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Synthesis, Spectroscopy, Electrochemistry, and Photochemistry of a Series of $M(bpym)_2Cl_2$ (M = Mn(II), Co(II), Ni(II), and Cu(II)) Complexes. Precursor Complexes in the Preparation of Polymetallic Systems

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Abstract

The synthesis, aqueous absorption and reflectance spectra, cyclic voltammetry and ligand field photochemistry of a series of $M(bpym)_2Cl_2$ (M = Mn(II), Co(II), Ni(II), Cu(II) and bpym = 2,2′-bipyrimidine) are reported here. Ligand field electronic spectral assignments are made by comparison to analogous $M(bpy)_2Cl_2(s)$ (bpy = 2,2′-bipyridine) and $M(bpym)_3^{2+}$ complexes. Ligand field absorption maxima are shifted to lower energy as a result of bpym loss *vs.* $M(bpym)_3^{2+}$ complexes. Metal to ligand charge transfer absorption energies increase as a result of d_M orbital stabilization *vs.* $M(bpym)_3^{2+}$ complexes. Cyclic voltammetry indicates ring opening upon reduction of the complexes. The complexes are photochemically inert ($\phi_{max} < 0.002$) at the irradiated wavelengths.

Introduction

Inorganic polymer synthesis is a rapidly developing field which nourishes diverse chemical applications such as efficient electrical conductors, surface coatings [1], synthetic models for the active site of cytochrome oxidase [2, 3], photocatalyzed processes and electron exchange processes [4–6]. Many recent studies have focused on the use of the aromatic nitrogen donor ligand 2,2′-bipyrimidine (bpym) with transition metals for generation of polymetallic systems. The peripheral nitrogen atoms of the bidentate bpym afford the opportunity for extensive polymetallic complexes, and studies indicate that bpym allows more effective electronic communication between bridged metal centers than most monodentate ligands [7, 8]. The use of bpym as both effective bridging group, and as a stable 2,2′-bipyridine (bpy) analog has been demonstrated in the preparation of several mono and bimetallic systems [2, 9–20]. We have previously reported a series of $M(bpym)_3^{2+}$ (M = Fe(II), Co(II), Ni(II), Cu(II)) complexes [18–20]. These molecules offer the restricted potential to serve as molecular hubs, through which other metals or molecular groups might be coordinated.

We now wish to report the preparation, spectroscopy, electrochemistry and photochemistry of a series of $[M(bpym)_2Cl_2]$ (M = Mn(II), Co(II), Ni(II), Cu(II)) complexes. In addition to retaining the potential to serve as a framework through which to bind remote metal centers, these complexes also possess labile coordination sites through which extensive modifications might be made to the metal center. For the series of complexes, we assign the ligand field (LF) and metal to ligand charge transfer (MLCT) transitions by comparison with analogous $M(bpym)_3^{2+}$ and $[M(bpy)_2Cl_2]$ complexes. Electrochemical results are reported and interpreted from models used on similar chelated complexes.

Experimental

Materials

Analytical reagent grade compounds and solvents were used for all preparations described in this work. 2,2′-Bipyrimidine was obtained from Alfa Inorganics (U.S.A.) or Lancaster Synthesis Ltd. (U.K.), and used without purification. Water used in electrochemistry was distilled. Argon was obtained from Linde, passed through a chromous solution, then dried by passing through $CaSO_4$ before use in solvent deoxygenation. Elemental analyses were performed by Atlantic Microlab, Atlanta, Ga., with satisfactory results obtained for all complexes.

Instrumentation

Electronic absorption spectra were recorded on a Beckman Model 5240 Spectrophotometer with matching quartz cells. Reflectance spectra were recorded on the same instrument fitted with a Beckman reflectance sphere. Samples were dry mounted

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on a piece of Watman filter paper which served as the sample holder. Cyclic voltammograms were recorded on a Bio Analytical Systems CV-18 Cyclic Voltammograph with a Hewlett Packard 7044A XY recorder. The glassy carbon working electrode (3.0 mm diameter) was polished with alumina prior to each scan. An Ag|AgCl (3 M KCl, nominally −0.044 V *vs.* SCE) reference electrode was used. All potentials are reported *vs.* SCE and are uncorrected for junction potentials. The potentials reported for oxidation couples $E_{1/2}$, are estimates obtained by averaging the anodic and cathodic peak potentials. Cyclic voltammograms were recorded in distilled H_2O using 0.10 M KCl as an electrolyte. Scan rates were varied from 50–300 mV/s.

Irradiation of samples was accomplished with a continuous beam photolysis apparatus consisting of an Ealing universal arc source lamp with a 200 W high pressure Hg lamp, 1 in diameter Oriel mercury line interference filters, an ESCO 4 in focal length fused quartz collimating lens and a thermostated cell compartment (controlled by a Fisher Model 90 constant temperature circulating both) all mounted on an Ealing optical railing. Intensities of the apparatus were measured by Reinecke actinometry at 546 nm, 577 nm and 691 nm as 1.90×10^{-6} E/min, 3.45×10^{-5} E/min, and 1.38×10^{-6} E/min respectively [35]. The solutions used for the photolysis studies were prepared, then deoxygenated with argon gas in the absorption cells prior to irradiation. Spectroscopic changes in the sample were determined at intervals throughout the photolysis. All spectroscopic measurements were corrected for thermal reaction by use of a dark sample. The ϕ_t for each time period of the reaction was plotted *vs.* percent reaction and the initial quantum yield obtained by extrapolation to 0% reaction.

Syntheses

Mn(bpym)₂Cl₂·2H₂O

$Mn(bpym)_2Cl_2$ was prepared by dissolving 0.0317 g (0.16 mmol) of $MnCl_2 \cdot 4H_2O$ in 10 ml of deoxygenated methanol and adding 0.1031 g (0.65 mmol) bpym as a solid, with rapid stirring. The bright yellow solution was left in the dark under argon for 4 h during which a yellow precipitate formed. After collection of the precipitate by filtration the product was washed with ethanol and dried by washing with ether and placed in a vacuum dessicator. Yield 0.0281 g (37%). *Anal.* Calc. for $C_{16}H_{12}N_8MnCl_2 \cdot 2H_2O$: C, 40.1; H, 3.3; N, 23.5. Found: C, 39.8; H, 2.5; N, 23.1%.

Co(bpym)₂Cl₂·3H₂O

$Co(bpym)_2Cl_2 \cdot 3H_2O$ was prepared by dissolving 0.038 g (0.16 mmol) of $CoCl_2 \cdot 6H_2O$ in 10 ml of deoxygenated ethanol and adding a solution of 0.050 g (0.32 mmol) of bpym dissolved in 10 ml of deoxygenated ethanol. After stirring in the dark for 1 h, the light pink precipitate was collected by centrifugation. After decanting the supernatent liquor, the product was washed with ethanol and centrifuged. This process was repeated three times. Finally the process was repeated with ether and the product was vacuum dried. Yield 0.055 g (0.12 mmol) 75%. *Anal.* Calc. for $C_{16}H_{12}N_8CoCl_2 \cdot 3H_2O$: C, 39.40; H, 3.5; N, 22.40. Found: C, 39.56; H, 2.7; N, 22.45%.

Ni(bpym)₂Cl₂·H₂O

$Ni(bpym)_2Cl_2 \cdot H_2O$ was prepared by dissolving 0.0376 g (0.16 mmol) $NiCl_2 \cdot 6H_2O$ in 10 ml of deoxygenated absolute ethanol. To this solution was added 0.050 g (0.32 mmol) bpym in 10 ml deoxygenated absolute ethanol with stirring. After 1 h the light green fine precipitate was collected by centrifugation, washed three times with absolute ethanol, then ether, and the product vacuum dried. Yield 0.044 g (63%). *Anal.* Calc. for $C_{16}H_{12}N_8NiCl_2 \cdot 1/2H_2O$: C, 42.25; H, 2.86; N, 24.60. Found: C, 42.35; H, 2.91; N, 24.41%.

Cu(bpym)₂Cl₂·3H₂O

$Cu(bpym)_2Cl_2 \cdot 3H_2O$ was prepared by dissolving 0.0426 g (0.32 mmol) of $CuCl_2$ in 10 ml of deoxygenated absolute ethanol and adding 0.100 g (0.64 mmol) bpym dissolved in 3 ml of deoxygenated absolute ethanol dropwise with stirring. After 1 h the green precipitate was collected by centrifugation, washed three times with absolute ethanol followed by ether, and vacuum dried. Yield, 0.0784 g (51%). *Anal.* Calc. for $C_{16}H_{12}N_8CuCl_2 \cdot 3H_2O$: C, 38.03; H, 3.50; N, 22.10. Found: C, 38.17; H, 2.43; N, 22.25%.

Results and Discussion

Synthesis

The preparation of $[M(bpym)_2Cl_2] \cdot nH_2O$ (M = Mn(II), Co(II), Ni(II) and Cu(II), $n = 1$–3) complexes involved direct addition of stoichiometric amounts of the metal chloride and two-fold bpym. The precipitates were extremely fine powders which passed through fine porosity (4–5 μm) sintered glass filtering funnels. The isolation and purification of the $[M(bpym)_2Cl_2]$ complexes was achieved through a repeated process of centrifugation and decantation of the mother liquor. Only the $[Cu(bpym)_2Cl_2]$ complex was soluble in a solvent (CH_3NO_2) other than H_2O.

Although the complexes $[Co(bpy)_2Cl_2]$ and $[Ni(bpy)_2Cl_2]$ have been prepared as the stepwise thermal decomposition products of $[Co(bpy)_2]Cl_2 \cdot H_2O$ and $[Ni(bpy)_3]Cl_2 \cdot 7H_2O$, relatively little is

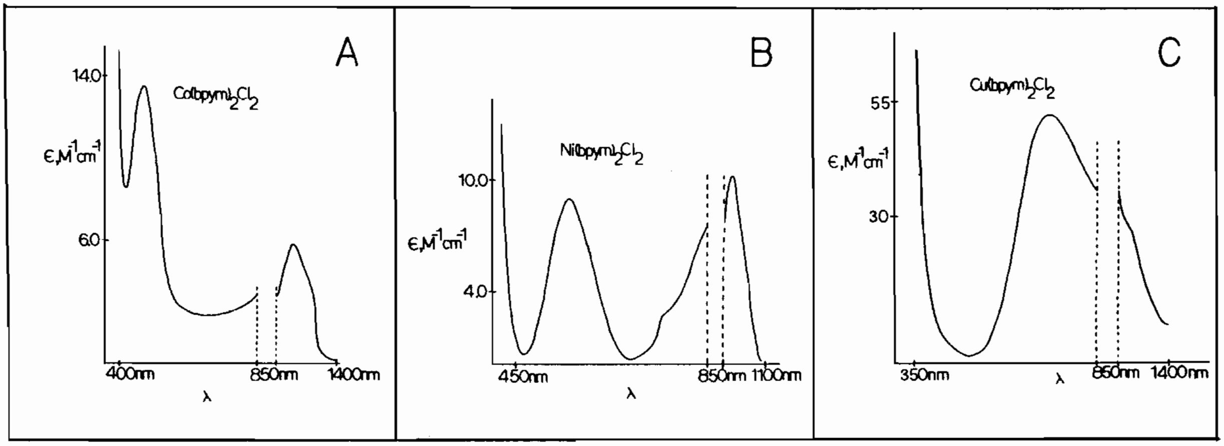

Fig. 1. Aqueous absorption spectra of: (a) Co(bpym)$_2$Cl$_2$, (b) Ni(bpym)$_2$Cl$_2$, and (c) Cu(bpym)$_2$Cl$_2$. Wavelength scale change at 850 nm.

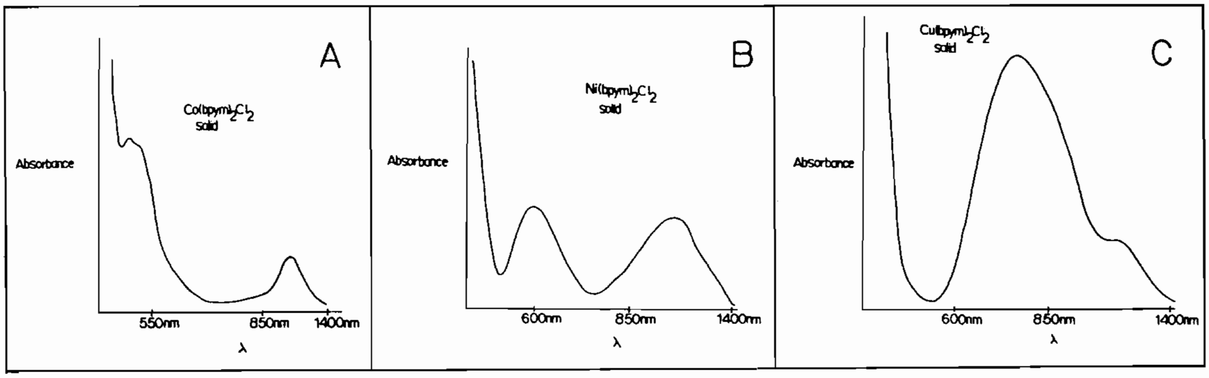

Fig. 2. Solid reflectance spectra of: (a) Co(bpym)$_2$Cl$_2$, (b) Ni(bpym)$_2$Cl$_2$, and (c) Cu(bpym)$_2$Cl$_2$. Wavelength scale change at 850 mn.

known about bipyridyl transition metal complexes containing fewer than three ligands per metal ion [21–23].

Electronic Spectra

The absorption spectra of all complexes were recorded in aqueous solution (Fig. 1) and as solid reflectance (Fig. 2). Because of rapid dissolution in H_2O, the aqueous spectra are most likely due to the M(bpym)$_2$(H$_2$O)$_2^{+2}$ species in solution.

Mn(bpym)$_2$Cl$_2$ in aqueous solution has no ligand field absorptions in the visible region of the spectrum but an intense intraligand absorption peak in the ultraviolet (Table I). Such absorption characteristics are typical of the d^{5}Mn^{2+} species with no spin allowed ligand field transitions [24]. Only the characteristic bpym $\pi^* \leftarrow \pi$ transition appears in the ultraviolet at wavelengths below 250 nm.

The Co(bpym)$_2$Cl$_2$ complex in aqueous solution exhibits two d–d transitions in the near infrared-visible spectrum at 1050 nm ($\epsilon = 5.9$ M^{-1} cm^{-1}) and 480 nm ($\epsilon = 13.5$ M^{-1} cm^{-1}) (Table I). These absorption maxima are similar, although lower energy, than analogous Co(bpym)$_3^{2+}$ and Co(bpy)$_3^{2+}$ absorptions. This may be understood by replacement of the relatively strong field π bonding bpym with the weaker field H_2O ligand. The assignments made by analogy to other Co^{2+} complexes are $^4T_2 \leftarrow {}^4T_1(F)$ at 1050 nm and $^4T_1(P) \leftarrow {}^4T_1(F)$ at 480 nm. While no MLCT absorption is observed, the $\pi^* \leftarrow \pi$ intraligand absorption is observed at 245 nm ($\epsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}). The solid reflectance spectrum of Co(bpym)$_2$Cl$_2$ also shows two absorptions at 1140 nm ($^4T_2(F) \leftarrow {}^4T_1(F)$ and 495 nm ($^4T_1(P) \leftarrow {}^4T_1(F)$). These reflectance maxima occur at lower energy than the aqueous absorptions, and may reflect the fact that in the solid state, the bound Cl$^-$ is a weaker ligand than H_2O. The values for [Co(bpym)$_2$Cl$_2$] also are at slightly lower energy than the previously reported Co(bpy)$_2$Cl$_2$ with peaks at 1120 nm and 490 nm, and demonstrate that bpym is a slightly weaker ligand than bpy [23].

The aqueous spectrum of Ni(bpym)$_2$Cl$_2$ shows two absorption maxima at 925 nm ($\epsilon = 6.6$ M^{-1} cm^{-1}) and 560 nm ($\epsilon = 5.8$ M^{-1} cm^{-1}) and a shoulder at 760 nm ($\epsilon = 3.0$ M^{-1} cm^{-1}). There has been

TABLE I. Electronic Spectra of some 2,2′-Bipyrimidine Transition Metal Complexes

Complex	λ (nm)	ε (M^{-1} cm^{-1})	Assignment	Reference
$Mn(bpym)_2Cl_2(aq)$	242		$\pi^* \leftarrow \pi$	
$Mn(bpym)_2Cl_2(s)$	242		$\pi^* \leftarrow \pi$	
$Co(bpym)_2Cl_2(aq)$	1050	5.9	$^4T_2 \leftarrow {}^4T_1(F)$	
	480	13.5	$^4T_1(P) \leftarrow {}^4T_1(F)$	
	245	3.2×10^4	$\pi^* \leftarrow \pi$	
$Co(bpym)_2Cl_2(s)$	1140		$^4T_2 \leftarrow {}^4T_1(F)$	
	495		$^4T_1(P) \leftarrow {}^4T_1(F)$	
$Co(bpy)_2Cl_2(s)$	1120 ± 10		$^4T_2 \leftarrow {}^4T_1(F)$	23
	490 ± 10		$^4T_1(P) \leftarrow {}^4T_1(F)$	
$Co(bpym)_3{}^{2+}(aq)$	990	5.2	$^4T_2 \leftarrow {}^4T_1(F)$	18
	472	18.7	$^4T_1(P) \leftarrow {}^4T_1(F)$	
	242	4.5×10^4	$\pi^* \leftarrow \pi$	
$Ni(bpym)_2Cl_2(aq)$	925	6.6	$^3T_2 \leftarrow {}^3A_2$	
	760	3.0	$^1E \leftarrow {}^3A_2$	
	560	5.8	$^3T_1 \leftarrow {}^3A_2$	
	260		MLCT	
	243	2.6×10^4	$\pi^* \leftarrow \pi$	
$Ni(bpym)_2Cl_2(s)$	1100		$^3T_2 \leftarrow {}^3A_2$	23
	655		$^3T_1 \leftarrow {}^3A_2$	
$Ni(bpy)_2Cl_2(s)$	1050 ± 10		$^3T_2 \leftarrow {}^3A_2$	
	625 ± 10		$^3T_1 \leftarrow {}^3A_2$	
$Ni(bpym)_3{}^{2+}(aq)$	870	6.0	$^3T_2 \leftarrow {}^3A_2$	18
	790	5.8	$^1E \leftarrow {}^3A_2$	
	535	9.8	$^3T_1 \leftarrow {}^3A_2$	
	370		MLCT	
	243	3.2×10^4	$\pi^* \leftarrow \pi$	
$Cu(bpym)_2Cl_2(aq)$	920	29.5	$^2B_1 \leftarrow {}^2A_1$	
	725	51.5	$^2E \leftarrow {}^2A_1$	
	(270)	5.7×10^3	MLCT	
	242	1.36×10^4	$\pi^* \leftarrow \pi$	
$Cu(bpym)_2Cl_2(s)$	1100		$^2B_1 \leftarrow {}^2A_1$	
	750		$^2E \leftarrow {}^2A_1$	
$Cu(bpym)_3{}^{2+}(aq)$	1320	37.4	$^2A_1 \leftarrow {}^2E$	20
	682	81.0	$^2E \leftarrow {}^2E$	
	300	4.4×10^3	MLCT	
	242		$\pi^* \leftarrow \pi$	

previous discussion concerning the assignment of the two low energy $^3T_2 \leftarrow {}^3A_2$ and $^1E \leftarrow {}^3A_2$ transitions, which as previously noted, are close to the crossover point for $Ni(bpym)_3{}^{2+}$ and $Ni(bpy)_3{}^{2+}$ complexes [18, 25–30]. In those complexes, the lowest energy peak was assigned to the $^3T_2 \leftarrow {}^3A_2$ transition. The di-substituted $Ni(bpym)_2(H_2O)_2{}^{2+}$ complex must have a weaker Dq/B than either $Ni(bpym)_3{}^{2+}$ or $Ni(bpy)_3{}^{2+}$ and thus the lowest energy transition is undoubtedly due to $^3T_2 \leftarrow {}^3A_2$, while the $^1E \leftarrow {}^3A_2$, which should be relatively unaffected by 10 Dq, remains the higher energy transition. The transition at 560 nm is unambiguously assigned as $^3T_1 \leftarrow {}^3A_2$. All d–d transitions for aqueous $Ni(bpym)_2Cl_2$ are at slightly lower energy than analogous $Ni(bpym)_3{}^{2+}$ transitions, reflecting a smaller d orbital splitting in the di-substituted complex. The MLCT for the aqueous $Ni(bpym)_2Cl_2$ complex appears as a shoulder at 260 nm on the side of the more intense $\pi^* \leftarrow \pi$ intraligand charge transfer at 243 nm ($\epsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}). The MLCT absorption at 260 nm occurs at higher energy than for $Ni(bpym)_3{}^{2+}$ [18]. This is probably due to stabilization of the Ni^{2+} $e_g{}^*$ orbitals because of weaker crystal field effects. Thus the MLCT $\pi^*{}_L \leftarrow e_g{}^*{}_M$ transition originates from a more stabilized level and requires more energy. Reflectance spectra of $Ni(bpym)_2Cl_2$ are similar to those previously reported for $Ni(bpy)_2Cl_2$ although shifted to lower wavelength because of weaker bpym *vs.* bpy bonding [23]. The $Ni(bpym)_2Cl_2$ solid spectrum

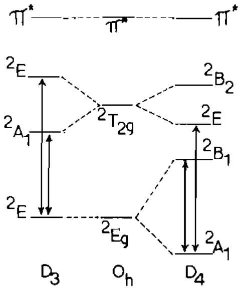

Fig. 3. Approximate molecular orbital diagram showing splitting of Cu(II) states in D_3, O_h and D_4 symmetry.

absorbances are also of lower energy when compared to the aqueous spectrum. This may be understood as being due to a weaker (Cl^-) ligand being bound in the solid state *vs.* (H_2O) in the aqueous solution.

The aqueous spectrum of $Cu(bpym)_2Cl_2$ shows two spin allowed transitions. The λ_{max} of the high energy absorption occurs at 725 nm ($\epsilon = 51.5$ M^{-1} cm^{-1}) while a shoulder appears on the lower energy side at 920 nm ($\epsilon = 29.5$ M^{-1} cm^{-1}). While aqueous $M(bpym)_2Cl_2$ (M = Mn(II), Co(II) and Ni(II)) complexes were similar in energy and shape with analogous $M(bpym)_3{}^{2+}$ complexes, the aqueous spectrum of $Cu(bpym)_2Cl_2$ was markedly different in λ_{max} and shape than the previously prepared $Cu(bpym)_3{}^{2+}$ and $Cu(bpy)_3{}^{2+}$ complexes. This may be explained by the fact that the d^9 bis-chelated $Cu(bpym)_2Cl_2(aq)$ complex is more susceptible to Jahn–Teller distortion than either $Cu(bpym)_3{}^{2+}$ or $Cu(bpy)_3{}^{2+}$. The interaction of many tris chelated bidentate Cu(II) complexes is not well defined and studies have interpreted the spectra of Cu(II) complexes in terms of both tetragonal and trigonal distortions [20, 26, 36]. While solution spectra of $Cu(bpym)_3{}^{2+}$ and $Cu(bpy)_3{}^{2+}$ have been interpreted using D_3 symmetry, the disubstituted aqueous $Cu(bpym)_2Cl_2$ complex is less confined to trigonal distortion and more likely to undergo normal tetragonal Jahn–Teller distortion. Even though the disubstituted positions are most likely forced to be *cis* because of steric bpym repulsions of the *trans* configuration, examples of tetragonal distortion have been shown to occur with complexes of the type $Cu(L{\cdot}L)_2(L'{\cdot}L')^{2+}$ [31]. Thus, in D_4 symmetry the ^2E ground state is split into $^2A_1 + {}^2B_1$ (Fig. 3). The spectrum assigned from this symmetry allows for the low energy absorption in D_3 symmetry ($^2A_1 \leftarrow {}^2E$) to increase in energy in D_4 symmetry ($^2B_1 \leftarrow {}^2A_1$) and the higher energy D_3 transition ($^2E \leftarrow {}^2E$) to decrease in energy in D_4 symmetry ($^2E \leftarrow {}^2A_1$). The lower symmetry D_4 ground state of aqueous $Cu(bpym)_2Cl_2$ may also explain the higher energy MLCT absorption (270 nm, $\epsilon = 5.75 \times 10^3$ M^{-1} cm^{-1}) as compared with the $Cu(bpym)_3{}^{2+}$ MLCT absorption (300 nm, $\epsilon = 4.4 \times 10^3$ M^{-1} cm^{-1}). The $\pi^* \leftarrow \pi$ intraligand transition was found to occur at 242 nm ($\epsilon = 1.3 \times 10^4$ M^{-1} cm^{-1}). The solid state reflectance spectrum of $Cu(bpym)_2Cl_2$ also exhibits two d–d ligand field absorptions occurring at 750 nm and 1100 nm. As with the other $M(bpym)_2Cl_2$ complexes, the solid state absorptions occurred at lower energy than aqueous spectra, most likely caused by weak field Cl^- replacement by stronger field H_2O in solution.

Electrochemistry and Photochemistry

The electrochemical reduction potentials and ligand field photochemical results are summarized in Table II. Cyclic voltammograms of the aqueous $M(bpym)_2Cl_2$ complexes are shown in Fig. 4.

The cyclic voltammogram of aqueous $Mn(bpym)_2Cl_2$ shows a totally irreversible wave at -1.09 V *vs.* SCE representing a $Mn^{2+/1+}$ reduction. A subsequent reduction wave at -1.28 V is also observed. However, since the initial complex irreversibly falls apart upon the one electron reduction, additional waves do not reflect reduction potentials of the initial complex.

The one electron reduction of the aqueous $Co(bpym)_2Cl_2$ complex occurs at -0.86 V *vs.* SCE. Although repetititve scans show reactant depletion and the anodic–cathodic peak separation ($\Delta E_{1/2}$) is 360 mV (at 100 mV/s) indicating electrochemical irreversibility [32], holding the potential at -0.50 V regenerates the wave height for subsequent scans. The results are similar to those observed for $M(bpym)_3{}^{2+}$ and $M(bpy)_3{}^{2+}$ complexes which are believed to undergo initial chelate ring opening on reduction followed by reclosure after reoxidation [17, 33, 34]. A second totally irreversible cathodic wave is observed at -1.23 V *vs.* SCE, and holding the potential at -0.50 V after scanning through this wave fails to regenerate the initial complex.

Ligand field irradiation of the $^4T_1(P) \leftarrow {}^4T_1(F)$ absorption on the low energy side at 546 nm produced no observable spectral changes, and $\phi_{max\ 546\ nm} < 0.002$.

The cyclic voltammetry of aqueous $Ni(bpym)_2Cl_2$ shows two cathodic waves at very close potential, with a single anodic return wave. The potential of the anodic return wave is independent of whether the scan was reversed after the first reduction wave only or after both reduction waves. $E_{1/2}(2+/1+)$ occurred at -0.86 V *vs.* SCE ($\Delta E_{1/2} = 360$ mV at 100 mV/s) and $E_{1/2}(1+/0)$ occurred at -0.89 V *vs.* SCE ($\Delta E_{1/2} = 420$ mV at 100 mV/s). While both waves are electrochemically irreversible, the anodic return wave suggests a bpym ring opening upon reduction followed by ring closure on reoxidation process may also occur.

The ligand field ($^3T_1 \leftarrow {}^3A_2$) photochemistry of aqueous $Ni(bpym)_2Cl_2$ at 571 nm showed no observable photochemistry with $\phi_{max\ 571\ nm} < 0.0005$.

TABLE II. Electrochemical and Photochemical Results of some Aqueous $M(bpym)_2Cl_2$ (M = Mn(II), Co(II), Ni(II) and Cu(II)) Complexes

Complex	$E_{1/2}$ (V)[a]	$\Delta E_{1/2}$ (mV)	ϕ_{max}[c]
$Mn(bpym)_2Cl_2(aq)$	−1.09[b] −1.28[b]	irr irr	
$Co(bpym)_2Cl_2(aq)$	−0.86 −1.23[b]	360 irr	<0.002 at 546 nm
$Ni(bpym)_2Cl_2(aq)$	−0.86 −0.89	360 420	<0.0005 at 577 nm
$Cu(bpym)Cl_2(aq)$	+0.13	300	<0.0005 at 691 nm

[a] Cyclic voltammograms recorded in 0.10 M KCl and reported *vs.* SCE. [b] Reduction peak potential only due to the absence of the reverse oxidation wave. [c] Photochemistry of aqueous solutions.

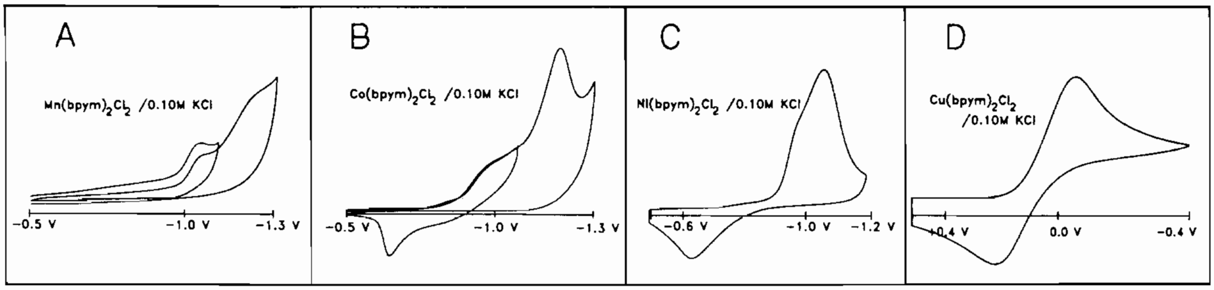

Fig. 4. Cyclic voltammograms of: (a) $Mn(bpym)_2Cl_2$, (b) $Co(bpym)_2Cl_2$, (c) $Ni(bpym)_2Cl_2$, and (d) $Cu(bpym)_2Cl_2$ recorded in aqueous 0.10 M KCl solution.

Cyclic voltammetry of aqueous $Cu(bpym)_2Cl_2$ shows a 2+/1+ reduction at $E_{1/2} = +0.13$ V *vs.* SCE ($\Delta E_{1/2} = 300$ mV at 100 mV/s). While successive scans reduce wave heights, prolonged electrolysis at +0.50 V regenerate approximate initial wave heights. Again, ring opening upon reduction followed by bpym ring reclosure after reoxidation appears to follow the same pattern as previously observed for $Cu(bpym)_3{}^{2+}$ [20].

Irradiation of aqueous $Cu(bpym)_2Cl_2$ at 691 nm into the $^2E \leftarrow {}^2A_1$ ligand field absorption band showed no observable photochemistry with $\phi_{max\ 691\ nm} < 0.0005$.

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