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Resonance Raman Spectroscopy of Ruthenium(II) and Osmium(II) Polypyridyl Complexes Containing the *N*-Methyl-4,4′-Bipyridinium Radical ($MQ^{\bullet}$) as a Ligand: Evidence for a M(dπ) → $MQ^{\bullet}(\pi^*)$ Metal-to-Ligand Charge Transfer (MLCT) Transition

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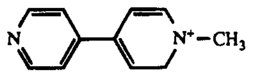
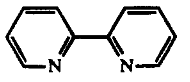
Introduction

In earlier studies, the electron-acceptor properties of N-methyl-4,4′-bipyridinium cation (monoquat, MQ^+) in polypyridyl complexes of Re(I), Ru(II), and Os(II) were detailed.[1,2] Ground- and excited-state resonance Raman measurements were employed to determine the sequence of events that occur after initial $M^{II}(d\pi) \rightarrow bpy(\pi^*)$ metal-to-ligand charge transfer (MLCT) excitation in these complexes (bpy is 2,2′-bipyridine).[3]

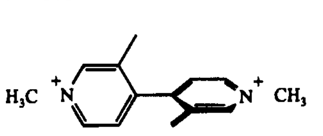


MQ^+

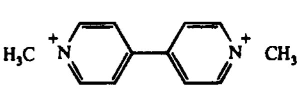


bpy

In *fac*-$[Re^I(bpy)(CO)_3(MQ^+)]^{2+}$, excited-state electron transfer ($bpy^{\bullet-}(\pi^*) \rightarrow MQ^+(\pi^*)$) occurs concomitant with a twisting of the monoquat rings from an inter-ring dihedral angle of ~47° to an angle of 0°.[3] A significant piece of evidence for this sequence came from comparisons of ground-state resonance Raman spectra for several monoquat analogs (*N,N*′-dimethyl-4,4′-bipyridine or methyl viologen, PQ^{2+}, and *N,N*′-dimethyl-3,3′-dimethyl-4,4′-bipyridine, Me_2PQ^{2+}) and their corresponding one-electron reduced forms ($PQ^{\bullet+}$ and $Me_2PQ^{\bullet+}$) to the excited-state resonance Raman spectrum of *fac*-$[Re^{II}(bpy)(CO)_3(MQ^{\bullet})]^{2+*}$.



Me_2PQ^{2+}



PQ^{2+}

While the above measurements were being performed, it was noted that polypyridyl complexes containing $MQ^{\bullet}$ as a ligand compared to free $MQ^{\bullet}$ display an additional, intense visible absorption band. Visible absorptions at ~360 and 600 nm for $MQ^{\bullet}$ are assigned to $\pi \rightarrow \pi^*$ ($MQ^{\bullet}$) and $\pi^* \rightarrow \pi^*$ ($MQ^{\bullet}$) transitions.

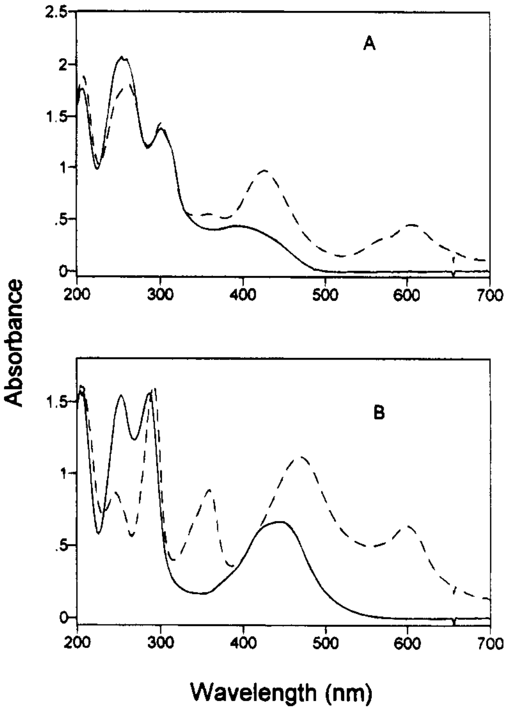


Figure 1. UV–visible absorption spectra of (A) $[(bpy)_2Os(CO)(MQ^+)]^{3+}$ (—) and electrochemically reduced form $[(bpy)_2Os(CO)(MQ^{\bullet})]^{2+}$ (– –) and (B) $[(bpy)_2Ru(MQ^+)_2]^{4+}$ (—) and electrochemically reduced form $[(bpy)_2Ru(MQ^{\bullet})_2]^{2+}$ (– –) in 0.1 M $[N(n\text{-}C_4H_9)_4](PF_6)$ CH_3CN solution.

Ground-state resonance Raman measurements have been used to assign electronic transitions based on the intensity enhancements in resonance Raman spectra.[4] Intensities are derived from electronic transitions near the exciting laser line. Resonance enhancements occur for those normal modes that undergo a change in equilibrium displacement between ground and excited states.[4] We report here the results of an excitation dependence study on bound and free $MQ^{\bullet}$ that allows the new absorption feature to be assigned to the MLCT transition, $M^{II}(d\pi) \rightarrow MQ^{\bullet}(\pi^*)$.

Experimental Section

Materials. Spectrograde CH_3CN (Burdick & Jackson) was used as received. The salts $[(bpy)_2Ru(MQ^+)_2](PF_6)_4$ and *cis*-$[(bpy)_2Os(CO)(MQ^+)](PF_6)_3$ were prepared as previously described.[1,5] *N*-Methyl-4,4′-bipyridinium cation (monoquat or MQ^+) was prepared as a PF_6^- salt using standard methods.[5] The reduced complexes $[(bpy)_2Ru(MQ^{\bullet})_2]^{2+}$ and $[(bpy)_2Os(CO)(MQ^{\bullet})]^{2+}$ and N-methyl-4,4′-bipyridinium radical ($MQ^{\bullet}$) were generated by controlled-potential electrolysis in a drybox under N_2 as previously described.[3] Tetra-*n*-butylammonium hexafluorophosphate, $[N(n\text{-}C_4H_9)_4](PF_6)$ or TBAH, was purchased from Aldrich, recrystallized from 2:1 (v:v) ethanol/H_2O twice, and thoroughly dried in a vacuum oven (72 h).

Measurements. The UV–visible absorption spectra were recorded on an HP 8452A diode array using a ~2-mm path length cell of our own design similar to the optically transparent thin-layer electrolytic (OTTLE) cell described by Krejcík *et al.*[6] Continuous-wave (CW)

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(1) (a) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708. (b) Westmoreland, T. D.; LeBozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952.

(2) Jones, W. E; Chen, P.; Bignozzi, C. A.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 793.

(3) Schoonover, J. R.; Chen, P.; Bates, W. D.; Dyer, R. B.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167.

(4) Clark, R. J. H.; Stewart, B. In *Structure and Bonding*; Springer-Verlag: New York, 1979; Vol. 36, pp 1–80.

(5) (a) Deusing, R. Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1990. (b) Chen, P.; Meyer, T. J. Unpublished results.

(6) Krejcík, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179.

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Table 1. Resonance Raman Band Energies (cm^{-1}) for (MQ$^•$), [(bpy)$_2$Ru(MQ$^•$)$_2$]$^{2+}$, and [(bpy)$_2$Os(MQ$^•$)(CO)]$^{2+}$ in 0.1 M TBAH/CH$_3$CN Solution at 298 K with Indicated Excitation Wavelengths (nm)

(MQ$^•$)		[(bpy)$_2$Ru(MQ$^•$)$_2$]$^{2+}$			[(bpy)$_2$Os(MQ$^•$)(CO)]$^{2+}$	
363.8	568.2	363.8	568.2	457.9	430.4	assignment[a]
		315		315	281	
		351	351	351	363	MQ$^•$ [ν(M−N)]
553		575		573	575	MQ$^•$
		665	663	665	665	ν(bpy)
715	713	728	727	727	728	MQ$^•$ [ν(CC) + γ(CCC)]
795	796	800	800	800	799	MQ$^•$ [ν(CC) + ν(NCH$_3$)]
974	975	988	986	986	986	MQ$^•$ [ν(CC) + γ(CCC)]
1025	1027	1005	1005	1005	1005	MQ$^•$ [ν(CN) + γ(CCN)]
1035	1035	1036	1037	1036	1036	MQ$^•$ [ν(CC) + γ(CCH)]
			1049	1048	1051	MQ$^•$
				1106		ν(bpy)
				1173		ν(bpy)
	1205	1206	1203	1206	1207	MQ$^•$
1215		1213		1212		MQ$^•$ [ν(CC) + γ(CCH)]
1233	1235	1238	1239	1239	1239	MQ$^•$ [γ(CCH) + ν(NCH$_3$)]
1267				1266		MQ$^•$ [γ(CCH)]/ν(bpy)
				1317		ν(bpy)
1333	1333	1346	1348	1348	1348	MQ$^•$ [γ(CCH) + ν(CC)ir]
1428	1428	1425		1425		MQ$^•$ [γ(NCH$_3$)]
1444	1446	1452				MQ$^•$/ν(bpy)
				1486	1489	ν(bpy)
1502	1504					MQ$^•$ [ν(CC) + γ(CCH)]
1525	1514	1516	1514		1514	MQ$^•$ [ν(CN) + γ(CCH)]
1540						MQ$^•$
		1563	1562	1562	1562	ν(bpy)
1579	1580	1602	1602	1602	1605	MQ$^•$ [ν(CC) + γ(CCH)
1648	1650	1652	1652	1652	1652	MQ$^•$ [ν(CC) IR + ν(CC)]
					1958	ν(CO)

[a] From ref 3.

resonance Raman spectra were obtained on ~1 mM samples in 0.1 M TBAH CH$_3$CN solutions at 298 K. The spectra were acquired on spinning samples by using a 135° back-scattering geometry. Laser excitation was supplied by employing either a Spectra-Physics 165-05 Ar$^+$, a Coherent INNOVA 90K Kr$^+$ laser, a Model 2045 Spectra-Physics Ar$^+$ laser, or a Coherent CR-599 dye laser with Stilbene 420. Data collection and processing was accomplished as previously described.[3,7] For the excitation-dependent spectra, the Raman bands of CH$_3$CN served as internal energy and intensity references.

Results and Discussion

The UV-visible absorption spectra for the metal complexes containing unreduced monoquat (MQ$^+$, dashed) and electrochemically reduced monoquat (MQ$^•$, solid) are shown in Figure 1. New bands appear at 360, 468, and 600 nm for [(bpy)$_2$Ru(MQ$^•$)$_2$]$^{2+}$ (B) and 360, 426, and 600 nm for *cis*-[(bpy)$_2$Os(CO)(MQ$^•$)]$^{2+}$ (A). The absorption increases near 360 and 600 nm are expected for MQ$^•$ complexes due to $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions of MQ$^•$, but the intense bands at 468 and 426 nm for the Ru(II) and Os(II) complexes, respectively, are new features. Intensity and relative energies of these features are consistent with metal-to-ligand charge (MLCT) transfer transitions with the Os$^{III/II}$ redox potential (+1.74 V vs SCE in CH$_3$CN) being more positive than the corresponding Ru$^{III/II}$ potential (+1.34 V).[8] There are contributions from M^{II}(dπ) $\rightarrow$ bpy(π^*) transition at 468 and 426 nm, but they cannot account for the large intensity change upon reduction.

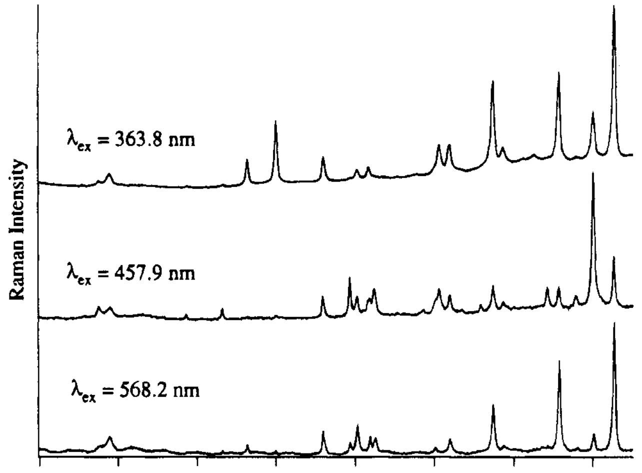

Figure 2. Excitation-dependent continuous wave (CW) resonance Raman spectra of [(bpy)$_2$Ru(MQ$^•$)$_2$]$^{2+}$ in 0.1 *m* [N(*n*-C$_4$H$_9$)$_4$](PF$_6$) CH$_3$CN solution (excitation wavelengths are indicated). The CH$_3$CN Raman bands are at 380, 920, and 1380 cm^{-1}. The spectra are of the same sample and have been normalized in intensity to the 920 cm^{-1} solvent band.

Raman spectra measured in resonance with free MQ$^•$ absorption bands near 360 and 600 nm (363.8- and 568.2-nm excitation) in CH$_3$CN display similar sets of Raman bands, Table 1. Likewise, resonance Raman measurements on [(bpy)$_2$Ru(MQ$^•$)$_2$]$^{2+}$ in CH$_3$CN (Figure 2) show analogous Raman bands using these same excitation lines (with some differences noted between bound MQ$^•$ and free MQ$^•$ in solution). Close inspection of the Raman spectra obtained with excitation at these two wavelengths reveals similar spectra with no enhancements for transitions involving the ancillary bipyridine ligands. The high frequency region (1300-1700 cm^{-1}) is particularly diagnostic

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(7) (a) Schoonover, J. R.; Timpson, C. J.; Meyer, T. J.; Bignozzi, C. A. *Inorg. Chem.* **1992**, *31*, 3185. (b) Bignozzi, C. A.; Argazzi, R.; Garcia, C. G.; Scandola, F.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 1652.

(8) (a) Westmoreland, T. D. Ph.D. Dissertation, The University of North Carolina at Chapel Hill, 1985. (b) Sullivan, B. P.; Abruna, H. Finklea, O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.

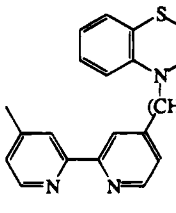
when comparison is made with data for paraquat (PQ^{2+}) and bpy, Table 1.[3]

While the spectra of $[(bpy)_2Ru(MQ^\bullet)_2]^{2+}$ with 363.8- and 568.2-nm excitation are similar, intensity differences are observed. The major differences are greater intensities for bands at 728, 800, 1206, 1346, and 1602 cm^{-1} with 363.8-nm excitation compared to 568.2-nm excitation. Higher intensities occur for bands at 986, 1005, and 1049 cm^{-1} with 568.2-nm excitation. The intensity differences may reflect the different orbital origins of the different transitions in the absorption spectra with the band at 360 nm attributable to $\pi \rightarrow \pi^*$ ($MQ^\bullet$) and the 600-nm band to a $\pi^* \rightarrow \pi^*$ ($MQ^\bullet$) transition.[9,10]

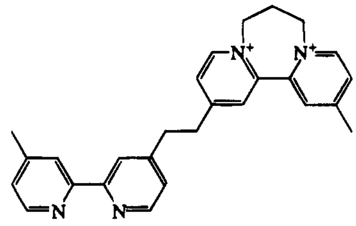
A greatly different intensity pattern is obtained with 457.9-nm excitation into the strong absorption band centered at 468 nm (Figure 2). The intense Raman bands in this spectrum can be attributed to $MQ^\bullet$. Bands are present that can be assigned to the bpy ligands, which gain intensity from the $Ru^{II}(d\pi) \rightarrow bpy(\pi^*)$ MLCT transition near 460 nm; however, their intensities are weak relative to the $MQ^\bullet$ bands. These data confirm the presence of an overlapping, monoquat-based transition in this region. The different intensity pattern for $MQ^\bullet$ bands measured with 457.9-nm excitation compared to 363.8 and 568.2 nm points to a different orbital origin for the absorption band at 468 nm. The most relevant intensity change occurs for the Raman band at 351 cm^{-1}, which gains intensity by a factor of *ca.* 2 for the spectrum measured with 457.9 nm excitation. This band is assigned as predominantly Ru-N($MQ^\bullet$) in character.[11] The large change in intensity for the Ru−N($MQ^\bullet$) stretch suggests a change in oxidation state at the metal in this electronic transition.

To investigate the nature of this transition further, resonance Raman spectra were measured for $[(bpy)_2Os(CO)(MQ^\bullet)]^{2+}$ with excitation into the intense band near 426 nm, Table 1. This complex has the added feature of a bound carbonyl ligand. For carbonyl containing complexes of this type (e.g. $[L_3Re(CO)_3]^{n+}$, $[L_2M(CO)_4]^{n+}$, and $[L_5Os(CO)]^{n+}$), the intensity of a carbonyl stretch is enhanced when the complexes are excited in resonance with their MLCT absorptions.[12] Resonance Raman spectra measured with 430.4-nm excitation reveal an intensity pattern very similar to that of the Ru complex with 457.9-nm excitation in terms of the $MQ^\bullet$ and bpy vibrations. The spectrum of the Os complex contains intense $MQ^\bullet$ bands with the same relative intensities, an enhanced Os−N($MQ^\bullet$) band at 363 cm^{-1}, very weak bpy bands, and an enhanced CO stretch at 1958 cm^{-1} (Table 1).

The intensity of these new absorption features, the data for the Os(II) complex, and the wavelength-dependent data for the Ru complex demonstrate the absorption bands at 426 and 468 nm to be largely $M^{II}(d\pi) \rightarrow MQ^\bullet(\pi^*)$.[13] These features are observed in time-resolved absorption difference measurements on chromophore-quencher complexes as well. In an earlier study on the donor−acceptor complex $[Ru^{II}(bpy\text{-}PTZ)_2(bpy\text{-}DQ^{2+})]^{4+}$ (bpy-PTZ is 10-[4-(4′-methyl-2,2′-bipyridin-4-yl)-butyl]-10H-phenothiazine and bpy-DQ^{2+} is 2-methyl-11-[2-(4′-methyl-2,2′-bipyridin-4-yl)ethyl]-6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazinediium-N11,N11′), a feature centered at ~450 nm was observed.[14]



bpy-PTZ



bpy-DQ^{2+}

The time-resolved absorption difference spectrum of the redox-separated state, $[(bpy\text{-}PTZ^{\bullet+})Ru^{II}(bpy\text{-}PTZ)(bpy\text{-}DQ^{\bullet+})]^{4+}$, resembles the absorption of the one-electron reduced complexes (Figure 1A) albeit with a much less intense visible band. This result is not unexpected given the similarity of bpy-DQ^{2+} to a bound MQ^+ ligand.

The decreased intensity can be rationalized by invoking weak electronic coupling between the metal center and the diquat radical cation ($DQ^{\bullet+}$) portion of the acceptor ligand due to the presence of an ethylene spacer between the bpy and diquat fragments.

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(9) Excitation profiles for the one electron reduced radical of *N,N*′-dimethyl-4,4′-bipyridine ($PQ^{\bullet 2+}$) demonstrated a complex pattern of enhancements due presumably to interference effects. Forster, M.; Girling, R. B.; Hester, R. E. *J. Raman Spectrosc.* **1982**, *12*, 36.

(10) Creutz, C. *Comments Inorg. Chem.* **1982**, *1*, 293.

(11) The Raman band associated with the Ru−N(bpy) stretch is at 376 cm^{-1} and therefore hidden under the solvent band at 380 cm^{-1}.

(12) (a) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015. (b) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1124. (c) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067. (d) Schoonover, J. R.; Meyer, T. J. Unpublished results.

(13) The strong intensity of the absorption features at 426 nm for $[(bpy)_2Os(CO)(MQ^\bullet)]^{2+}$ and 468 nm for $[(bpy)_2Ru(MQ^\bullet)_2]^{2+}$ preclude their assignment as a ligand-to-metal charge transfer transition. The lowest unfilled orbital at the metal is $d\sigma^*$, and a $MQ^\bullet(\pi^*) \rightarrow M^{II}(d\sigma^*)$ transition would be very weak by symmetry arguments.

(14) (a) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519. (b) Ryu, C. K.; Wang, R.; Schmehl, R. H.; Ferrere, S.; Ludwikow, M.; Merkert, J. W.; Headford, C. E.; Elliott, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 430. (c) Larson, S. L.; Cooley, L. F.; Elliott, C. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1992**, *114*, 9504.