately 50 μL min^{-1} with nitrogen nebulizing gas. The source temperature was held at 300°C.

3. Results and discussion

Synthesis of the target complexes was performed using common synthetic methods for ruthenium polypyridine complexes. The quaternary amines were prepared by NBS bromination of the methyl group of 5-methyl-1,10-phenanthroline followed by reaction with the tertiary amine. ^{1}H-NMR provided convincing evidence of purity. In particular, the region showing the 5 methyl protons at ~5 ppm was diagnostic for complexes containing the quaternary amine or other substituents. In each case only a single resonance was observed in this region consistent with the expected product. Integration of the aromatic peaks and the amine methyl peaks provided additional evidence for the presence of the appropriate numbers of quaternary amines.

The electrospray mass spectrometry of the complexes showed a consistent fragmentation pattern. Each spectrum showed a fragment consistent with formal homolytic cleavage of all of the trimethylamines from the 5-methyl positions and no molecular ion peak. Figure 1 shows the major fragments for the mixed complex $[Ru(TMAphen)(bpy)_2]^{3+}$. In this specific example, the most abundant ion containing ^{102}Ru appears at $m/z = 303.5$. The ion has an overall charge of 2+ and results from the loss of the trimethylamine cation. The most abundant ion obtained with $[Ru(TMAphen)_2(bpy)]^{4+}$ appears at $m/z = 322.0$. The ion has an overall charge of 2+ and derives from the loss of two trimethylamine cations. The complex $[Ru(TMAphen)_3]^{5+}$ follows the trend with the most abundant ion appearing at $m/z = 340.5$. The uncomplexed TMAphen yielded two major fragments. One at $m/z = 252.1$ which is the parent ion and a smaller, but significant fragment, at $m/z = 193.0$ produced by the loss of the trimethylamine moiety. These ions had an overall charge of 1+.

The fragmentation pattern is unusual. For comparison, parent ions are observed with complexes containing 5-methylphenanthroline, 5-bromomethylphenanthroline or 5-hydroxymethylphenanthroline and fragmentation at the 5 methyl position is not observed.

In light of the mass spectral data and the possibility that the benzylic substituent might be susceptible to hydrolysis in aqueous soloution, the stability of the

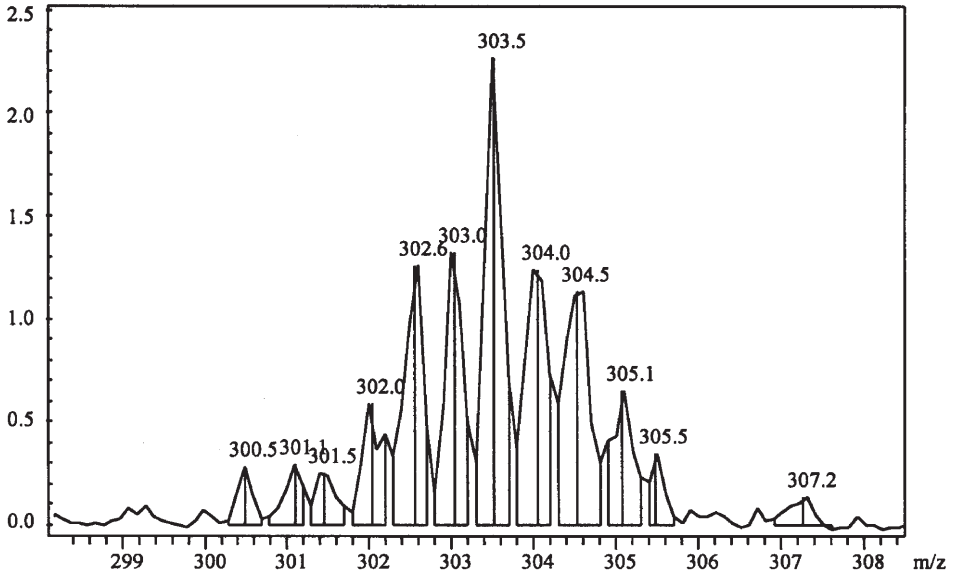

Figure 1. A portion of the electrospray mass spectrum showing the major fragment cluster obtained with $[Ru(TMAphen)bpy)_2]^{3+}$.

$[Ru(TMAphen)_3]^{2+}$ with respect to hydrolysis of the amine was investigated. ^{1}H-NMR of samples in D_2O showed no changes after 24 h at 50°C followed by 1 h of reflux. Furthermore, the free TMAphen ligand showed no indication of hydrolysis after 1 h at reflux. These experiments demonstrate that the complexes containing TMAphen are stable for extended periods in aqueous solution over the pH range 5–8.

In order to test the impact of the benzylic substitution on the photophysical properties of the complex, the temperature dependencies of the excited-state lifetimes of the $[Ru(TMAphen)_3]^{2+}$ and $[Ru(mephen)_3]^{2+}$ were obtained in water and acetonitrile. Over the temperature range studied the excited-state lifetimes decreased in a near linear manner with increasing temperature in every case. The results are illustrated in figure 2. The temperature dependence data were fitted to the equation

$$k_{obs} = k_r + k_{nr} + A_1 \exp\left(-\frac{\Delta E_1}{RT}\right) \quad (1)$$

This equation has been used previously by Van Houten and Watts [18,19] to describe the temperature dependence of the emission lifetime of the excited state of $[Ru(bpy)_3]^{2+}$. Although a wider temperature range than used is generally desirable, the focus of the measurements in the current study is a comparison of the substituted and unsubstituted complexes and the temperature range chosen revealed sufficient changes in emission lifetime for an informative comparison. Table 1 summarizes the rate constants obtained with these complexes. In order to estimate the error in the experiment, data from duplicate samples prepared over a period of several weeks were obtained. Duplicate plots of the emission lifetime as a function of temperature were superimposable with no significant deviations from best-fit lines. Proof of this statement is illustrated in figure 2

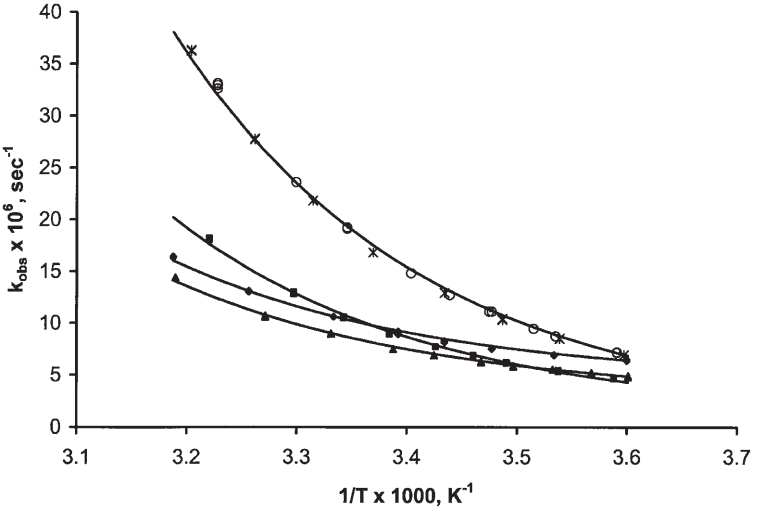

Figure 2. Plot of the observed rate constant for the decay of the excited state versus the inverse temperature obtained with $[Ru(TMAphen)_3]^{5+}$ in acetonitrile (■) and in 0.1 M H_2SO_4 (▲) and $[Ru(mephen)_3]^{2+}$ in acetonitrile (○, ✱) and in 0.1 M H_2SO_4 (◆).

Table 1. Summary of excited-state decay parameters obtained with $[Ru(TMAphen)_3]^{5+}$ and $[Ru(mephen)_3]^{2+}$.

Complex	Solvent	τ_0 (nsec[a])	$k_r + k_{nr}$	A_1	ΔE_1 (cm^{-1})
$[Ru(mephen)_3]^{2+}$	acetonitrile	620	1×10^5	5×10^{12}	3000
$[Ru(TMAphen)_3]^{2+}$	acetonitrile	1100	1×10^5	3×10^{12}	3000
$[Ru(mephen)_3]^{2+}$	0.1 M H_2SO_4	1100	5×10^5	1×10^{12}	3000
$[Ru(TMAphen)_3]^{2+}$	0.1 M H_2SO_4	1300	3×10^5	1×10^{12}	3000

[a]Measured at 22°C in absence of oxygen.

with data for $[Ru(mephen)_3]^{2+}$ obtained in acetonitrile. The data shown were acquired from two separate experiments separated by several weeks. The kinetic parameters are listed with one significant figure in table 1 which is consistent with the sensitivity of the least-squares fitting procedure to the three parameters.

Equation (1) has been interpreted using a simple two state model. The first state (actually a collection of several states of very similar energy) is the emitting charge transfer state characterized by decay to the ground state via radiative, k_r, and nonradiative processes, k_{nr}. A second state, possibly a d–d state, is thermally populated from the charge transfer state and characterized by rapid decay to the ground state, A_1. ΔE_1 describes the energy gap between the CT state and the d–d state. The data given in table 1 for the complexes in 0.1 M H_2SO_4 indicate that complexes containing the quaternary amine share almost identical decay parameters with the unsubstituted complex. This is consistent with the initial hypothesis that the benzylic substituent would have little impact on the photophysical parameters. It may also reflect the fact, that in both cases, the complexes are hydrophobic with no strong solvent interactions. The 5+ overall charge apparently has no measurable effect. The results obtained for the

Table 2. Summary of Ru(II)/Ru(III) redox potentials[a] for the series $[Ru(TMAphen)_x bpy_{3-x}]^{2+x}$.

$[Ru(bpy)_3]^{2+}$	1.30
$[Ru(mephen)_3]^{2+}$	1.28
$[Ru(bpy)_2(TMAphen)]^{3+}$	1.33
$[Ru(bpy)(TMAphen)_2]^{4+}$	1.32
$[Ru(TMAphen)_3]^{5+}$	1.30

[a]Complexes dissolved in 0.1 M TBAH in acetonitrile. All potentials were measured with respect to a SCE reference electrode.

complexes dissolved in acetonitrile on the other hand show a significant difference between the substituted and unsubstituted complexes with nearly a two fold change in excited-state lifetime. The fact that the $[Ru(mephen)_3]^{2+}$ has a shorter excited-state lifetime in acetonitrile was unexpected. The data listed in table 1 indicate that the shorter excited-state lifetime can be attributed to the larger value of A_1 which implies a faster rate of decay of the d–d excited state. $[Ru(TMAphen)_3]^{5+}$ exhibits a similar but smaller enhancement of A_1 in acetonitrile. The value of ΔE_1 for all of the complexes are the same within experimental error.

Electrochemical measurements were performed on the series of mixed ligand complexes containing TMAphen and bpy to determine the impact of the quaternary amine substitution and the resulting increased charge on the Ru(II)/Ru(III) reduction potential. In this study, we have only examined the redox reactions occurring over the range of potentials from −0.2 to 1.7 V versus SCE. In each example, the potential corresponds to oxidation of the ruthenium(II) to ruthenium(III) by analogy to $[Ru(bpy)_3]^{2+}$ which has been thoroughly studied. Table 2 summarizes these reduction potentials and reveals only minor differences in the Ru(III)/Ru(II) potentials within the series of complexes despite the range in overall charge, 2+ to 5+. All complexes showed reversible electrochemistry over the range examined. The fact that the potentials are essentially identical indicates that the difference between the solvation energies of the reduced and oxidized forms of the complexes is approximately constant and independent of the charge on the complex.

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References

[1] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky. *Coord. Chem. Rev.*, **84**, 85 (1988).
[2] D.P. Rillema, G. Allen, T.J. Meyer, D. Conrad. *Inorg. Chem.*, **22**, 1617 (1983).
[3] S.D. Ernst, W. Kaim. *Inorg. Chem.*, **28**, 1520 (1989).
[4] Y. Kawanishi, N. Kitamura, S. Tazuke. *Inorg. Chem.*, **28**, 2968 (1989).
[5] A.P.B. Lever. *Inorg. Chem.*, **29**, 1217 (1990).
[6] M. Sykora, J.R. Kincaid. *Inorg. Chem.*, **34**, 5852 (1995).

[7] B. Durham, F. Millett. *J. Chem. Ed.*, **74**, 636 (1997).
[8] G. Engstrom, R. Rajagukguk, A.J. Saunders, C. Patel, S. Rajagukguk, T. Merbitz-Zahradnik, K. Xiao, G. Pielak, B. Trumpower, C.-A. Yu, L. Gu, B. Durham, F. Millett. *Biochemistry*, **42**, 2816 (2003).
[9] D. Zaslasvsky, R.C. Sadoski, S. Rajagukguk, L. Geren, F. Millett, B. Durham, R.B. Gennis. *Proc. Natl. Acad. Sci.*, **101**, 10544 (2004).
[10] F. Millett, B. Durham. *Photosynthesis Research*, **84**, 1 (2004).
[11] D.M. Fraser, S.M. Zakeeruddin, M. Grätzel. *J. Electroanal. Chem.*, **359**, 125 (1993).
[12] S.M. Zakeeruddin, D.M. Fraser, M-K. Nazeeruddin, M. Grätzel. *J. Electroanal. Chem.*, **337**, 253 (1992).
[13] B.P. Sullivan, D.J. Salmon, T.J. Meyer. *Inorg. Chem.*, **17**, 3334 (1978).
[14] R.A. Krause. *Inorg. Chem. Acta*, **22**, 209 (1977).
[15] J. Gallagher, C.B. Chen, C.Q. Pan, D.M. Perrin, Y-M. Cho, D.S. Sigman. *Bioconjugate Chem.*, **7**, 413 (1996).
[16] G.C. Walter, D.G. Nocera, S. Swavey, K.J. Brewer. *Inorganic Synthesis*, **34**, 66 (2004).
[17] E. Ioachim, E.A. Medlycott, G.S. Hanan, F. Loiseau, S. Campagna. *Inorg. Chim. Acta*, **359**, 766 (2006).
[18] J. Van Houten, R.J. Watts. *J. Amer. Chem. Soc.*, **98**, 4853 (1976).
[19] J. Van Houten, R.J. Watts. *Inorg. Chem.*, **17**, 3381 (1978).