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Preparation and Investigation of the Spectral and Electrochemical Properties of Mixed-Ligand Ruthenium(II) Complexes Containing 1,8-Naphthyridines[1]

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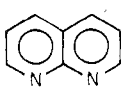
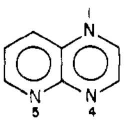
Mixed-ligand complexes of the form $Ru(bpy)_2L^{2+}$ and $Ru(phen)_2L^{2+}$, L = 1,8-naphthyridine (napy), 2,7-dimethyl-1,8-naphthyridine, 2-methyl-1,8-naphthyridine, and pyrido[2,3-*b*]pyrazine, have been prepared and isolated as their PF_6^- salts. The formulations were confirmed by elemental analysis and conductivity measurements while the purity of the compounds was judged by the single maximum observed in the ac polarograms. The solution spectra of the mixed-ligand complexes are characterized by a high-intensity ($\epsilon \sim 10^4$) metal-to-ligand charge-transfer band at ~450 nm and $\pi \rightarrow \pi^*$ intraligand UV transitions. The energies and intensities of these absorptions are compared with previously reported $Ru(bpy)_2X_2^{2+}$ complexes. The reduction potentials (Ru^{3+}/Ru^{2+}) for the napy mixed-ligand complexes were determined using both cyclic voltammetry and ac polarography and the reversibility of the electrochemical couples was established. The $E_{1/2}$ values do not vary greatly from those observed for the $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes thus indicating that the stability of the Ru(II) state has not been significantly altered by the replacement of a phen or bpy with a napy type ligand.

Introduction

The tris(2,2′-bipyridine) and tris(1,10-phenanthroline) complexes of ruthenium(II) have generated considerable interest due largely to their luminescence[3,4] and photogalvanic properties.[5] In addition to the aforementioned complexes, a large number of mixed-ligand complexes which contain these diimines have been synthesized and studied.[6,7] In the course of our investigations of the coordinating nature of the naphthyridines, we have prepared mixed-ligand complexes of the form $Ru(bpy)_2L^{2+}$ and $Ru(phen)_2L^{2+}$ where L = 1,8-naphthyridine (napy), 2-methyl-1,8-naphthyridine (2-mnapy), 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy), and pyrido[2,3-*b*]pyrazine (ppyz) and have examined their spectral and electrochemical properties. This work was undertaken in the hope that we could improve our understanding of the disposition of four-membered-ring chelating agents, especially when coordinated to a metal center exhibiting a high degree of metal-to-ligand π back-bonding.



napy



ppyz

Our interest with the heterocycle ppyz lies in its potential to act as (1) a bidentate chelate using N-4 and N-5, (2) a bridging bidentate ligand using N-1 and either N-4 or N-5, and (3) a monodentate ligand using either N-1, N-4, or N-5. A simple Hückel π-electron charge calculation[8] and an alkylation study[9] have suggested N-5 to be the most basic nitrogen of the aromatic system. Stoklosa et al.[8] have reported the ligand to behave in a "stepped" bridging fashion using N-1 and N-5, while the work reported herein indicates bidentate chelate ligation (N-1, N-8).

Experimental Section

Materials. 2,7-dmnapy, 2-mnapy, and napy were synthesized by standard literature methods.[10,11] ppyz was prepared using the procedure of Leese and Rydon,[12] which was slightly modified by increasing the extraction time from 4 h to a minimum of 48 h. Ligand purity was ascertained by C, H, and N analyses and ^1H NMR spectroscopy. $Ru(bpy)_2Cl_2 \cdot 2H_2O$ and $Ru(phen)_2Cl_2$ were prepared using a procedure provided by Professor Meyer.[13] Tetraethylammonium hexafluorophosphate (TEAH) was prepared by the addition of an aqueous solution of tetraethylammonium chloride to aqueous NH_4PF_6, recrystallized twice from a hot 1:1 ethanol–water mixture and dried at 80 °C for 12 h. Acetonitrile (Eastman "Spectro") and reagent grade acetone and nitromethane were used without further purification. All other solvents and chemicals were of commercially available reagent quality.

Preparation of $[Ru(bpy)_2L](PF_6)_2$ and $[Ru(phen)_2L](PF_6)_2$, L = napy, 2-mnapy, and 2,7-dmnapy. For a typical preparation, $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (260 mg, 0.5 mmol) was suspended in ~40–50 mL of deaerated water in a 100-mL one-necked round-bottom flask. The flask, fitted with a condenser, was heated at reflux under argon for 1 h. A deaerated aqueous solution or deaerated aqueous acetone (1:1 v/v) solution of the appropriate ligand (1.5 mmol) was then added to the deep red-brown solution. Gentle heating was continued for 2 h and the resulting solution (color ranged from bright orange to red-orange) was cooled in an ice bath. Addition of saturated aqueous NH_4PF_6 caused precipitation of a solid. The reaction flask was removed from the argon atmosphere and the solid was collected by vacuum filtration. This material was dissolved in ~20 mL of acetone, filtered, and reprecipitated by addition of 150 mL of anhydrous ether. The recovered solid was dried for 12 h over P_4O_{10}.

Preparation of $[Ru(bpy)_2ppyz](PF_6)_2$ and $[Ru(phen)_2ppyz](PF_6)_2$. The procedure was similar to the above with the exception that a 5:1 ratio of ppyz:$Ru(diimine)_2Cl_2$ was employed. Addition of aqueous NH_4PF_6 to the resulting brown solution yielded a black-brown material. Purification was afforded by chromatographic separation using a 8 cm × 1 cm silica gel (mesh 100–200) column with acetonitrile as eluent. Approximately 100 mg of crude product was dissolved in a minimal quantity of acetonitrile; the solution was placed on the column and eluted with acetonitrile leaving a black-brown ring at the top. Addition of ether to the reddish brown eluent produced a precipitate of the same color. The material collected by vacuum filtration was dissolved in ~10 mL of acetone, filtered, and reprecipitated by addition of 100 mL of anhydrous ether. The recovered solid was dried for 12 h over P_4O_{10}.

Measurements. An industrial Instruments Model RC-16B2 conductance bridge was used to determine the molar conductivity, Λ_m, of reagent grade acetone solutions of the new complexes at a concentration of 10^{-3} M. The experimental results were compared to the value for $[Ru(bpy)_3](PF_6)_2$, a known 1:2 electrolyte, at the same approximate concentration.

The infrared (4000–600 cm^{-1}) spectra of Nujol–Fluorolube mulls of the complexes supported between sodium chloride windows were obtained with a Perkin-Elmer Model 621 double-beam grating spectrophotometer.

All visible and UV spectra were obtained from solutions using a Cary Model 14 recording spectrophotometer. The sample was dissolved in the indicated solvent and a spectrum obtained using matched quartz 1-cm cells at a scan speed of 10 Å/s. For Beer's law determinations, absorbance measurements of a successively diluted standard solution were obtained at constant wavelength. A least-squares linear regression of a minimum of four data points was then utilized to calculate the reported molar absorptivity.

All electrochemical measurements were obtained using "Spectro Grade" acetonitrile dried over 4-Å molecular sieves with 0.1 M tetraethylammonium hexafluorophosphate (TEAH) as supporting electrolyte. The potential values reported are vs. the saturated sodium

Table I. Analytical and Conductivity Data for $[Ru(bpy)_2L](PF_6)_2$ and $[Ru(phen)_2L](PF_6)_2$

L	% C		% N		% H		Λ_m,[a] cm² mho	Concn × 10³, M
	Calcd	Found	Calcd	Found	Calcd	Found		
			$[Ru(bpy)_2L](PF_6)_2$					
phen	43.49	43.31	9.51	9.32	2.76	2.66		
2,7-dmnapy	41.82	41.85	9.75	9.76	3.04	3.26	254	0.98
2-mnapy	41.09	41.01	9.92	10.20	2.83	2.75	251	1.00
napy	40.34	40.43	10.08	10.39	2.66	2.48	254	0.99
ppyz	38.86	38.86	11.75	11.94	2.54	2.34	224	1.02
			$[Ru(phen)_2L](PF_6)_2$					
bpy	44.98	44.61	9.25	9.25	2.66	2.62		
2,7-dmnapy	44.89	45.03	9.23	9.26	2.88	2.64	248	0.97
2-mnapy	44.25	44.21	9.39	9.35	2.70	2.52	252	1.01
napy	43.59	43.26	9.53	9.32	2.52	2.67	242	1.02
ppyz	42.18	42.26	11.10	11.23	2.40	2.32	236	1.00

[a] $[Ru(bpy)_3](PF_6)_2$ was used as the standard for a 1:2 electrolyte: 233 cm² mho at a concentration of 1.02×10^{-3} M.

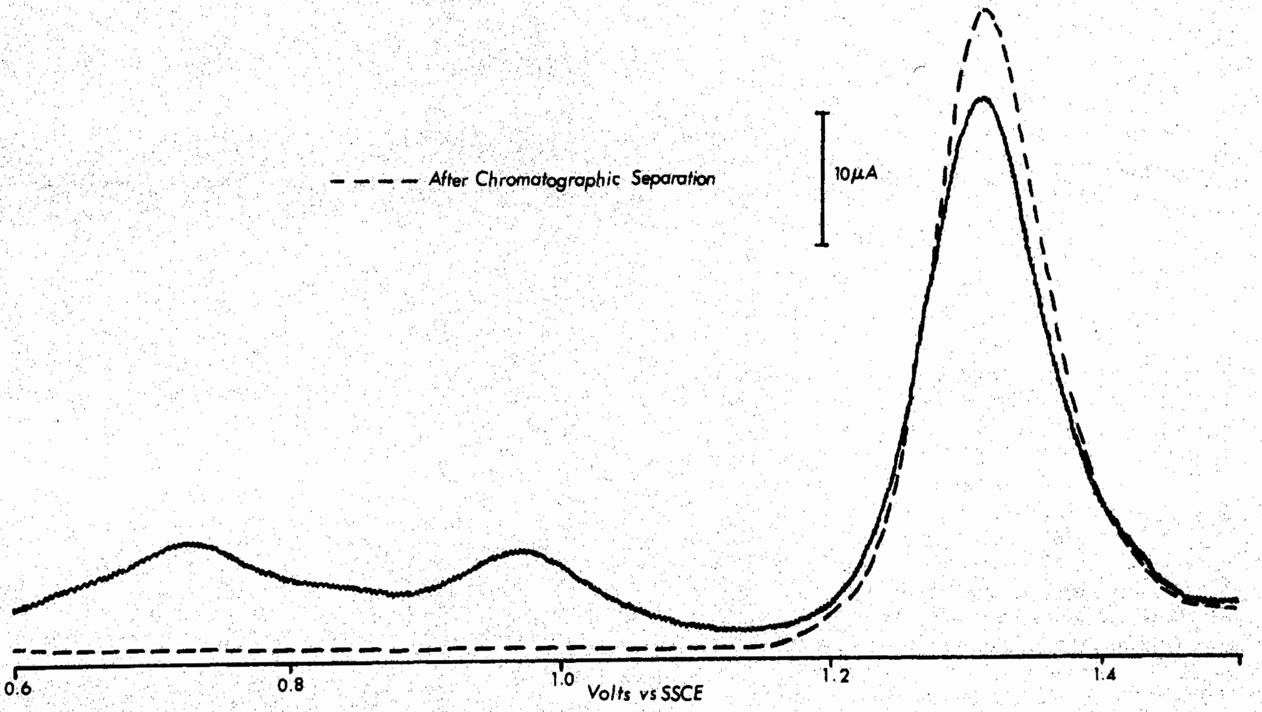


Figure 1. Ac polarograms of impure and pure $[Ru(bpy)_2ppyz](PF_6)_2$ (4.0×10^{-4} M) in acetonitrile solution (0.1 M TEAH).

chloride calomel electrode (SSCE) at 25 ± 2 °C. A three-electrode system (working electrode, auxiliary platinum wire counterelectrode, and the SSCE connected by means of a Luggin capillary) was used in conjunction with a Princeton Applied Research Model 174A polarographic analyzer, a Model 174/50 AC polarographic interface accessory, and a Model 122 lock-in amplifier. The working surface was a Beckman platinum electrode, pretreated prior to each electrochemical run.[14] Before the start of an experiment, the solution was degassed with N_2 and the internal resistance compensation circuit of the Model 174/50 interface was adjusted to a point just below oscillation as detected by an oscilloscope. The mode of operation was either cyclic voltammetry or alternating current polarography (70 Hz).

Microanalyses for carbon, hydrogen, and nitrogen were performed by the Analytical Services Laboratory of Ohio University.

Results and Discussion

Preparations. The preparations described in the Experimental Section employed *cis*-dichlorobis(diimine)ruthenium(II) (diimine = bpy or phen) to generate a solution[15] of $[Ru(diimine)_2(H_2O)Cl]^+$ which undergoes substitution in the presence of excess naphthyridine ligands, L, to produce $[Ru(diimine)_2L]^{2+}$. The complexes were recovered as PF_6^- salts and are soluble in acetone and acetonitrile with decreasing solubility in nitromethane, ethanol, and methanol. The conductivity measurements and analyses of the mixed-ligand complexes, Table I, are consistent with the proposed 1:2 electrolyte composition.

It is interesting to note that acceptable analyses consonant with the $[Ru(phen)_2L](PF_6)_2$ and $[Ru(bpy)_2L](PF_6)_2$ formulations were also obtained for complexes prepared under conditions in which the ratio of ligand to $Ru(diimine)_2Cl_2$ was only slightly greater than 1 and reflux time with ligand was approximately 45 min. However, ac polarograms of these preparations revealed the presence of other ruthenium species. The impurities were eliminated by the use of a greater ligand to $Ru(diimine)Cl_2$ mole ratio and by column chromatography.

The presence of impurities was especially pronounced in complexes obtained from the reactions with ppyz; the initially recovered ppyz complexes were black-brown and after chromatographic separation and recrystallization appeared reddish brown. The ac polarograms of $[Ru(bpy)_2ppyz](PF_6)_2$ before and after chromatography are shown in Figure 1. Chromatographic separation was not required for the remaining mixed-ligand complexes as judged from the single maximum observed in the ac polarogram.

The identity of the impurities is unknown but most probably is a mixture of $[Ru(bpy)_2(H_2O)_2]^{3+}$ and dihydroxo-bridged

Table II. Visible and Ultraviolet Spectral Data for $[Ru(bpy)_2L](PF_6)_2$

	λ_{max}, nm					
L	Nitromethane	Acetone	Acetonitrile	$\tilde{\nu}$,[a] μm^{-1}	$10^{-4}\epsilon$,[a] M^{-1} cm^{-1}	Assignment
2,7-dmnapy	453	453	453	2.21	1.26	MLCT
			286	3.49	7.92	$\pi \rightarrow \pi^*$
			254	3.93	2.51	$\pi \rightarrow \pi^*$
			243[b]	4.12		
2-mnapy	452	452	434	2.30	1.13	MLCT
			286	3.50	5.07	$\pi \rightarrow \pi^*$
			255[b]	3.92		
			243	4.12	2.21	$\pi \rightarrow \pi^*$
napy	445	450	434	2.30	1.12	MLCT
			286	3.49	5.26	$\pi \rightarrow \pi^*$
			253[b]	3.95		
			243	4.12	2.25	$\pi \rightarrow \pi^*$
ppyz	436	436	434	2.30	1.02	MLCT
			284	3.52	5.00	$\pi \rightarrow \pi^*$
			254[b]	3.93		
			245	4.08	2.07	$\pi \rightarrow \pi^*$
phen	449	449	449	2.23	1.57	MLCT
			286	3.49	6.32	$\pi \rightarrow \pi^*$
			264	3.79	5.76	$\pi \rightarrow \pi^*$
bpy	450	450	450	2.22	1.40	MLCT
			284	3.52	7.92	$\pi \rightarrow \pi^*$
			253[b]	3.95		
			243	4.12	2.56	$\pi \rightarrow \pi^*$

[a] Obtained in acetonitrile. [b] Shoulder on main band.

Ru(III) species.[15] This tentative identification was suggested by the isolation of a dark green material from a solution of "$Ru(bpy)_2(H_2O)Cl^+$" which had been treated under the general preparation conditions described in the Experimental Section with the exception that no ligand was present. The addition of NH_4PF_6 to this hot aqueous solution of "$Ru(bpy)_2(H_2O)Cl^+$" produced a small quantity of a dark green precipitate which gave a visible maximum at 660 nm in acetonitrile and ac polarographic maxima suggestive of the impurity peaks shown in Figure 1.

Ultraviolet-Visible Spectra. The UV and visible spectra of a large number of six-coordinate $[Ru(bpy)_2L_2]^{2+}$ complexes where L = monodentate ligand have been studied by Bryant et al.[7] The absorbance spectra for these complexes are characterized by the intense $\pi \rightarrow \pi^*$ bipyridine intraligand transitions in the UV and by two metal-to-ligand charge-transfer (MLCT) bands: the main one is at ~450 nm and a second of lesser intensity is between 340 and 390 nm. The maximum at ~450 nm is broad and often has distinct shoulders while the maximum between 340 and 390 nm is not observed for some complexes, e.g., $[Ru(bpy)_3]^{2+}$, $Ru(bpy)_2(CN)_2$, and $[Ru(bpy)_2(CH_3CN)_2]^{2+}$.[7] The visible spectra of these general types of complexes are sensitive to the presence of π-back-bonding ligands. A blue shift or a small red shift in the MLCT band relative to $Ru(bpy)_3{}^{2+}$ has been shown to be demonstrative of the ability of the ligand to stabilize the t_{2g} level by π back-bonding to a degree equivalent to bpy while substantial red shifts are observed when L possesses only σ-donor properties. The intensity of the main visible maximum systematically decreases on proceeding from the tris- to bis- to mono(bipyridine) complexes, supporting the contention that the absorption involves a transition to bipyridine.[7]

For $Ru(bpy)_2L_2{}^{2+}$ complexes, containing an unsaturated ligand L, no separate d (Ru(II)) → L band was observed[7] and it was concluded that this band is most likely hidden under the envelope of the more intense MLCT transition involving bipyridine. However, Meyer et al.[16] have also studied similar complexes and in several instances where L = pyridine–amine bidentate ligands have assigned high-energy shoulders on the main visible band as a d (Ru(II)) → π^* (pyridine) transition.

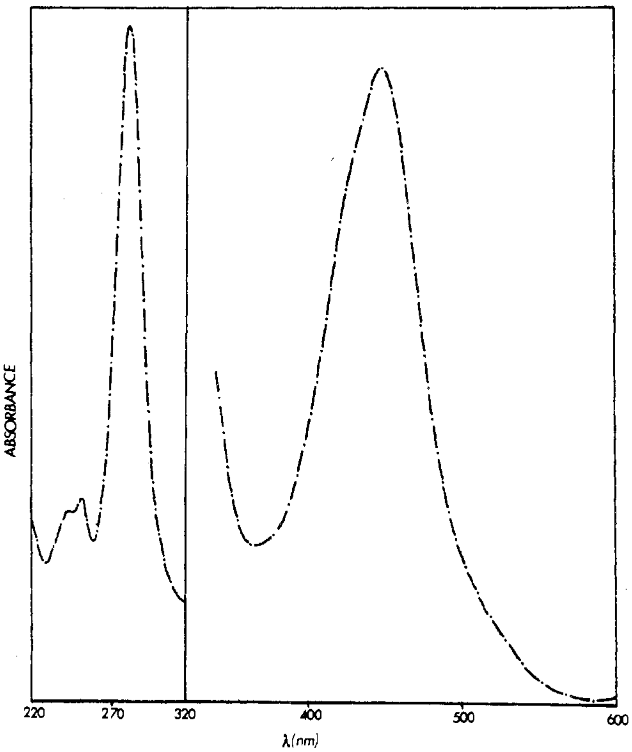


Figure 2. Electronic spectrum of $[Ru(bpy)_2(2,7\text{-dmnapy})]^{2+}$ in acetonitrile. The concentration of the complex was 6.1×10^{-5} M in the visible and 1.1×10^{-5} M in the UV region.

Table III. UV Spectral Data for Naphthyridines and Pyrido[2,3-*b*]pyrazine in Methanol

	λ_{max} nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}		λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
napy	306	5.2	2,7-dmnapy	315	9.1
	301	5.3		308	8.6
	294	4.8		303	8.3
	255	4.3		248	5.3
2-mnapy	312	6.0	ppyz	314	12
	303	5.9		307	8.7
	298	5.6		302	8.4
	253			258	3.8

The UV spectra of the $Ru(bpy)_2L_2{}^{2+}$ complexes suggest that the first $\pi \rightarrow \pi^*$ transition of bipyridine at ~290 nm does not shift significantly from the band maximum of the $Ru(bpy)_3{}^{2+}$ complex when L has π-acceptor character. Further, the intensity of this $\pi \rightarrow \pi^*$ maximum is lowered successively as the number of coordinated bipyridine decreases.[7]

The absorption maxima for the mixed-ligand bipyridine and naphthyridine complexes of ruthenium(II) are recorded in Table II. These complexes all show $\pi \rightarrow \pi^*$ bands at 286 nm and near 243 nm, Figure 2, both in agreement with energies previously observed for $[Ru(bpy)_2L_2]^{2+}$ complexes.[7] UV data for the uncomplexed ligands are presented in Table III. Their electronic structure has been discussed by Mason.[17] The molar absorptivities, ϵ, of the 2-mnapy, napy, and ppyz mixed-ligand complexes reveal the expected lowered intensity for the first intraligand band in the UV when compared to the $Ru(bpy)_3{}^{2+}$ complex. This lowering is a consequence of the loss of a bipyridine molecule and replacement by a naphthyridine ligand. Surprisingly, the mixed bpy–2,7-dmnapy complex is of similar intensity to $Ru(bpy)_3{}^{2+}$. The Ru(2,7-

Table IV. Visible and Ultraviolet Spectral Data for $[Ru(phen)_2L](PF_6)_2$

	λ_{max}, nm					
L	Nitromethane	Acetone	Acetonitrile	$\tilde{\nu}$,[a] μm^{-1}	$10^{-4}\epsilon$,[a] M^{-1} cm^{-1}	Assignment
2,7-dmnapy	448	448	448	2.23	1.40	MLCT
			262	3.82	9.12	$\pi \rightarrow \pi^*$
2-mnapy	446	446	417[b]	2.40	1.38	MLCT
			262	3.82	8.15	$\pi \rightarrow \pi^*$
napy	438	445	426	2.35	1.45	MLCT
			413[c]	2.42		
			262	3.82	7.59	$\pi \rightarrow \pi^*$
ppyz	429	430	428	2.34	1.20	MLCT
			262	3.82	7.97	$\pi \rightarrow \pi^*$
bpy	448	448	448	2.23	1.65	MLCT
			430[c]	2.32		
			284[c]	3.52		
			262	3.82	9.17	$\pi \rightarrow \pi^*$
phen	446	446	446	2.24	1.99	MLCT
			262	3.82	12.5	$\pi \rightarrow \pi^*$

[a] Obtained in acetonitrile. [b] Very broad maximum. [c] Shoulder on main band.

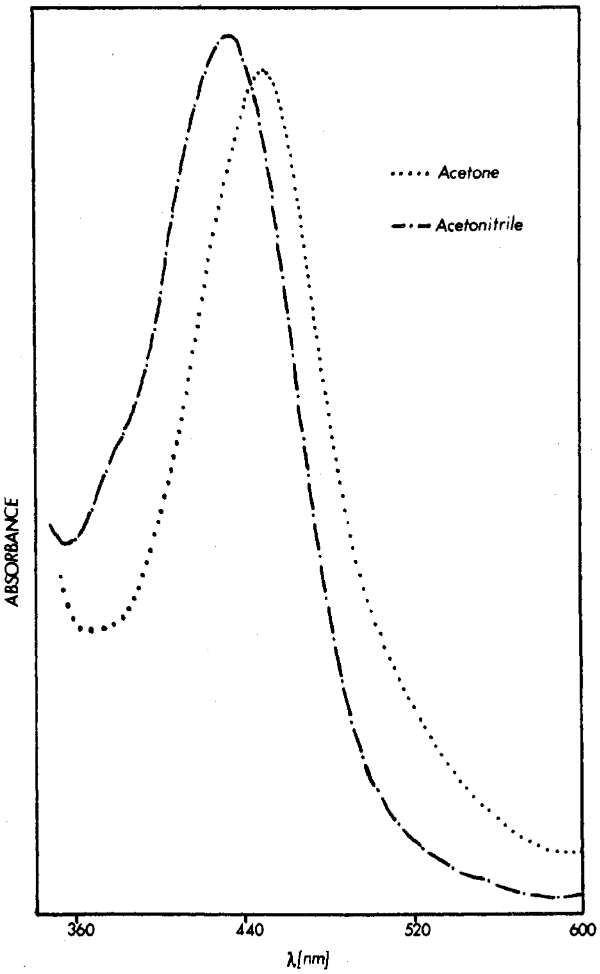


Figure 3. Visible spectra of $[Ru(bpy)_2(2\text{-}mnapy)]^{2+}$ in acetone (7.5 × 10^{-4} M) and acetonitrile (8.1 × 10^{-4} M).

dmnapy)$_3^{2+}$ complex[17] has a $\pi \rightarrow \pi^*$ absorption at 283 nm, ϵ 5.00 × 10^4, which suggests that the observed intensity of the $\pi \rightarrow \pi^*$ transition for the mixed-ligand complex probably reflects an increment due to a $\pi \rightarrow \pi^*$ transition on the coordinated 2,7-dmnapy molecule as well as that due to the bipyridine ligands. The $\pi \rightarrow \pi^*$ absorptions for coordinated napy and 2-mnapy in $Ru(napy)_4^{2+}$ and $Ru(2\text{-}mnapy)_4^{2+}$ occur at higher energy and apparently do not contribute measurably to the intensity of the band observed at 286 nm for the mixed bpy–napy and bpy–2-mnapy complexes.[17]

The similarity in energy for the first d $\rightarrow$ π^* transition of the mixed-ligand bpy complexes to that of the tris(bipyridine) complex demonstrates that the naphthyridine ligands have π-acceptor character toward the ruthenium(II) center. The UV spectral data for the mixed-ligand phenanthroline complexes are presented in Table IV and parallel the bipyridine analogues.

The visible region for each of the mixed-ligand bpy complexes consists of a single asymmetrical band of high intensity near 450 nm. The spectra are devoid of any other absorption to 700 nm. The observed band undergoes a solvent shift for several of the complexes upon dissolution in acetonitrile (Table II and Figure 3). Prior study of the $Ru(napy)_4^{2+}$ and $Ru(2\text{-}mnapy)_4^{2+}$ complexes[18] in acetonitrile has shown that solvolysis occurs and that one of the manifestations of such substitution is a change in energy of the MLCT band (for the $Ru(napy)_4^{2+}$ complex a blue shift of 68 nm occurs upon dissolution in acetonitrile). Similar observations with the $(2\text{-}mnapy)_4$ complex suggested the hypothesis that the change in energy of the 450-nm band of the mixed bpy–napy complexes in acetonitrile may result from substitution of one of the coordinated napy positions by a solvent molecule to give the complex $[Ru(bpy)_2(napy)(CH_3CN)]^{2+}$ in solution. Meyer et al. have reported that the complexes $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ and $[Ru(bpy)_2py(CH_3CN)]^{2+}$ possess λ_{max} at 425 nm, ϵ 8.59 × 10^3, and 437 nm, ϵ 7.73 × 10^3.[19] Any proposed mixed bpy–napy–acetonitrile complex should, to a good approximation, exhibit spectral properties similar to those of the bpy–pyridine–acetonitrile complex. The bpy–napy and bpy–2-mnapy complexes upon dissolution in acetonitrile displayed a λ_{max} close in energy to 437 nm; however, the calculated molar absorptivities (Table II) are 45% higher than those reported for the bpy–pyridine–actonitrile complex[19] suggesting the presence of bidentate naphthyridine. Additionally, acetonitrile solutions of the bpy–napy complexes were refluxed and then added to an excess of ethyl ether to precipitate a solid. The recovered solid did not show any evidence in the IR for coordinated acetonitrile. These results, along with the single ac polarographic peak (vide infra), signify that acetonitrile substitution is not occurring in this instance and that the hypothesized $[Ru(bpy)_2(napy)(CH_3CN)]^{2+}$ substitution product is not present.

The visible spectral data and general behavior of the phen–napy mixed-ligand complexes (Table IV) are similar to the bpy–napy analogues. The anomalous solvent shift is observed with the napy and 2-mnapy complexes and is particularly pronounced with a broad maximum resulting for the latter complex.

In general it can be said for both series of mixed-ligand complexes, $Ru(bpy)_2L^{2+}$ and $Ru(phen)_2L^{2+}$, that the near-invariancy of the λ_{max} of these complexes in nitromethane and acetone when compared to the $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes supports the contention that the naphthyridines are participating in synergic back-bonding and thereby stabilizing the t_{2g} level of ruthenium(II).

Electrochemistry. The electrochemistry of the mixed-ligand complexes was studied by cyclic voltammetry and ac polarography using a platinum-button electrode in acetonitrile containing 0.1 M TEAH as supporting electrolyte. The half-wave potentials, $E_{1/2}$, are recorded in Table V. These values were calculated from the average of the peak potentials for the oxidation and reduction waves of the cyclic voltammograms[20] and agree with the maxima obtained from the ac polarographic runs; Figure 4 contains the result for

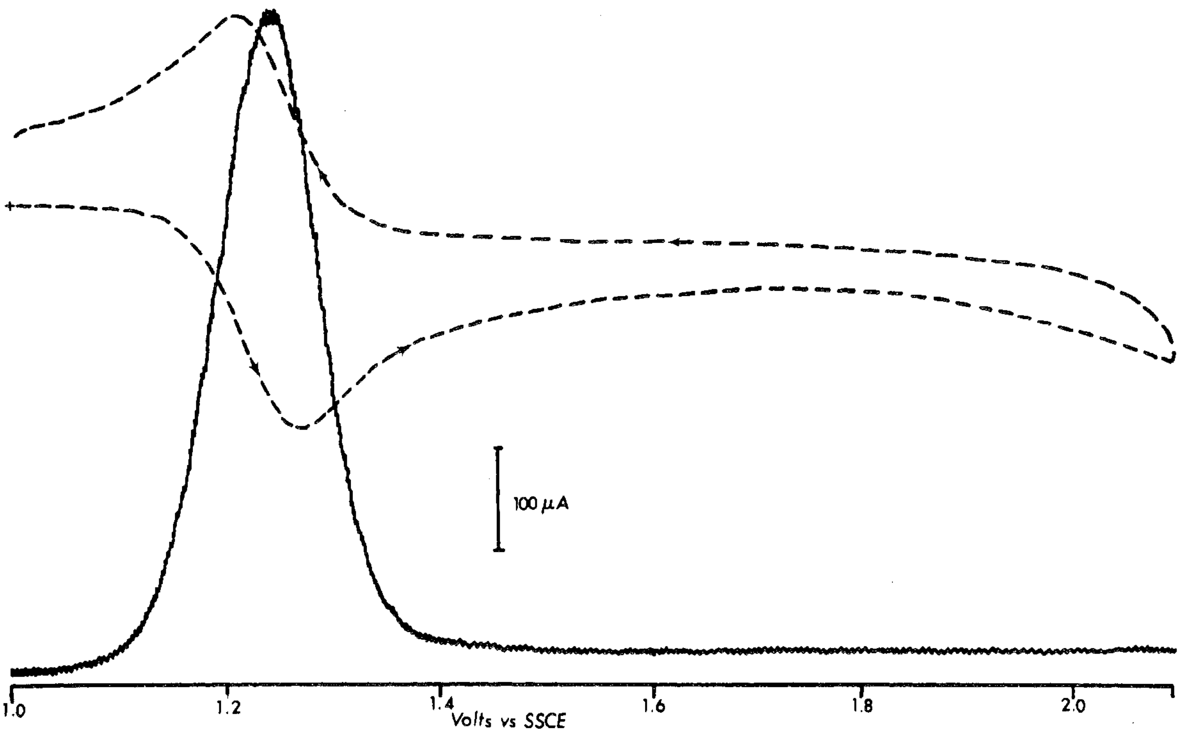


Figure 4. Cyclic voltammogram and ac polarogram of $[Ru(phen)_2(2\text{-mnapy})]^{2+}$ (1.0×10^{-3} M) in acetonitrile solution (0.1 M TEAH).

Table V. Voltammetric Data for the Mixed-Ligand Complexes $[Ru(bpy)_2L](PF_6)_2$ and $[Ru(phen)_2L](PF_6)_2$ in 0.1 M TEAH-Acetonitrile

	$E_{1/2}$, V[a]	
L	$[Ru(bpy)_2L]$-$(PF_6)_2$	$[Ru(phen)_2L]$-$(PF_6)_2$
2,7-dmnapy	1.32	1.33
2-mnapy	1.25	1.26
napy	1.26	1.27
ppyz	1.32	1.33
phen	1.29	1.30
bpy	1.29	1.30

[a] The reported values are vs. the SSCE at 25 ± 2 °C and are the average of the anodic and cathodic peaks from the cyclic voltammograms. The ac polarographic maxima coincide with this potential.

$[Ru(phen)_2(2\text{-mnapy})]^{2+}$ which is representative for all complexes.

The electrochemical reversibility of the reactions was ascertained by two methods:[21] (1) using the peak separation (ΔE_p) from the cyclic voltammogram; (2) observing the half-peak width of the ac polarogram. Under the experimental conditions, the reversible couple $[Ru(bpy)_3]^{2+} \rightarrow [Ru(bpy)_3]^{3+} + e^-$ gave a ΔE_p of 70 mV, which was used as the criterion of electrochemical reversibility.[22] The ΔE_p for entire series of complexes ranged between 70 and 80 mV at a scan rate of 200 mV/s. The ac polarograms of the mixed-ligand complexes were symmetrical and had half-peak widths varying between 90 and 95 mV from 50 to 500 Hz. Therefore, the complexes were judged to be reversible by both criteria.[21]

Coordinated phen and bpy are known to act as π acceptors from appropriate orbitals on a metal and as a consequence the lower oxidation states of a metal may be stabilized. When a bpy molecule is replaced in $[Ru(bpy)_3]^{2+}$ by ligands capable only of σ donation, the $E_{1/2}$ of the Ru^{3+}/Ru^{2+} couple decreases significantly, indicative of a destabilization of Ru(II).[23,24] However, when bpy is substituted by ligands capable of π acceptance, the change in $E_{1/2}$ is not dramatic.[16]

The naphthyridine ligands have shown a π-back-bonding propensity when ligated to ruthenium(II)[18] and the $E_{1/2}$ potentials in Table V merit comment based on this. The mixed-ligand complexes containing 2,7-dmnapy have a potential more positive than the $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes. This compares well with the finding that $[Ru(2,7\text{-dmnapy})_3]^{2+}$ apparently stabilizes Ru(II) better than phen or bpy as evidenced by its $E_{1/2}$ of 1.37 V. The decrease in $E_{1/2}$ for the mixed-ligand complexes of napy and 2-mnapy relative to the tris complexes of phen and bpy supports the conclusion reached previously for the $Ru(napy)_4^{2+}$ and $Ru(2\text{-mnapy})_4^{2+}$ complexes, i.e., that napy and 2-mnapy are less effective in stabilizing the ruthenium(II) oxidation state.[18]

The question of acetonitrile solvolysis arose from the experience with the $Ru(napy)_4^{2+}$ and $Ru(2\text{-mnapy})_4^{2+}$ complexes[18] as well as the anomalous solvent shift of the λ_{max}. The ac polarograms of the mixed-ligand complexes using acetonitrile as a solvent indicated only one peak from 0 to 2 V vs. SSCE (Figure 4). This peak did not change nor did a new one appear when polarograms were obtained intermittently up to 2 days after dissolution of the complex. If substitution of one or both of the coordinated napy or 2-mnapy sites by acetonitrile had occurred, the $E_{1/2}$ values should have shifted anodically relative to the $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes.[19] This did not occur and in fact the values shifted the other way as previously explained. Therefore, acetonitrile solvolysis of coordinated napy and 2-mnapy in the mixed-ligand complexes is not operative under the conditions investigated.

A study of the luminescent properties of the new complexes reported in this paper is presently being conducted.

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Registry No. $[Ru(bpy)_2(phen)](PF_6)_2$, 60828-38-8; $[Ru(bpy)_2(2,7\text{-dmnapy})](PF_6)_2$, 62601-28-9; $[Ru(bpy)_2(2\text{-mnapy})](PF_6)_2$, 62571-42-0; $[Ru(bpy)_2(napy)](PF_6)_2$, 62571-40-8; $[Ru(bpy)_2(ppyz)](PF_6)_2$, 62571-38-4; $[Ru(phen)_2(bpy)](PF_6)_2$, 60828-39-9; $[Ru(phen)_2(2,7\text{-dmnapy})](PF_6)_2$, 62571-36-2; $[Ru(phen)_2(2\text{-mna-}$

py)]$(PF_6)_2$, 62601-26-7; $[Ru(phen)_2(napy)](PF_6)_2$, 62571-34-0; $[Ru(phen)_2(ppyz)](PF_6)_2$, 62571-32-8; $[Ru(bpy)_3](PF_6)_2$, 60804-74-2; $[Ru(phen)_3](PF_6)_2$, 60804-75-3; napy, 254-60-4; 2-mnapy, 1569-16-0; 2,7-dmnapy, 14903-78-7; ppyz, 322-46-3; $Ru(phen)_2Cl_2$, 15453-59-5; $Ru(bpy)_2Cl_2$, 19542-80-4.

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Dimethyl Compounds of Platinum(II). 1. Oxidative Addition Reactions Involving Group 4 Element–Halogen Bonds

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Reactions of $PtMe_2(N\text{-}N)$ (N-N = 2,2′-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) with methyltin– or aryltin–halogen compounds SnR_nCl_{4-n} (R = Me, Ph; n = 0–3), lead diphenyl dichloride, $PbPh_2Cl_2$, and lead triphenyl chloride, $PbPh_3Cl$, proceeded via an oxidative addition involving the Sn–Cl or Pb–Cl bond to give the new compounds $PtMe_2Cl(N\text{-}N)(SnR_nCl_{3-n})$ and $PtMe_2Cl(N\text{-}N)(PbPh_mCl_{3-m})$ (m = 1, 2) in almost quantitative yield. The compounds and their reactions were studied by ^1H NMR spectroscopy. Exchange reactions of $PtMe_2Cl(bpy)(SnR_nCl_{3-n})$ with SnR'_mCl_{4-m} and reactions with MeI showed that their relative stability decreased in the order $SnPhCl_2 > SnMeCl_2 > SnPh_2Cl > SnMe_2Cl > SnPh_3 > SnMe_3$. With MeI no reaction was observed, $PtMe_3Cl(bpy)$ was formed, or $PtMe_3I(bpy)$ depending upon the stability of the platinum–tin bond. In contrast with the SnR_nCl_{4-n} compounds themselves, the platinum–tin compounds were not affected by Lewis bases such as H_2O, ROH, pyridine, and PPh_3. Although there was evidence that the platinum–lead bonds were stronger than the corresponding tin bonds, the former compounds decomposed in CH_2Cl_2 solution except $PtMe_2Cl(Ph_2Me_2phen)(PbPh_2Cl)$, which was stable. In addition a halogen exchange between $PtMe_3Cl(bpy)$ and MeI was observed.

Introduction

The formation of Pt–M bonds (M is a group 4 element: Si, Ge, Sn, or Pb) by oxidative addition of group 4 compounds to Pt(0)[1–6] or Pt(II)[6–10] compounds has received considerable attention.

Recently it was clearly established[1] that oxidative addition of SnR_3X (R = Me, Ph; X = Cl, Br, I, OH, NO_3) to Pt $(C_2H_4)(PPh_3)_2$ proceeded by "insertion" of platinum in the Sn–C bond rather than in the Sn–X bond, as was described earlier.[2] Similarly oxidative addition of $SiRX_2H$ to square-planar Rh(I) and Ir(I) compounds involved the M–H instead of the M–X bond.[11,12] Reactions of MR_3H compounds (R = Me, Ph; M = Si, Ge, Sn) with Pt(0) compounds probably proceed via oxidative addition of M–H to platinum, followed by reaction with another molecule R_3MH. This results in H_2 elimination or again oxidative addition.[5–7] Also reactions of $SiMe_nCl_{3-n}H$ (n = 0, 1) with Pt(0) compounds proceeded similarly and did not involve rupture of the Si–Cl or Si–C bond.[5,6] Oxidative addition of $SnMe_3H$ to Pt(II) also involved the Sn–H bond.[8–10]

Since no oxidative additions of MR_nCl_{4-n} (R = Me, Ph; M = Si, Ge, Sn, Pb; n = 0–3) with Pt(II) compounds are known, we became interested in reactions of MR_nCl_{4-n} with $PtMe_2(bpy)$, a compound which is known to undergo oxidative additions very readily.[13] The results of this investigation with tin and lead compounds are presented in this paper.

Experimental Section

General Information. Although the compounds prepared in this study were stable in air, several of the starting materials were susceptible to atmospheric moisture. Therefore all preparations were carried out in a dry nitrogen atmosphere. The abbreviations bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, Ph_2Me_2phen = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, and pic = 4-picoline are used in the text.

Chemicals. Tin and lead alkyl or aryl chlorides are commercially available and were used without further purification. Reagent grade solvents were dried and distilled prior to use. ^1H NMR spectra in CH_2Cl_2 were recorded on a Varian HA100 NMR spectrometer. Melting and decomposition points were recorded on a DTA apparatus, Du Pont Model 900, and were checked visually. Elemental analyses were performed by Childers Laboratories, Milford, N.J. Analytical data are summarized in Table I.

Preparation of $PtMe_2(bpy)$. Bipyridine (8.4 mmol) was added with rapid stirring to a warm solution (60 °C) of $[PtMe_2(SEt_2)]_2$[13] (4 mmol) in benzene (about 100 mL). As soon as all the bipyridine had dissolved, stirring was stopped. After 5 min at 60 °C and subsequently 24 h at 5 °C the red needles of $PtMe_2(bpy)$ were collected on a filter and vacuum-dried for 1 h; yield 85% (two fractions). $PtMe_2(phen)$ was