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Tris Complexes of Ruthenium(II) with 2-(2-pyridyl)-1,8-naphthyridine and 5,6-dihydrodipyrido-[2,3-b:3′,2′-j]-1,10-phenanthroline. Syntheses, Spectroscopic and Electrochemical Characterization

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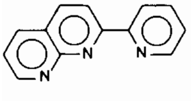
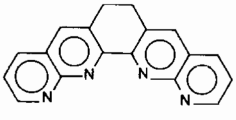
Ruthenium(II) complexes with empirical formula $[Ru(pynapy)_3](PF_6)_2$ and $[Ru(dinapy)_3](PF_6)_2$ where pynapy is 2-(2-pyridyl)-1,8-naphthyridine and dinapy is 5,6-dihydrodipyrido-[2,3-b:3′,2′-j]-1,10-phenanthroline have been prepared. Room temperature electronic absorption spectra, emission spectra and lifetimes at 77 K along with cyclic voltammetric data for these complexes are reported and compared with those for $Ru(bpy)_3^{2+}$.

Introduction

Current interest in $Ru(bpy)_3^{2+}$ stems from its luminescence [1], photosensitization of electron and energy transfer processes [2], photochemistry [3], and from its photocatalytic role in solar energy conversion [4]. Such interest has prompted the investigation of a variety of related ruthenium polypyridine complexes which have included tris-chelated ruthenium(II) complexes with substituted bipyridines [5], mixed ligand Ru(II) complexes of the form $Ru(bpy)_2L^{2+}$ where L is a chelating nitrogen donor ligand [5, 6], and trisubstituted Ru(II) complexes with bidentate nitrogen heterocycles [7]. As part of our current investigations [8] of the ligating ability of multidentate, substituted 1,8-naphthyridines, tris complexes with 2-(2-pyridyl)-1,8-naphthyridine (pynapy) and 5,6-dihydrodipyrido[2,3-b:3′,2′-j]-1,10-phenanthroline (dinapy) have been prepared. The ligands are represented by the following structures:



pynapy



dinapy

The present paper describes the syntheses, the absorption, emission and electrochemical properties of these complexes in comparison with those of $Ru(bpy)_3^{2+}$.

Experimental

Materials

Ruthenium trichloride trihydrate was used as obtained from Aldrich Chemical Co., Inc. $K_2[RuCl_5(H_2O)]$ [9], 2-(2-pyridyl)-1,8-naphthyridine (pynapy) [10] and 5,6-dihydrodipyrido[2,3-b:3′,2′-j]-1,10-phenanthroline (dinapy) [11] were synthesized following published procedures. Ligand purity was ascertained by melting point and mass spectral data. Spectrophotometric grade acetonitrile and methanol were used without further purification unless stated otherwise. Tetra-n-butylammonium perchlorate (TBAP) was recrystallized from ethyl acetate and dried in a vacuum dessicator over P_2O_5. All other materials used were analytical reagent grade.

Preparation of Complexes

$[Ru(pynapy)_3](PF_6)_2$

Pynapy (91 mg) was dissolved in 3 ml of glycerol and added to a dark green solution of ruthenium complex prepared by suspending $K_2[RuCl_5(H_2O)]$ (41 mg) in 7 ml of glycerol and heating at 95–100 °C for 24 hours. The resultant deep red solution was heated further at 70 °C for 1 day. Saturated aqueous NH_4PF_6 solution and 20 ml water were added to precipitate a red solid which was collected by vacuum filtration, washed well with water, alcohol and ether,

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and then air-dried. The product was dissolved in dichloromethane and reprecipitated by addition of anhydrous ether. The fine powder recovered was vacuum-dried for one day. Yield, 88%. *Anal.* Calcd. for $[Ru(C_{13}H_9N_3)_3](PF_6)_2$: C,46.26; H, 2.69; N, 12.45. Found: C, 46.41, H, 2.94; N, 12.59.

$[Ru(dinapy)_3](PF_6)_2 \cdot H_2O$

The procedure described above for $[Ru(pynapy)_3](PF_6)_2$ was used to synthesize the dark blue tris-chelated dinapy complex. Yield, 94%. *Anal.* Calcd. for $[Ru(C_{18}H_{12}N_4)_3](PF_6)_2 \cdot H_2O$: C, 51.39; H, 3.03; N, 13.32. Found: C, 51.16; H, 2.98; N, 13.32.

Physical Measurements

Elemental analyses were done by Schwartzkopf Microanalytical Laboratory. UV and visible spectra were recorded on either a Cary 14 or Cary 15 spectrophotometer with 1-cm quartz cells at room temperature. Molar extinction coefficients were calculated from a least-squares linear regression of absorbance data at four different concentrations. Molar conductivities, Λ_M, were determined for 1 mF solutions of the complexes in acetone using a conductivity meter type CDM 2e No. 191500 (The London Company). Cyclic voltammetry was performed with a Chemtrix polarographic potentiostat (type 201) and an amplifier (type 300) unit. A conventional three-electrode cell was employed with a Pt ball working electrode, a Pt wire auxiliary electrode, and an aqueous saturated sodium chloride calomel electrode (SSCE) as reference. The solvent employed was spectrophotometric grade acetonitrile previously dried over 4 Å molecular sieves. The solutions were 5×10^{-4} *M* ruthenium complex in 0.1 *M* TBAP–CH_3CN, and were deaerated with argon. $E_{1/2}$ values were taken as the average of the anodic and cathodic peak potentials. Electrochemical reversibility was judged on the basis of the following [12]: (a) the separation of the anodic and cathodic peak potentials (ΔE_p) is 59/n mV where n is the number of electrons involved in the redox process; (b) the ratio of the anodic and cathodic peak currents ($_ai_p/_ci_p$) is unity. $[Ru(bpy)_3](PF_6)_2$ was used as the standard in the reversibility experiments. Potential-step coulometry to determine n values from Faraday's law was performed using a platinum thin-layer electrode described elsewhere [13]. Luminescence spectra of the ligands were obtained with a Perkin-Elmer Model MPF-3 fluorescence spectrophotometer while the emission spectra of the complexes were measured as described previously [14] with a few modifications: a Corning CS 7-60 filter was used to improve spectral purity and intensity corrections were done using a Digital PDP 11 computer. The excitation wavelength was 365 nm. Luminescence lifetimes were measured in EtOH/MeOH glass at 77 K using the 3rd harmonic of a Nd-YAG laser, a Perkin Elmer dense flint prism monochromator, an EMI 9808B photomultiplier tube (S-1 response) and a Tektronix 7904 oscilloscope with 7B85 time base and 7A13 amplifier terminated at 50 Ω. The traces were photographed and the mean of 3 least squares fitted values are reported.

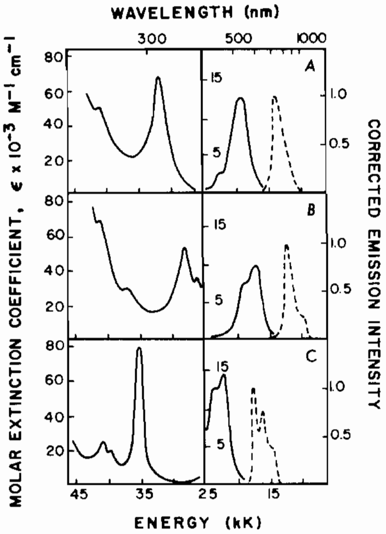

Fig. 1. Room temperature absorption (——) and low temperature (77 K) emission (------) spectra of complexes: A, $Ru(pynapy)_3^{2+}$; B, $Ru(dinapy)_3^{2+}$; C, $Ru(bpy)_3^{2+}$.

Results and Discussion

The tris complexes were readily obtained in excellent yields with glycerol as the reducing medium. The analytical results and conductivity data [15] support the $[RuL_3]^{2+}2PF_6^-$ formulation of the complexes. The compounds are intensely colored, air-stable and soluble in common organic solvents like acetone, dichloromethane and acetonitrile. Staniewicz and Hendricker [9] have prepared tris and tetrakis Ru(II) complexes with 2,7-dimethyl-1,8-naphthyridine and 1,8-naphthyridine, respectively. In these complexes, the naphthyridine ligands presumably bind to the metal ion through the peri-nitrogen atoms to form a four-membered chelate ring. It was suggested that the facile acetonitrile solvolysis of the tetrakis complexes was a consequence of the strain in the four-membered ring. In view of the strain imposed by the short bite (2.2 Å) [9] of the naphthyridine nitrogen atoms, it seems likely that complexation of pynapy and dinapy to the metal ion occurs through the nitrogen atoms of the bipyridine moiety.

The absorption and emission spectra of $Ru(pynapy)_3^{2+}$ and $Ru(dinapy)_3^{2+}$ along with those of

TABLE I. Spectral Data for the Ligands and Corresponding Tris Complexes.

Compound	Absorption[a]	Emission[b]	
	ν_{max}, kK (10^{-4} ϵ_{max}, M^{-1} cm^{-1})	ν_{max}, kK	Lifetime, μs
pynapy	30.0(2.09), 31.3(2.29), 34.4(1.34) 35.6(1.49), 36.8(1.44), 41.0(3.38) 42.2(3.33)	22.0[c,d]	1.21×10^6 [d]
dinapy	27.5(2.75), 28.6(2.37), 36.4(1.13) 37.7(1.20), 43.9(4.23)	25.2[c], 20.7[c,d]	0.84×10^6 [d]
bpy	35.6(1.34), 42.9(0.96)[e]	23.0[e,d]	0.963×10^6 [f,d]
Ru(pynapy)$_3^{2+}$	19.0(1.25), 31.5(6.94), 40.8(5.03)	13.6	0.503
Ru(dinapy)$_3^{2+}$	17.1(0.99), 18.1sh(0.75), 25.6sh(3.15) 27.9(5.22), 36.8(3.03), 41.2(6.46)	11.9	0.179
Ru(bpy)$_3^{2+}$ [g]	22.2(1.40), 35.2(8.00), 39.5sh, 41.2(2.50)	16.4[h]	0.85[h]

[a] The room temperature absorption spectra of the ligands and the complexes in this study were measured in MeOH and CH_3CN, respectively. [b] The emission spectra (77 K) for all compounds studied were measured in EtOH–MeOH glasses (4:1; v/v). [c] Uncorrected emission maximum. [d] Phosphorescence. [e] From reference 26. [f] D. H. W. Carstens and G. A. Crosby, *J. Mol. Spectrosc.*, *34*, 113 (1970). [g] Reference 9. [h] P. J. DeLaive, J. T. Lee, H. W. Sprintschnik, H. Abruna, T. J. Meyer and D. G. Whitten, *J. Am. Chem. Soc.*, *99*, 7094 (1977).

Ru(bpy)$_3^{2+}$ are shown in Fig. 1. The positions of the absorption maxima and corresponding extinction coefficients as well as the emission maxima and lifetimes are summarized in Table I. Like its bipyridine analogue [1], Ru(pynapy)$_3^{2+}$ and Ru(dinapy)$_3^{2+}$ display prominent $t_{2g} \rightarrow \pi^*$ metal to ligand charge transfer bands in the visible region and intraligand bands in the ultraviolet. Relative to Ru(bpy)$_3^{2+}$, the MLCT band is shifted to progressively lower energies with an attendant decrease in band intensity in going from the pynapy to the dinapy complex. These shifts (3.2 and 5.1 kK) are much greater than those observed in analogous tris complexes with 2-(2′-pyridyl)quinoline [16] and 2,2′-biquinoline [16] in which benzene rings are fused to the bipyridine fragment of the ligands, and are consistent with stronger electron-withdrawing capacity of the additional nitrogen atoms in pynapy and dinapy. It has been proposed [16] that the red shifts in the quinoline complexes may result from either or both of two factors: (a) a decrease in the energy of the π^* level of the ligands compared to bpy, and (b) an increase in the energy of the metal ion (t_{2g}) orbitals in the complexes. The electrochemical data (*vide infra*) seem to indicate that both are operative in the complexes under study. It is also noted that there are parallel red shifts in the lowest energy intraligand π–π^* bands of the complexes relative to Ru(bpy)$_3^{2+}$ as expected for ligands with more extended aromatic π-systems [17].

The ligands pynapy and dinapy show strong visible emission at lower energies (22.0 and 20.7 kK, respectively) than bipyridine (23.0 kK) with phosphorescence lifetimes of 1.21 and 0.84 sec at 77 K. The emission band at 25.2 kK for dinapy is probably due to fluorescence. Like Ru(bpy)$_3^{2+}$, the pynapy and dinapy complexes undergo emission both in room temperature fluid and low temperature (77 K) glass solutions. Comparison of their emission spectra with that of Ru(bpy)$_3^{2+}$ reveals the following spectral changes: (1) the energy of the band maxima decreases in the order Ru(bpy)$_3^{2+}$ > Ru(pynapy)$_3^{2+}$ > Ru(dinapy)$_3^{2+}$; (2) while the emission band of Ru(bpy)$_3^{2+}$ in EtOH-MeOH glass displays 1.3 kK vibrational progression observed also in other related ruthenium compounds [5, 16], the emission band of the subject complexes, although unsymmetrical, are devoid of any structure under the same conditions; and (3) the emission lifetimes decrease in the same order as in (1). It is generally agreed that the emission of Ru(bpy)$_3^{2+}$ arises from a d–π^* MLCT excited state [18] although the assignment of the electronic structure of this state has been varied [19]. The emission bands of Ru(pynapy)$_3^{2+}$ and Ru(dinapy)$_3^{2+}$ are assigned similarly based on four considerations, namely, (1) the emission is too low in energy to arise from ligand fluorescence or phosphorescence; (2) Pynapy and dinapy are expected to provide a high crystal field strength such that the lowest d–d excited states are well above the ~14 kK emitting level [20]; (3) the correlation of the energy of the emission band with (i) the frequency of the visible CT absorption band; *i.e.* as the MLCT band decreases in energy in the order Ru(bpy)$_3^{2+}$ > Ru(pynapy)$_3^{2+}$ > Ru(dinapy)$_3^{2+}$, the emission band energy changes accordingly, and (ii) the first reduction potentials of the free ligands: *i.e.* as the reduction potential decreases in the order bpy > pynapy > dinapy, the

TABLE II. Cyclic Voltammetric Data for the Ligands and Tris Complexes.

Compound	$E_{1/2}$, V[a,b]				
	Oxidation	Reduction			
		I	II	III	IV
pynapy	none up to +2V	−1.66			
dinapy	none up to +2V	−1.33			
bpy	none up to +2V	−2.12[c]			
$Ru(pynapy)_3^{2+}$	1.08	−0.99	−1.23	−1.53	−1.87(i)
$Ru(dinapy)_3^{2+}$	0.97	−0.83	−1.06	−1.36	−1.71(i)
$Ru(bpy)_3^{2+}$	1.24	−1.34	−1.52	−1.75	−2.13(i)

[a] The halfwave potentials, $E_{1/2}$, were measured in 0.1 *M* TBAP–CH_3CN against SSCE at 23 ± 1 °C. The sweep rate was 100 mV/sec. [b] i = irreversible. [c] Reference 21.

emission energy decreases correspondingly; and (4) the excited state lifetimes are comparable to that for $Ru(bpy)_3^{2+}$.

Relevant electrochemical data for the ligands and complexes in 0.1 *M* TBAP–CH_3CN are compiled in Table II. Data for bpy and $Ru(bpy)_3^{2+}$ are included for comparison. All the three complexes display a reversible one-electron oxidation wave assignable to the Ru(III)/Ru(II) couple [21]. Since the oxidation of $Ru(bpy)_3^{2+}$ involves removal of an electron from the t_{2g} metal orbitals, the electrode potential provides evidence for the relative energy of the t_{2g} levels [9]. The half-wave potential for the Ru(III)/Ru(II) couple in the pynapy and dinapy complexes are 160 mV and 270 mV less anodic than for $Ru(bpy)_3^{2+}$. This implies that the t_{2g} levels in $Ru(pynapy)_3^{2+}$ and $Ru(dinapy)_3^{2+}$ are much higher than in $Ru(bpy)_3^{2+}$ and hence, may account in part for the decrease in energy of the MLCT absorption bands. Each complex shows three reversible one-electron reduction waves which, for $Ru(bpy)_3^{2+}$, correspond to the successive addition of an electron to the bipyridine ligand in the complex to form $[Ru(bpy)_2(bpy^-)]^+$, $[Ru(bpy)(bpy^-)_2]^0$ and $[Ru(bpy^-)_3]^{-1}$ [21, 22]. Whether the added electron resides in each bipyridine or is delocalized over the entire ligand system is still unresolved [23]. The pynapy and dinapy complexes are much more easily reduced relative to $Ru(bpy)_3^{2+}$ as reflected in the less negative potentials for the three reduction waves. For the former, the spacing between the successive reduction steps of 240 to 300 mV are larger than that for the corresponding spacing of 180 to 230 mV for $Ru(bpy)_3^{2+}$. The less cathodic potentials for the reduction of the pynapy and dinapy complexes imply that the LUMO(π^*) in these complexes are lower in energy than that in the bipyridine analogue. Likewise, this may account for the observed energy decrease of the MLCT absorption band. The fourth cathodic wave for $Ru(bpy)_3^{2+}$ has been assigned [21] to the reduction of free bipyridine labilized upon decomposition of the complex at extremely negative potentials. For the pynapy and dinapy complexes, the fourth wave is observed at potentials significantly more negative than the reduction of the free ligands; moreover, the spacing between this wave and the one immediately preceding it is comparable to the spacing between the first three successive reductions of the complexes. Consequently, the fourth reduction wave may be tentatively assigned to the addition of a fourth electron to the complex. This behavior is not unusual; for example, tris(4,4′-dicarboxyethyl-2,2′-bipyridine)ruthenium(II) which contains strongly electron-withdrawing CO_2Et substituents on bipyridine shows six quasi-reversible one-electron reduction waves [24].

It is altogether not surprising that the spectral and electrochemical behavior of $Ru(pynapy)_3^{2+}$ and $Ru(dinapy)_3^{2+}$ parallels that of $Ru(bpy)_3^{2+}$ since the pynapy and dinapy ligands may be viewed as pyrido-substituted bipyridines. However, it is observed that the shifts in the positions of the absorption and emission bands and in the redox potentials that have resulted from this substitution are quite pronounced and unique for the complexes under study. For example, the shifts in the absorption and emission band maxima are much greater than those observed for 2,2′-biquinoline [16], 4,4′-dimethyl-2,2′-bipyridine [24], 4,4′-diphenyl-2,2′-bipyridine [25], 6,6′-dimethyl-2,2′-bipyridine [5], 4-(triethylphosphonio)-2,2′-bipyridine [26] and 4-nitro-2,2′-bipyridine [26] indicative of the greater effect of pyrido-substitution on the bipyridine ligand.

In summary, the MLCT absorption bands and emission bands of $Ru(pynapy)_3^{2+}$ and $Ru(dinapy)_3^{2+}$ occur at much lower energies than those of

$Ru(bpy)_3^{2+}$; the lifetimes of their MLCT excited states are shorter. The +2/+3 oxidation potentials are shifted to less positive values suggesting less stabilization of the Ru^{2+} state by pynapy and dinapy. The +2/+1, +1/0, 0/−1 reduction potentials are much less negative indicating that $Ru(pynapy)_3^{3+}$ and $Ru(dinapy)_3^{3+}$ are significantly stronger oxidants than $Ru(bpy)_3^{3+}$. And lastly, a fourth reduction potential for each of the two complexes represents the formation of a −2 species not observed for $Ru(bpy)_3^{2+}$.

$Ru(pynapy)_3^{2+}$ and $Ru(dinapy)_3^{2+}$ display spectral and electrochemical properties similar to those of $Ru(bpy)_3^{2+}$. In view of the current interest in $Ru(bpy)_3^{2+}$ as a photosensitizer, the replacement of bipyridine ligands for pynapy and dinapy has yielded new complexes with modified properties that further increase the range of donor energies available for photosensitization processes.

Acknowledgements

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