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Synthesis and Spectral and Electrochemical Properties of Di-2-pyridyl Ketone Complexes of Ruthenium and Their Reactions

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Di-2-pyridyl ketone (dpk) complexes of ruthenium(II) have been synthesized and characterized by analytical spectroscopic and electrochemical data. Attempts to prepare a diaquo complex from [Ru(dpk)$_2$Cl$_2$] by hydrolysis in the presence of Ag$^+$ resulted in addition of H_2O to the coordinated dpk. The *gem*-diol complex [Ru(dpk·H$_2$O)$_2$]$^{2+}$ produced is readily oxidized on heating in air with simultaneous loss of H$^+$. The synthesis of 1,1-di-2-pyridylethanol and its ruthenium complex has also been reported.

Introduction

There has been a lot of interest in recent years in the chemistry of ruthenium complexes of 2,2′-bipyridines and bipyridine-like ligands, for a variety of reasons.[1,2] Tris(2,2′-bipyridine)ruthenium(II) undergoes unique photoinduced electron-transfer reactions[3] and is under investigation as a photocatalyst for the direct homogeneous photodecomposition of water[4] and as a component in photogalvanic[5] and photoelectrochemical cells.[6] Oxidation of water to molecular oxygen, which is of great importance as a means of converting light energy to chemical energy, has been shown to be catalyzed by aquo and oxo complexes of ruthenium containing bipyridine or related ligands.[7-9] In a recent paper from this laboratory, we have shown that dipyridyl ketone (dpk) can act as a chelating $\overset{\frown}{\mathrm{N\ N}}$ ligand in its Cu(I) complexes, which are efficient photocatalysts for norbornadiene to quadricyclane conversion.[10] In order to have at our disposal new mononuclear ruthenium(II) complexes that may be able to catalyze water oxidation to O_2, we attempted to synthesize compounds of the type $\mathrm{RuL_2(H_2O)_2}^{2+}$ (L = dpk), but did not succeed owing to complications arising out of water addition to coordinated dpk. In this paper, the synthesis and spectral and electrochemical properties of di-2-pyridyl ketone complexes of ruthenium and their reactions are reported.

Experimental Section

All reactions were carried out with dry and distilled solvents. Elemental analysis was done on a Carlo Erba 1106 instrument, and infrared spectra were recorded on a Perkin Elmer 781 spectrophotometer. The far-IR spectrum was recorded by using a Nicolet 170 SX FT-IR instrument, and a Perkin-Elmer LS5 luminescence spectrometer was used for emission measurements. A Pye-Unicam SP8-100 instrument was used to record UV–visible spectra of the compounds, and NMR spectra were recorded on a Burker CW 80 MHz instrument. Cyclic voltametric experiments were carried out by using a PAR Model 174A polarographic analyzer, a Model 175 universal programmer, a Model RE 0074 X-Y recorder, and a Model 377A cell system. A glassy-carbon working electrode, platinum-wire auxiliary electrode, and a saturated calomel electrode were used for cyclic voltammetric measurements. 2,2′-Bipyridine, di-2-pyridyl ketone, silver perchlorate, and methyl iodide were purchased from Aldrich and used without further purification. Ru(bpy)$_2$Cl$_2$ (bpy = 2,2′-bipyridine) was synthesized by a literature-reported procedure.[11]

Synthesis of Ru(dpk)$_2$Cl$_2$·2H$_2$O (1) and [Ru(dpk)(CO)Cl$_2$(DMF)]·2H$_2$O (2). RuCl$_3$·3H$_2$O (1 g, 3.8 mmol) and di-2-pyridyl ketone (1.47 g, 8 mmol) were mixed in 25 mL of DMF under N_2 and heated under reflux for 3 h. The reaction mixture was allowed to cool and DMF partly removed under vacuum. Acetone (10 mL) was then added and the dark-colored solution kept at 0 °C overnight. A dark blue precipitate of **1** was obtained, which was collected by filtration, washed repeatedly with acetone, and dried under vacuum (1 mm). Yield = 1.3 g (60%).

Anal. Calcd for $\mathrm{RuC_{22}H_{20}N_4O_4Cl_2}$: C, 45.8; H, 3.5; N, 9.7. Found: C, 45.6; H, 3.4; N, 10.1. A 1 × 10^{-3} M solution in DMF of **1** was nonconducting.

The filtered solution was evaporated to dryness, and the residual solid was crystallized from CH$_3$CN. Dark wine red crystals of (2) were obtained, which were collected by filtration and dried under vacuum (1 mm). Yield = 0.18 g (~10%).

Anal. Calcd for $\mathrm{RuC_{15}H_{19}N_3O_5Cl_2}$: C, 36.3; H, 3.8; N, 8.5. Found: C, 36.3; H, 3.5; N, 8.8. A 1 × 10^{-3} M solution of **2** in DMF was nonconducting.

Direct Synthesis of [Ru(dpk)(CO)Cl$_2$(DMF)]·2H$_2$O (2). RuCl$_3$·3H$_2$O (1 g, 3.8 mmol) and di-2-pyridyl ketone (0.7 g, 4 mmol) were mixed in 25 mL of DMF under N_2 and heated under reflux for 3 h. The red reaction mixture was allowed to cool and DMF was completely removed under vacuum (1 mm). The residue was dissolved in CHCl$_3$ and the insoluble portion, which was almost entirely Ru(dpk)$_2$Cl$_2$, was separated by filtration. The chloroform solution was concentrated and left overnight at 0 °C after addition of a small amount of ether. Deep red crystals of **2** were obtained, which were collected and dried under vacuum (1 mm). Yield = 0.94 g (50%).

Preparation of [Ru(dpk)$_2$(CH$_3$CN)$_2$](ClO$_4$)$_2$·2H$_2$O (3). Ru(dpk)$_2$Cl$_2$ (0.2 g, 0.35 mmol) and AgClO$_4$ (0.18 g, 0.86 mmol) were refluxed in 20 mL of CH$_3$CN under N_2 for 2 h. A red-violet solution was obtained, which was filtered to remove the suspended AgCl. The filtrate was concentrated and crystallized with the addition of a small amount of ether. A crop of maroon crystals were obtained, which was collected and dried under vacuum (1 mm). Yield = 0.23 g (85%). Anal. Calcd for $\mathrm{RuC_{26}H_{26}N_6O_{12}Cl_2}$: C, 39.7; H, 3.3; N, 10.7. Found: C, 39.8; H, 3.1; N, 10.5. A 1 × 10^{-3} M solution of **3** in DMF had a conductivity of 110 Ω^{-1} indicating a 1:2 electrolyte.

Preparation of [Ru^{II}(dpk)$_2$](ClO$_4$)$_2$·3H$_2$O (4). Ru(dpk)$_2$Cl$_2$ (0.2 g, 0.35 mmol) and AgClO$_4$ (0.18 g, 0.86 mmol) were refluxed in dry acetone under N_2 for 2 h to give a pink-violet solution, which was filtered to remove AgCl. The filtrate on cooling to 0 °C deposited dark violet crystals. Yield = 0.14 g (55%). Anal. Calcd for $\mathrm{RuC_{22}H_{22}N_4O_{13}Cl_2}$: C, 36.5; H, 3.0; N, 7.8. Found: C, 36.2; H, 3.2; N, 8.2. Conductivity of a 1 × 10^{-3} M solution of **4** in DMF was 125 Ω^{-1} indicating a 1:2 electrolyte.

Preparation of [Ru(bpy)$_2$(dpk)]Cl$_2$·3H$_2$O (5). Ru(bpy)$_2$Cl$_2$ (0.484 g, 1 mmol) was dissolved in 20 mL of dry EtOH and dipyridyl ketone (0.202 g, 1.1 mmol) was added. The reaction mixture was refluxed for 3 h under N_2. At the end of the period, the solution was concentrated and cooled to 0 °C to give dark red crystals, yield = 0.55 g (76%). Anal. Calcd for $\mathrm{RuC_{31}H_{30}N_6O_4Cl_2}$: C, 51.5; H, 4.1; N, 11.6. Found: C, 51.5; H, 4.2; N, 11.3. Conductivity of a 1 × 10^{-3} M solution of **5** in DMF was 115 Ω^{-1} indicating a 1:2 electrolyte.

The corresponding hexafluorophosphate salt could be prepared by dissolving the chloride in EtOH and adding excess NH$_4$PF$_6$ in EtOH. A brick red precipitate of [Ru(bpy)$_2$dpk](PF$_6$)$_2$ was obtained, which was

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dried under vacuum (1 mm). Yield = 0.64 g (90%).

Preparation of [Ru(dpk·H_2O)$_2$](ClO_4)$_2$·4H_2O (6). Ru(dpk)$_2$$Cl_2$ (0.2 g, 0.35 mmol) and $AgClO_4$ (0.18 g, 0.86 mmol) were refluxed in 15 mL of degassed H_2O under N_2 for 1 h. A pink solution was obtained at this stage with precipitation of white AgCl. The reaction mixture was filtered under N_2, and excess sodium perchlorate was added. The solution was then concentrated and cooled when dark-colored crystals started to deposit. The crystals were collected and dried under vacuum (1 mm). Yield = 0.12 g (46%).

Anal. Calcd. for $RuC_{22}H_{28}N_4O_{16}Cl_2$: C, 34.0; H, 3.6; N, 7.2. Found: C, 34.0; H, 3.5; N, 7.5. The conductivity of a 1 × 10^{-3} M solution of **6** in DMF was 120 Ω^{-1} indicating a 1:2 electrolyte.

Preparation of [Ru^{III}(dpk·OH)$_2$]ClO_4·2H_2O (7). The pink solution obtained in the above procedure turned to yellow on heating in air. The reaction mixture was filtered to remove AgCl, and excess sodium perchlorate was added. The solution was concentrated and cooled. Pale yellow crystals were obtained, which were collected and dried under vacuum (1 mm). Yield = 0.85 g (38%). Anal. Calcd for $RuC_{22}H_{22}N_4O_{10}Cl$: C, 41.3; H, 3.4; N, 8.8. Found: C, 41.5; H, 3.3; N, 8.7. The conductivity of a 1 × 10^{-3} M solution of **7** in DMF was 65 Ω^{-1} indicating a 1:1 electrolyte.

Preparation of [Ru(dpk·OCH_3)$_2$]ClO_4·2H_2O (8). Ru(dpk)$_2$$Cl_2$ (0.2 g, 0.35 mmol) and $AgClO_4$ (0.18 g, 0.86 mmol) were refluxed in MeOH under N_2 for 3 h to give a yellow solution. The solution was filtered to remove the suspended AgCl, and the filtrate was taken to dryness. The solid residue was crystallized from acetone to give pale yellow crystals, which were collected and dried under vacuum (1 mm). Yield = 0.12 g (52%). Anal. Calcd for $RuC_{24}H_{26}N_4O_{10}Cl$: C, 43.2; H, 3.9; N, 8.4. Found: C, 42.9; H, 3.6; N, 8.5. The conductivity of a 1 × 10^{-3} M solution of **8** in DMF was 61 Ω^{-1} indicating a 1:1 electrolyte.

Synthesis of 1,1-Di-2-pyridylethanol (LH) (9). MeMgI was first prepared by adding an ether solution of MeI (3.408 g, 24 mmol) dropwise under N_2 to Mg turnings (0.86 g, 25 mmol) in a three-necked flask cooled in an ice bath. Di-2-pyridyl ketone (2.20 g, 12 mmol) was dissolved in dry ether in a two-necked flask under N_2, and the ether solution of MeMgI was transferred to this flask through syringe under N_2 pressure. The reaction mixture was stirred for 2 h at room temperature, and 20 mL of 20% NH_4Cl was then added slowly. The reaction mixture was extracted repeatedly with ether, and the combined ether extracts were washed three times with 20% NH_4Cl solution. The ether extract was then dried over anhydrous Na_2SO_4, and the solvent was removed to yield a viscous liquid. Yield = 1.830 gms (76%). NMR ($CDCl_3$) δ (ppm relative to TMS): 1.97 (s, CH_3), 7.07 (m, 1 H), 7.7 (m, 2 H), 8.45 (m, 1 H).

Preparation of [Ru^{II}(LH)$_2$]Cl_2·2H_2O (10). $RuCl_3$ (0.135 g, 0.5 mmol) and 1,1-di-2-pyridylethanol (0.22 g, 1.1 mmol) were dissolved in 15 mL of dry and degassed ethanol. The reaction mixture was refluxed for 16 h under N_2 leading to a dark red solution. The solution was cooled to room temperature and filtered under N_2 to get a clear solution. The clean dark solution was concentrated and cooled and dark brown crystals were obtained. The crystals were collected and dried under vacuum (1 mm). Yield = 0.17 g (56%). Anal. Calcd for $RuC_{24}H_{28}N_4O_4Cl_2$: C, 47.4; H, 4.6; N, 9.2. Found: C, 47.2; H, 4.6; N, 8.9. The conductivity of a 1 × 10^{-3} M solution of **10** in DMF was 112 Ω^{-1} indicating a 1:2 electrolyte.

Preparation of [Ru^{III}L_2]ClO_4·2H_2O (11). To the dark red solution obtained in the above procedure, was added 6 mL of a saturated solution of $NaClO_4$ in EtOH. The solution was then concentrated by heating in air when the color changed to yellow. The solution on cooling gave yellow crystals, which were collected and dried under vacuum (1 mm). Yield = 0.16 g (52%). Anal. Calcd for $RuC_{24}H_{26}N_4O_8Cl$: C, 45.4; H, 4.1; N, 8.8. Found: C, 45.6; H, 3.9; N, 8.7. The conductivity of a 1 × 10^{-3} M solution of **11** in DMF was 62 Ω^{-1}, indicating a 1:1 electrolyte.

Results and Discussions

Preparation of the Complexes. The precursor to most of these complexes, Ru(dpk)$_2$$Cl_2$, was synthesized by the procedure reported by Meyer et al.[11] Stoichiometric amounts of $RuCl_3$·3H_2O and dpk were reacted in DMF (DMF = dimethylformamide) for 3 h under N_2 and Ru(dpk)$_2$$Cl_2$ (**1**) was formed in high yields. However small amounts of the carbonylated compound Ru(dpk)(CO)Cl_2(DMF) were also produced (see Experimental Section) from this reaction. The formation of the carbonylated complex is not surprising as such complexes have been reported to be formed with $RuCl_3$ and 6,6′-dimethylbipyridine in DMF, under conditions similar to ours.[12] The hindered dipyridyl ketone ligand greatly favors DMF decarbonylation. The compound Ru(dpk)(CO)Cl_2(DMF) (**2**) could also be produced in high yield by reacting $RuCl_3$·3H_2O with molar equivalents of dpk in DMF.

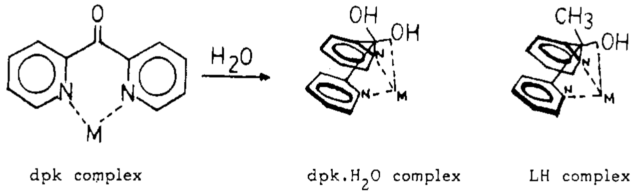

Figure 1. Possible structures for metal complexes of dpk, dpk·H_2O, and LH.

The bis(acetonitrile) compound [Ru(dpk)$_2$(CH_3CN)$_2$]$^{2+}$ (**3**) could be readily prepared by solvolysis of the corresponding dichloro compound in the presence of Ag^+ in CH_3CN.[13] All attempts to substitute acetonitrile in the bis(acetonitrile) complex with other ligands, like bpy, dpk, or acetone, failed to give any reaction. The compound was inert to thermal substitution even under quite severe conditions. We thought that it would be easier to replace acetone with other ligands in the bis(acetone) compound, [Ru(dpk)$_2$(acetone)$_2$]$^{2+}$, which could then act as a precursor for tris-chelated complexes. In order to synthesize [Ru(dpk)$_2$(acetone)$_2$]$^{2+}$, Ru(dpk)$_2$$Cl_2$ was refluxed with $AgClO_4$ in dry acetone for 2 h. However instead of the expected bis(acetone) compound, [Ru(dpk)$_2$](ClO_4)$_2$ (**4**), having two tridentate dpk ligands, was obtained in good yield. All attempts to react [Ru(dpk)$_2$]$^{2+}$ with bpy or dpk to produce tris-chelated complexes failed to give any reaction. Methods based on reduced forms of ruthenium chloride or on "ruthenium blue"[14] and used previously by others to prepare tris-chelated ruthenium(II) complexes of sterically hindered diimine ligands[15,16] also turned out to be unsuccessful with dpk. It appears that it is not possible to coordinate more than two chelating dpk ligands on to a Ru(II) center because of its steric bulk, and a tris-chelated complex like [Ru(dpk)$_2$(bpy)]$^{2+}$ is also not favored. Interestingly [Ru(bpy)$_2$(dpk)]$^{2+}$ (**5**) could be synthesized quite readily by refluxing Ru(bpy)$_2$$Cl_2$ with dpk in EtOH.

Attempts to prepare a diaquo complex of the type [Ru(dpk)$_2$(H_2O)$_2$]$^{2+}$ by hydrolysis of the corresponding dichloro compound in the presence of Ag^+ did not succeed owing to a competing reaction of addition of H_2O to coordinated dpk to produce [Ru(dpk·H_2O)$_2$](ClO_4)$_2$ (**6**). Such additions of water across the ketone of a N,N-coordinated dpk to produce *gem*-diols have been reported earlier.[17] The disposition of OH groups in the coordinated *gem*-diol can provide an opportunity for tridentate chelation through the OH group[18] (See Figure 1).

Although in the absence of X-ray crystallographic data the structure of [Ru(dpk·H_2O)$_2$](ClO_4)$_2$ (**6**) remains uncertain, it is possible to have tridentate chelation of dpk·H_2O as described in Figure 1. Interestingly **6** undergoes spontaneous oxidation in solution on heating in air with the simultaneous loss of H^+ to produce yellow [Ru(dpk·OH)$_2$]ClO_4 (**7**). A reaction similar to that in water takes place in methanol to produce [Ru(dpk·OCH_3)$_2$]ClO_4 (**8**). In an attempt to understand the process of oxidation of **6** to **7**, we have synthesized a related ligand 1,1-di-2-pyridyl ethanol (LH) and prepared its ruthenium complex [Ru(LH)$_2$]Cl_2 (**10**) (see Experimental Section). It is to be noted that the coordination behavior of LH and dpk·H_2O in metal complexes are expected to be very similar (Figure 1). Attempts to isolate **10** as a perchlorate salt led to spontaneous oxidation to produce [RuL_2]ClO_4 (**11**). In a recent paper from this laboratory, the copper complex of LH and its oxidation product have been characterized by X-ray structure determinations.[19] We find

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Table I. Absorption Spectra and Electrochemical Properties of Di-2-pyridyl Ketone Complexes of Ruthenium in Dimethylformamide

compd	λ_{max} ($10^{-3}\epsilon$)[a]	$E^{3+/2+}$ [b]	$E^{2+/+}$ [c]
$Ru(bpy)_3^{2+}$	451 (14), 345 (6.5), 323 (6.5)	1.29	−1.31
$Ru(bpy)_2Cl_2$	550 (9.0), 375	0.30[c]	
$Ru(dpk)_2Cl_2$	590 (4.5), 398 (5.1), 277 (9.1)	0.61	−1.06
$Ru(dpk)(CO)Cl_2(DMF)$	539 (2.9), 366 (9.8)	0.88	−0.79
$[Ru(dpk)_2(CH_3CN)_2]^{2+}$	535 (7.4), 365 (14.1)	1.31	−0.81
$[Ru(dpk)_2]^{2+}$	703 (4.4), 512 (7.0)	1.31	−1.32
$[Ru(bpy)_2(dpk)]^{2+}$	498 (8.2), 424 (8.5), 286 (40.0)	1.34	−0.82
$[Ru(dpk{\cdot}H_2O)_2]^{2+}$	382 (0.6)		
$[Ru(dpk{\cdot}OH)_2]^{+}$	427 (4.7), 366 (S), (12.8), 342 (14.7)	−0.89	
$[Ru(dpk{\cdot}OCH_3)_2]^{+}$	424 (4.3), 365 (S), 340 (14.0)	−0.45	
$[RuL_2]^{+}$	424 (S) (5.4), 375 (16.3), 352 (16.1)	−0.61	

[a] λ_{max} values are in nm; ϵ units in M^{-1} cm^{-1}. [b] Potentials are in V vs SSCE. S denotes shoulder. [c] Taken from: Johnson, E. C.; Sullivan, B. P.; Salmon, D. J.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 2211.

that LH acts as a tridentate ligand for the mononuclear copper center as depicted in Figure 1, and oxidation of the copper complex is accompanied by a simultaneous loss of H^+ from the coordinated ligand. It is possible that the ruthenium complexes of LH and $dpk{\cdot}H_2O$, **10** and **6**, have similar tridentate coordination through the two pyridyl N'S and the hydroxy group (Figure 1). The oxidation of the ruthenium complexes **6** and **10** involve simultaneous deprotonation of the coordinated ligand as has been observed by an X-ray structure determination for the copper complex.[19] Consequently the oxidized complexes **7**, **8**, and **11** possibly have a tridentate alkoxide coordinated to the metal center. The oxidation of **6** to **7** has been followed by NMR. The NMR spectrum of $[Ru(dpk{\cdot}H_2O)_2](ClO_4)_2$ in $(CD_3)_2CO$ had peaks at 7.77 (m), 8.25 (m), and 8.90 ppm (m), corresponding to coordinated pyridine ligands. The solution when warmed in air turned yellow, and the NMR signals completely disappeared. Although the failure to observe an NMR signal for **7** could be a result of a trace Ru(III) impurity, the NMR results coupled with the conductivity data indicating a 1:1 electrolyte suggest **7** to be a Ru(III) compound.

Spectroscopic Properties. The infrared spectrum of $Ru(dpk)_2Cl_2$ has a ν_{CO} peak at 1665 cm^{-1}. The insignificant shift of the carbonyl stretching frequency in the compound from that of the free dipyridyl ketone (1690 cm^{-1}) suggests a N,N-coordination of the ligand.[17] ν_{Ru-Cl} peaks are observed at 291 and 315 cm^{-1} showing that the Cl's are indeed coordinated to the ruthenium atom. Comparable values have been observed for $Ru(bpy)_2Cl_2$.[20] $Ru(dpk)_2Cl_2$ also has two peaks at 246 and 258 cm^{-1} due to $\nu_{RuN(py)}$,[21] which suggest a cis configuration for the $Ru(dpk)_2$ coordination plane. Only one RuN–(pyridine) stretch would be expected if it had a trans configuration.[22]

$Ru(dpk)(CO)Cl_2(DMF)$ has a terminal ν_{CO} peaks at 1950 cm^{-1} and a peak at 1680 cm^{-1} corresponding to the C=O of N,N-coordinated dpk. Comparable terminal ruthenium carbonyl frequencies have been observed earlier for $RuL(CO)Cl_2(DMF)$ (L = 6,6′-dimethylbipyridine).[12] All the dpk complexes display many characteristic peaks for N,N-coordinated dpk; these are not considered further. $[Ru(dpk)_2(CH_3CN)_2](ClO_4)_2$ and the other perchlorato complexes show bands at 1100 and 620 cm^{-1} due to ClO_4^- and at 3400 cm^{-1} due to H_2O. The complexes derived from LH, $dpk{\cdot}H_2O$, and $dpk{\cdot}OCH_3$, as expected, do not have any ν_{CO} peaks in the infrared spectra.

The visible absorption maxima of the complexes are given in Table I. The intense low-energy absorption bands observed in $Ru(bpy)_2X_2$ (X = halide, CN^-, etc.) have been assigned to metal-to-ligand charge-transfer (MLCT) transitions of the type $d\pi(Ru) \rightarrow \pi^*(bpy)$.[23,24] By analogy, the high extinction coefficients measured for the visible bands of $Ru(dpk)_2Cl_2$ in Table I strongly suggest the MLCT nature of the corresponding transitions. Di-2-pyridyl ketone being a stronger π acceptor ligand than bpy induces a red shift (40 nm) of the MLCT band from the corresponding bpy complexes. The $\pi \rightarrow \pi^*$ transitions characteristic of the coordinated diimine ligands occur in the UV region of the spectra. The energy of the MLCT transition in the dpk complexes is also dependent on the nature of the ancillary ligands coordinated at the cis position. Thus a large blue shift occurs on replacing Cl^- by the strong π acceptor CH_3CN in $[Ru(dpk)_2(CH_3CN)_2]^{2+}$. Some typical electronic spectra are shown in Figure 2. The spectrum of $[Ru(bpy)_2(dpk)]^{2+}$ has two intense low-energy absorptions at 498 and 424 nm. It is interesting to note that the distinction between the MLCT transitions involving the two different ligands is clear, with the $d\pi \rightarrow \pi^*(dpk)$ transition occurring at a lower energy than the corresponding $d\pi \rightarrow \pi^*(bpy)$ transition. However the luminescence spectrum of the compound at room temperature in DMF shows only a single emission peak at 710 nm. The low energy of the emission suggests that the emitting excited state in $[Ru(bpy)_2(dpk)]^{2+}$ is of MLCT nature.[25]

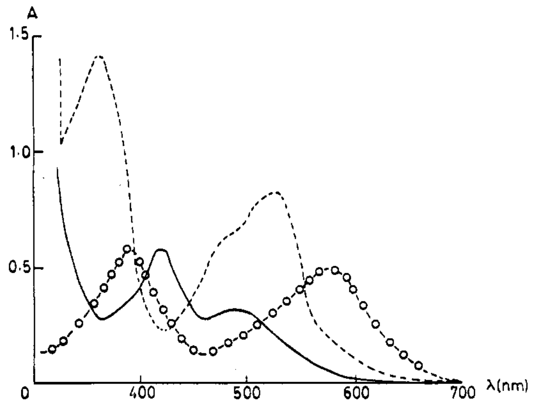

Figure 2. Visible absorption spectra of 1 × 10^{-4} M solutions in DMF of $Ru(dpk)_2Cl_2$(-O-), $[Ru(dpk)_2(CH_3CN)_2]^{2+}$ (---), and $[Ru(bpy)_2(dpk)]^{2+}$ (—).

The visible absorption bands in $[Ru(dpk)_2]^{2+}$ (**4**) are red shifted by about 110 nm from that in $Ru(dpk)_2Cl_2$. This large red shift is due to the coordination through the C=O group in dpk, which considerably lowers the electron density on the bound ligand. The absorption spectra of the Ru(II) complexes indicate that, for the dpk ligand, strong electronic coupling exists between the rings due to the ketonic bridging group. Since upon hydration the bridging carbon should become tetrahedral, the absorption spectra of $[Ru(dpk{\cdot}H_2O)_2]^{2+}$ look very much like those of pyridine complexes where the metal–ligand charge-transfer bands shift to higher energies and extinction coefficients decrease. The spectra of the ruthenium(III) complexes **7**, **8**, and **11** are very similar and have absorption peaks around 425 nm that can be assigned to ligand-to-metal charge-transfer transition.

Electrochemical Properties. The redox properties of the complexes are summarized in Table I. $E_{1/2}$ values were determined by cyclic voltammetry, and the differences in peak positions ΔE_p, $\Delta E_p = E_p(ox) - E_p(red)$, were scan rate dependant. Plots of the square root of the sweep rate vs ΔE_p gave intercepts that varied from 60 to 70 mv, indicative of reversible one-electron-transfer processes.[26] The uncoordinated ligand dpk is reduced at −1.33 V whereas the coordinated ligand in $[Ru(dpk)_2(CH_3CN)_2]^{2+}$ is

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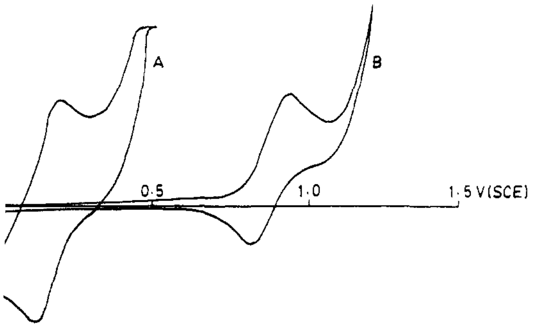

Figure 3. Cyclic voltammograms of (A) $Ru(dpk)_2Cl_2$ and (B) $[Ru(bpy)_2(dpk)]^{2+}$. Conditions: glassy-carbon electrode: scan rate 100 mv/s; DMF-TEAP (0.1 N) solution.

reduced at −0.81 V versus SCE. This is consistent with the reported data for ruthenium heterocyclic complexes where the free ligand is reduced at more negative potentials than when coordinated to ruthenium(II).[27] For the mixed-ligand complex $[Ru(bpy)_2(dpk)]^{2+}$, reduction occurs first at dpk, which has a lower π^* level than bpy, and the pattern of reduction is

$$[Ru(bpy)_2(dpk)]^{2+} + e^- \rightarrow [Ru(bpy)_2(dpk^-)]^+$$
$$E_{1/2} = -0.82 \text{ V}$$

The cyclic voltammograms of two representative dpk complexes are shown in Figure 3. As reported earlier, for MLCT excited states where excited-state distortion is relatively small, excited-state redox potentials can be estimated from ground-state redox potentials and the excited-state emission energy by $E_{1/2}{}^{3+/2+*} = E_{1/2}{}^{3+/2+} - E_{Em}$ and $E_{1/2}{}^{2+*/+} = E_{1/2}{}^{2+/+} + E_{Em}$.[28] By this calculation, for $[Ru(bpy)_2(dpk)]^{2+}$, $E(Ru^{3+/2+*}) = -0.41$ V and $E(Ru^{2+*/+}) = 0.93$ V. The data suggests that $[Ru(bpy)_2(dpk)]^{2+*}$ is a poor reductant compared to $[Ru(bpy)_3]^{2+*}$ but is a better oxidant due to enhanced $d\pi-\pi^*$ interaction.

For the Ru(III) complexes **7**, **8**, and **11**, irreversible oxidation peaks were observed at 1.3, 1.33, and 1.14 V, respectively. These are possibly ligand-based oxidations, and oxidative degradation of the ligand leads to irreversibility.

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Registry No. **1**, 116971-19-8; **2**, 116971-20-1; **3**, 116971-22-3; **4**, 116971-24-5; **5**, 116971-25-6; **6**, 116971-27-8; **7**, 116971-29-0; **8**, 116971-31-4; **9**, 29280-39-5; **10**, 116971-32-5; **11**, 116971-34-7; DMF, 68-12-2; $Ru(bpy)_2Cl_2$, 15746-57-3; $[Ru(bpy)_2(dpk^-)]^+$, 116971-35-8; $Ru(bpy)_3{}^{2+}$, 15158-62-0; di-2-pyridyl ketone, 19437-26-4.

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Hexaaza Macrocyclic Metal Complexes Containing Biimidazole. 1. Synthesis and Characterization of Nickel(II), Copper(II), and Palladium(II) Complexes of 2,7-Dimethyl-3-6-(1,1′-(2,2′-biimidazolo))-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene

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New Ni(II), Cu(II), and Pd(II) metal complexes of the macrocycle 2,7-dimethyl-3-6-(1,1′-(2,2′-biimidazolo))-1,3,6,8,11,14-hexaazacyclohexadeca-1,7-diene have been synthesized and characterized. The Pd(II) complex, which is proposed to contain three 5-membered rings, one 9-membered ring, and two imine linkages, was obtained as an air-stable, insoluble, yellow, diamagnetic compound. Corresponding orange to blue Ni(II) complexes were obtained as the diamagnetic iodide or perchlorate species and paramagnetic chloro and bromo complexes. The Cu(II) complex was obtained as a blue paramagnetic perchlorate complex. FT-IR, NMR, and electronic spectral data have been used to confirm macrocycle formation from metal–trien complexes reacting with 1,1′-diacetyl-substituted 2,2′-biimidazole in water/dioxane or 2-propanol/dioxane mixtures at pH 5. The formation of these amorphous complexes demonstrates how ring formation can be achieved over 1,1′-diacetyl-2,2′-biimidazole hydrolysis due to the metal ion template effect.

Introduction

Metal template syntheses of multidentate and macrocyclic ligands have been established over the last two decades as offering high-yielding and selective routes to new ligands and their complexes.[1] Transition-metal complexes involving triethylenetetramine (trien) have received a large amount of attention because of the several configurations in which the tetradentate ligand can coordinate metal centers.[2-4] Considerable attention has also been given to the metal complexing ability of 2,2′-biimidazole.[5-8] Because of the ease of formation of alkanyl derivatives of 2,2′-biimidazole,[9] the formation of polydentate Schiff-base ligands is made possible by the reaction of metal–trien complexes with derivatives of biimidazole. In this paper we report the preparation and spectral characterization of three new 16-membered macrocyclic complexes based on the reaction of 1,1′-diacetyl-2,2′-biimidazole (I) and Ni(II)–, Cu(II)–, and Pd(II)–triethylene-

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