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Synthesis and Characterization of Ruthenium Ammine Complexes Containing the Asymmetric Ligand Pyrazine Carboxylate

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The preparation and chemical properties of the ruthenium ammine complexes $[(NH_3)_nRu\text{mcpy}]^+$ *(n = 4, 5;* mcpy *= pyrazine carboxylate) are described. The* mcpy *ligand functions as either a mono- or bi-dentate ligand, depending upon ammine coordination. When* mcpy *acts as a bidentate ligand, two MLCT's are observed in the visible spectrum* (λ_{max} *= 520 and 420 nm). Polyvinylalcohol film studies identify the low energy band as a Ru-pyrazine MLCT and the high energy band as a Ru–metallocycle MLCT. For the pentaammine complex,* $E_{1/2}$ *= 0.51 V compared to 0.37 V for the tetraammine species. Multiple coordination by* mcpy *decreases the extent of metal π backbonding relative to the monodentate complex.*

Introduction

The redox properties of ruthenium compounds have been under extensive investigation over the last decade in an effort to develop and understand the potential of these compounds as catalysts, particularly in the auto-oxidation of water [1]. Judicious choice of ligands with π-acceptor capacity has resulted in a series of ruthenium complexes that exhibit a wide range of redox potentials [2]. The majority of such ligands have been nitrogen heterocycles which allow significant electron transfer of electron density from the Ru t_{2g} orbitals to the π* orbitals of the ligands.

When 2,5-pyrazine dicarboxylate (dcpy) is used as a bridging ligand between two ruthenium metal centers, the degree of electron delocalization is substantially diminished if compared to analogous complexes containing unsubstituted pyrazine as a ligand bridge [3]. This decrease in the extent of electron transfer is attributed to the presence of a multiply coordinated ligand bridge. Work in this laboratory is focusing on the use of pyrazine monocarboxylate (*mcpy*) as an asymmetric, multidentate ligand in ruthenium coordination complexes. This anion offers the advantage of selective coordination as either a mono- or bi-dentate ligand. This paper reports the preparation and properties of ruthenium tetraammine and pentaammine complexes containing *mcpy*.

Experimental

Materials

All materials were reagent grade. The starting materials $[Ru(NH_3)_5Cl]Cl_2$ and *cis*-$[Ru(NH_3)_4Cl_2]Cl$ were prepared from $[Ru(NH_3)_6]Cl_3$ (ICN K & K) according to literature procedures [4]. The *mcpy* ligand was prepared as the potassium salt of pyrazinecarboxylic acid (Aldrich) by dissolving the acid in 2 *M* KOH and precipitating with ethanol. Polyvinylalcohol (PVA) films were prepared according to Ref. [5].

Syntheses

$[Ru(NH_3)_5mcpy]ClO_4$ *(1)*

Complex *1* was prepared in an argon atmosphere by reducing $[Ru(NH_3)_5Cl]Cl_2$ (0.500 g) in 20 ml of distilled deaerated water over Zn/Hg amalgam and then adding the resultant pale yellow solution to a three-fold excess of potassium pyrazinemonocarboxylate. The maroon solution was stirred for 2 hours, filtered and evaporated to dryness. The solid was then dissolved in a minimum amount of saturated aqueous NH_4ClO_4. The product was precipitated by the addition of excess absolute ethanol. The deep purple precipitate was filtered, washed with absolute ethanol and air dried.

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TABLE I. Absorption Maxima of Ammineruthenium(II) Complexes in Aqueous Solution.

Complex	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	Reference
$[Ru(NH_3)_5$*mcpy*$]^+$	478	6500	this work
$[Ru(NH_3)_4$*mcpy*$]^+$	520	4200	this work
	420		
$[Ru(NH_3)_5pyrazine]^{2+}$	472	10700	[7]
$[Ru(NH_3)_4Hdcpy]^+$	557	4900	[3]
	435	3400	

*[Ru(NH$_3$)$_4$*mcpy*]PF$_6$ (2)*

The synthesis of complex *2* is analogous to that of complex *1* except that the starting material was *cis*-$[Ru(NH_3)_4Cl_2]Cl$ and NH_4PF_6 was used as the precipitating agent. *Anal.* Calcd.: C, 13.7; H, 3.4; N, 19.2; F, 26.1%. Found: C, 13.9; H, 3.9; N, 18.4; F, 26.6%.

Instrumentation

Absorption spectra were recorded on Cary 219, Perkin-Elmer Lambda 3 (UV-Vis region) and Cary 14 (near IR) spectrophotometers. A Perkin-Elmer 283B IR spectrophotometer was used to obtain IR spectra of the monomers prepared in KBr disks. Cyclic voltammograms were measured on an IBM 225 Voltammetric Analyzer using a glassy carbon working electrode, platinum wire counter electrode, and a saturated standard calomel electrode as a reference electrode. The reduction potentials were obtained in 0.1 *M* KCl aqueous solutions and the values reported are *vs.* NHE using the $Ru(NH_3)_6^{3+/2+}$ couple (E° = +0.05 V) [6] as a standard. A Beckman Century SS-1 Expanded Scale pH Meter was used for pH measurements.

Results and Discussion

Spectral Characterization

The visible absorption spectra of *1* and *2* are typical of ammine ruthenium nitrogen heterocyclic complexes. The absorption maxima are shown in Table I. Complex *1* exhibits a single metal-to-ligand charge transfer (MLCT) absorption. The spectrum of the tetraammine complex, *2*, contains two MLCT bands as expected from previous work with substituted pyridine ligands. The source of the second MLCT has been ascribed to the unsaturated metallocyclic ring which is the result of bidentate coordination by the *mcpy* ligand [8]. However, assignment of the two peaks is problematic. In a study using σ-substituted pyridines as bidentate ligands in ruthenium tetraammine complexes, Alvarez, *et al.* observed that the higher energy band was relatively insensitive to the nature of the σ-substituent while the lower energy band did vary with different substituents. Thus, the shorter wavelength band was attributed to the Ru-pyridine chromophore. This assignment neglects any effect on the ring π system from an electron withdrawing substituent.

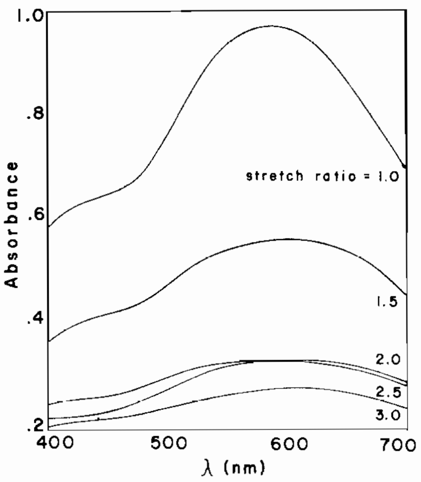

Fig. 1. Absorption spectra of $[(NH_3)_4Ru$*mcpy*$]PF_6$ in PVA film.

Spectral evidence for the *mcpy*–tetraammine complex suggests that the lower energy band is the Ru–pyrazine MLCT and the higher energy band therefore results from a Ru–metallocycle MLCT. Figure 1 shows the absorption spectra of complex *2* in PVA film. The peak positions are shifted compared to the values reported in Table I due to solvent effects, but the band shapes and relative intensities are maintained. Because molecules tend to align in the direction of a molecular axis (in this case the N_{ammine}–Ru–N_{mcpy} axis) any electronic transitions occurring along that axis are most effected as the PVA films are stretched. Although no linear dichroism was observed as the film was stretched, the absorbance at 590 nm decreased significantly more than the absorbance at 435 nm. This rapid

TABLE II. Carbonyl Stretching Frequencies of *mcpy* Complexes.

	$\nu_{C=O}$ (asym)	δ	ν_{C-O} (sym)
H*mcpy*	1718	1314	1390
K*mcpy*	1621		1390
$[(\mathrm{NH_3})_5\mathrm{Ru}\mathit{mcpy}]\mathrm{ClO_4}$	1631		1365
$[(\mathrm{NH_3})_5\mathrm{Ru}\mathit{mcpy}]\mathrm{ClO_4}^{a}$	1730	1409	1313
$[(\mathrm{NH_3})_4\mathrm{Ru}\mathit{mcpy}]\mathrm{PF_6}$	1640		1365
$[(\mathrm{NH_3})_4\mathrm{Ru}\mathit{mpcy}]\mathrm{PF_6}^{a}$	1632		1365

[a] Precipitated in 0.1 *M* HCl.

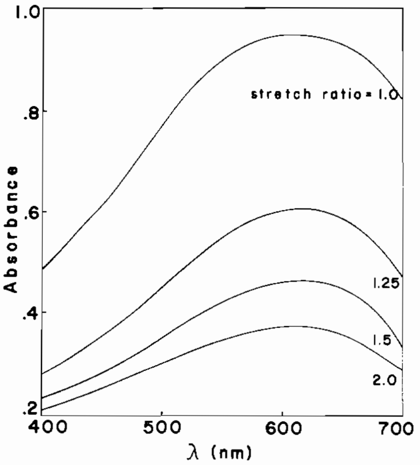

Fig. 2. Absorption spectra of $[(\mathrm{NH_3})_5\mathrm{Ru}\mathit{mcpy}]\mathrm{ClO_4}$ in PVA film.

diminution in intensity at 590 nm parallels the behavior of the Ru–pyrazine MLCT observed for complex *1* (Fig. 2).

Further support for the assignment of the low energy band as the Ru–pyrazine MLCT is found in the spectra of the binuclear species $[(\mathrm{NH_3})_5\mathrm{Ru}\text{-}\mathit{mcpy}\mathrm{Ru}(\mathrm{NH_3})_4]^{3+,4+}$. As reported elsewhere [9], the spectrum of the 3+ dimer is similar to that of the tetraammine monomer with a MLCT absorption at 574 nm and a shoulder at 490 nm. After partial oxidation to the mixed valence 4+ dimer, the high energy shoulder is no longer present and a single band is observed (λ_{max} = 582 nm). The Ru–metallocycle transition is lost due to the decreased π-donor ability of Ru(III).

Infrared

Infrared spectra of *1* and *2* were useful in determining the mode of ligand coordination to the ruthenium metal center. Table II lists some of the peaks observed in the carboxylate stretching region from 1800 to 1200 cm^{-1}.

Upon deprotonation $\nu_{C=O}$ for the free ligand shifts to lower energy and ν_{C-O} moves to higher energy. The bands are reassigned as asymmetric and symmetric stretches, respectively, to denote the loss of double and single bond character. The observed shift of ν_{sym} to higher energy and lowering of ν_{asym} for the protonated form of *1* indicates that the carboxylate moiety is not bound to the ruthenium atom. It is interesting to note that unlike pyrazine carboxylic acid [10] no N•••H–O bands were observed in the protonated complex *1*. Although IR evidence does not distinguish which ring nitrogen is bound to ruthenium, steric considerations suggest that the nitrogen in the *meta-* position is the most likely point of attachment. This assignment is supported by comparison of the pK$_a$ of the complex *versus* that of the free ligand.

Spectrophotometric determination of the pK$_a$ of *1* (3.0 ± 0.2) showed that the basicity of the ligand (pK$_a$ of the carboxylate function is 2.92 [11]) was not enhanced upon complexation in contrast to other nitrogen heterocyclic ligands [12]. Because protonation occurs at the carboxylate group rather than directly to the ring, the additional capacity for charge delocalization that occurs upon complexation to a ruthenium ammine moiety is not a significant factor in the ligand basicity. The pK$_a$ value reported is in agreement with the pH-dependent electrochemical measurements which are discussed below.

Recrystallization of *2* in 0.1 *M* HCl produced no change in the IR spectrum, so oxygen is considered to occupy a ruthenium coordination site. Only minor changes were recorded for the pH-dependent visible spectra of *2* and a conclusive pK$_a$ was not obtained.

Cyclic Voltammetry

Cyclic voltammograms for *1* and *2* are shown in Fig. 3. Complex *1* exhibits typical reversible behav-

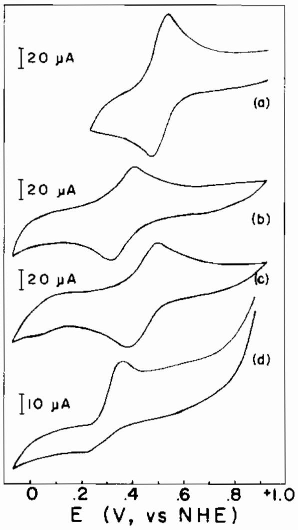

Fig. 3. Cyclic voltammograms in 0.1 *M* KCl. (a) $[(NH_3)_5$-Ru*mcpy*$]^+$, pH = 7.0 (b–d) $[(NH_3)_4$Ru*mcpy*$]^+$, pH = 7.0 (b); 1.9 (c); 11.9 (d).

ior with $E_{1/2}$ = 0.51 ± 0.01 V (*vs.* NHE). The reduction potential has a linear dependence on pH (slope = –0.03 V/pH unit) at $pH < 3.2$. At $pH > 3.2$, $E_{1/2}$ does not vary. For complex *2*, $E_{1/2}$ is 0.37 V or 140 mV more negative than complex *1*, reflecting the decreased dπ backbonding to the bidentate *versus* the monodentate *mcpy* ligand. In acidic media, $E_{1/2}$ shifts to more positive potentials. In basic solutions, though, the cyclic voltammogram of *2* exhibits irreversible behavior. A likely explanation for this behavior is that the carboxylate coordination site is replaced with hydroxide ion. If so, the substitution reaction is fully reversible for the carboxylate bound complex is recovered upon neutralization of the alkaline solution.

Conclusions

The mode of coordination of the asymmetric *mcpy* ligand in ruthenium pentaammine and tetraammine complexes has been characterized by electrochemical and spectroscopic techniques. Variations in the intensity of MLCT bands in stretched PVA film were particularly useful for the assignment of the origins of the MLCT transitions.

The characterizations of the two *mcpy* complexes reported here demonstrate how π-backbonding can be modified through coordination with a multidentate ligand. When the *mcpy* ligand is bound through a ring nitrogen only, a substantial degree of metal electron density can be transferred to the ligand, but when *mcpy* acts as a bidentate ligand, there is a decrease in dπ–π^* backbonding. Investigation of the diminished electron transfer capacity that arises from multiple coordination is currently being extended to electron delocalization in mixed valence complexes based on the *mcpy* bridging ligand [9].

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