ridine and pyrazine complexes better bases, but would be much less effective for the 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene complexes.

The net effect of the pentaammineruthenium(II) moiety on the electronic charge of the ligand was determined by a study of change in the chemical shifts of the protons of the ligands on complexation. It was found that the pentaammineruthenium(II) group polarized electron density toward itself, making the ligand slightly electron deficient. This was determined by the diamagnetic shifts found for all para protons and the protons on para substituents. The polarization was less than that of a proton, which is to be expected, since the polarization of charge is based on the charge to volume ratio of the polarizing agent. The charge to volume ratio is certainly much smaller for Ru(II) ion than for a proton. This result would predict that the basicities of the 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene complexes would be intermediate between the basicity of the free ligand and the monoprotonated ligand. This was found to be the case.

Acknowledgments. This work was supported generously by grants from the NIH and NSF.

Charge Delocalization in Pentaammineruthenium(II) Complexes. II. A Study of Dipentaammineruthenium(II) Complexes of Pyrazine, 4,4'-Bipyridine, and 1,2-Bis(4-pyridyl)ethylene[1]

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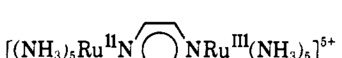
Abstract: The dipentaammineruthenium complexes with pyrazine, $(NH_3)_5Ru{-}NC_4H_4N{-}Ru(NH_3)_5{}^{4+}$, 4,4'-bipyridine, $(NH_3)_5Ru{-}(C_5H_4N)_2{-}Ru(NH_3)_5{}^{4+}$, and 1,2-bis(4-pyridyl)ethylene, $(NH_3)_5Ru{-}NC_5H_4C_2H_4C_5H_4N{-}Ru(NH_3)_5{}^{4+}$, were subjected to both chemical and electrochemical oxidations in order to study the "II–III" species. The 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene analogs of the previously characterized II–III type of complex with pyrazine could not be produced by either chemical oxidation or electrochemical oxidation. The characteristic near-ir band of the pyrazine II–III dimer does not exist for the other two ligands, and the cyclic voltammetry study indicated one two-electron change in the oxidation. Thus the properties of these latter systems can be described as mixtures of the II–II and III–III complexes, with no special stability to the II–III complex.

It has been reported[3] that μ-pyrazine-bis(pentaammineruthenium(II)) undergoes oxidation by silver ion to form



$[(NH_3)_5Ru^{II}NC_4H_4NRu^{III}(NH_3)_5]^{5+}$

which has a broad, intense absorption in the near-infrared. This absorption is attributed to the transition [2, 3] → [3, 2]*, *i.e.*, the Franck–Condon[4] barrier to electron transfer required for a transition between two centers with the same chemical composition but differing in environment due to their different charges. By use of the Marcus–Hush theory,[5–7] the rate of electron transfer may be approximated from the energy of the near-infrared absorption.

If this interpretation of the occurrence of the near-infrared absorption of the above complex is correct, it would be interesting to see how different bridging groups would affect the rate of electron transfer between the ruthenium centers. For this reason, the preparation of the "Ru(II)–Ru(III)" complexes of μ-4,4-bipyridinebis(pentaammineruthenium(II)) and μ-1,2-bis(4-pyridyl)ethylene-bis(pentaammineruthenium(II)) was attempted both by chemical and electrochemical means.

Experimental Section

Chemical Oxidation of the "Ru(II)–Ru(II)" Complexes. Oxidation of the μ-pyrazine-bis(pentaammineruthenium(II)) complex was accomplished in two well-defined steps by potentiometric titration with Ce(IV)[3]. Production of the Ru(II)–Ru(III) species was also achieved by oxidation with silver ion. Since only the Ru(II)–Ru(III) species was desired for the dipentaammineruthenium(II) complexes of 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene, and since these complexes proved to be sensitive to the highly acidic conditions used in ceric oxidations, the oxidations were attempted with silver ion.[1]

The addition of a stoichiometric amount of $AgNO_3$ to solutions of the dipentaammineruthenium(II) complexes of 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethylene was performed in a nitrogen-atmosphere glovebox. D_2O was used as the solvent so that near-infrared spectra could be taken. The solutions were filtered through glass wool to remove the black metallic silver formed during the oxidation.

Near-Infrared Spectra. A Cary-14 recording spectrometer was used to record near-infrared spectra from 700 to 2500 nm. The solutions were placed in deaerated, matched quartz cells. The cell compartment was maintained at 25°.

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[2] Address correspondence to this author at the University of California, Irvine, Calif. 92664.

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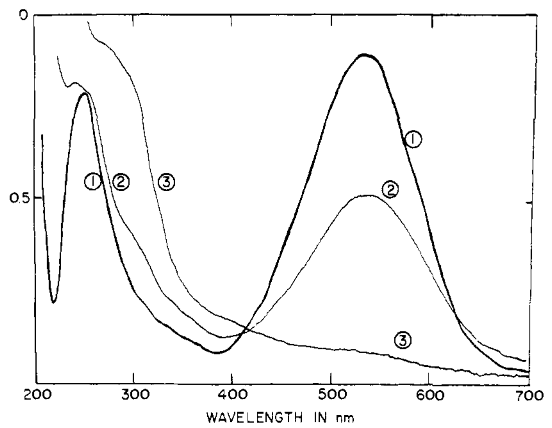


Figure 1. The visible and ultraviolet absorption spectrum of (1) μ-4,4′-bipyridine-bis(pentaammineruthenium(II)) (**1**), (2) $AgNO_3$ + **1**, 1:1, same concentration as **1**, (3) excess $AgNO_3$ + **1**, same concentration of **1**.

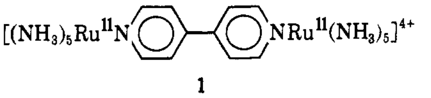
Cyclic Voltammetry. An H-cell and stand tube were prepared according to Lingane and Laitinen.[8]

The solutions used for the cyclic voltammetry measurements were 0.01 *M* in the complex and 0.1 *M* in KCl. In a typical measurement, 40 ml of the aqueous solution was used. The solution was deaerated with purified helium for 15 min before use. The presence of oxygen was readily evident from measurement of the current at − 0.7 V *vs.* sce.[9]

The triangular wave was generated by a Chemtrix Type 205 polarographic time base unit. The cyclic voltammograms were recorded on a Textronix RM 564 storage oscilloscope with a Chemtrix Type 310 readout amplifier as input. The oscilloscope was equipped with a Textronix C-12 Polaroid camera unit. Desired runs were photographed from the screen of the storage oscilloscope. The measurements were made at 25°, with a mercury drop life of 6–10 sec.

Results and Discussion

The visible spectrum of complex **1** did not show large shifts on addition of a stoichiometric amount of silver ion (Figure 1). This result, however, was similar to that seen for the analogous pyrazine complex[3] and left open the possibility that the near-infrared region might contain interesting information. The spectrum of the "oxidized species" in this region, however, resembled spectra of the Ru(II)–Ru(II) and Ru(III)–Ru(III) complexes and provided no new information. At the concentrations of the solution used (0.01 *M*) and with the path lengths of the cells (up to 2 cm), a peak with an extinction coefficient of 10^2 should be easily seen. The reported extinction coefficient for the pyrazine Ru(II)–Ru(III) complex is 6.5×10^3. From the ultraviolet and visible spectrum and the near-infrared spectrum, the existence of a Ru(II)–Ru(III) species could not be verified. The spectra could arise from a combination of the spectra of the Ru(II)–Ru(II) complex and the fully oxidized species, which is assumed to be the Ru(III)–Ru(III) complex.



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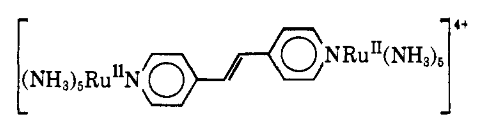
Very similar results were obtained in a similar experiment performed with the complex



Again, no new peaks were evident in the near-infrared for a solution of stoichiometric amounts of the complex and silver ion. In this case, however, the fully oxidized species was light sensitive, quickly turning green.

To overcome skepticism at this point, the reported Ru(II)–Ru(III) complex was prepared and the near-infrared spectrum indeed showed a band with λ_{max} at about 1575 nm with an extinction coefficient of the same magnitude as quoted above by Creutz and Taube.[3]

It was hoped that evidence for the Ru(II)–Ru(III) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)-ethylene might be obtained by electrochemical means. It was also of interest to see if the oxidation step(s) is (are) reversible.

An electrochemical method, cyclic volammetry, which provides rapid scanning of a voltage range and provides a recognized criterion for reversibility has been developed extensively for various types of electrochemcial processes, including oxidations, and reductions in which the product reacts before the cycle is completed.[10–13] In this method, a triangular wave potential is applied to the electrode (in our case, a dropping mercury electrode) with the current recorded as a function of voltage. During the redox cycle, the substrate is reduced in the negative voltage scan and in the positive scan, the reduced form is reoxidized if it has not reacted chemically in the interim.

For a reversible process, the separation of the anodic and cathodic peak currents is 57 mV, and the magnitude of the peak currents should be equal. For irreversible processes, the separation of the peaks is greater and the slope of the plot discussed above varies considerably. In processes involving reactions of the electrochemically produced species, the peak currents are generally not equal.

In the oxidation of the dipentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)-ethylene by cyclic voltammetry, each of the cyclic voltammograms shows a reversible two-electron process, as indicated by the 60-mV separation of the anodic and cathodic peaks and the equal magnitudes of the peak currents for both directions of the process.

The cyclic voltammetry of μ-pyrazine-bis(pentaammineruthenium(II)) produced a voltammogram with two irreversible processes occurring during the cycle. They were identified as irreversible because the separation of the peaks is greater than 57 mV.

The results from the cyclic voltammetry study and the near-infrared spectra of the dipentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene indicate that neither silver ion oxidation nor electrochemical oxidation of the complexes produces the Ru(II)–Ru(III) complex in either case.[14]

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(14) NOTE ADDED IN PROOF. S. A. Adeyemi, *et al.*, *J. Amer. Chem. Soc.*, 94, 300 (1972), have found that the dimers of 4,4′-bipy and 1,2-bis(4-pyridyl)ethylene complexes of $Ru^{II}(bipy)_2$ exhibit only one oxidation wave at $E_{1/2}$ = 0.84 and 0.82 V, respectively.

Conclusion

It was hoped that the effect of different "bridging groups" between pentaammineruthenium(II) and pentaammineruthenium(III) groups could be ascertained by a study of the near-infrared spectra of the Ru(II)–Ru(III) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene. Neither chemical means nor electrochemical means (*via* cyclic voltammetry), however, could be shown to produce these complexes by oxidation of the analogous Ru(II)–Ru(II) complexes. It appeared evident from the cyclic voltammograms of the dipentaammineruthenium(II) complexes of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene that these complexes undergo reversible two-electron oxidation and reduction. The mechanism of the oxidation (*e.g.*, it could be simultaneous one-electron withdrawal from each end of the complex, or a two-electron withdrawal from one end, perhaps followed by an electronic reorganization) is not elucidated by the cyclic voltammetry results.

One of the puzzling and disappointing aspects of this study is the noninteraction between the metal ions in the dimers of 4,4′-bipyridine and 1,2-bis(4-pyridyl)ethylene as compared to the strong interaction found in the pyrazine dimer. We are now further investigating other pyrazine-like dimer systems in order to determine the particular feature of this system that leads to its rather interesting properties.

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Effects of Donor Nonideality on Molecular Complex Equilibria[1]

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Received June 28, 1971

Abstract: A treatment of molecular complex equilibrium is proposed that takes nonideality of the excess component into account by using activities from vapor pressure data. It is shown, using an nmr study of the benzene–caffeine complex in carbon tetrachloride as an example, how using donor activities removes the concentration scale dependence of the shift of the pure complex and brings equilibrium constants derived for mole fraction and molal scales into their proper infinite-dilution relationship. Traditional plots of the data using the usual ideal mixture of species approximation give good linear plots even for the molal scale, which artificially increases the nonideality. Thus, straight-line plots cannot be used as a criterion for the absence of nonideality effects.

In the last 20 years the experimental work devoted to studies of molecular complexes has been voluminous. It is summarized in numerous books and reviews.[2-9] There are good reasons for this work to be done. Besides understanding donor–acceptor complexes themselves, the basic interactions are of considerable importance in determining conformation of proteins and nucleic acids. Because of the significance of this work, it is important that the data obtained for simple molecular complexes rest on a secure theoretical foundation. Unfortunately, several groups of workers have pointed out that this foundation is far from secure.[10-13] It is the purpose of this paper to continue this discussion and to point out at least one way to strengthen this foundation.

A great deal of the effort mentioned above has been devoted to obtaining association constant data for large numbers of complexes as well as parameters relating to the structure of the complex such as absorbancy indices, dipole moments, nmr shifts, enthalpies of formation, etc. The problem is that there is coupling between the microscopic model which one uses to interpret the experimental data and the values of the association constant and structural parameters which one calculates. Thus, it is necessary to verify the model in order to assess the reliability of the results, and often it is impossible to do this because of the nature of the system.[13]

In what follows, we wish to use an nmr study of the benzene–caffeine complex in CCl_4 as an example of the kinds of difficulties which one runs into in studies of weak molecular complexes and to suggest a more adequate model than the one presently used.

Theory

Consider the case where there is only a 1:1 association equilibrium between a donor molecule, D, and an acceptor molecule, A, to form complex, AD

$$A + D = AD \qquad (1)$$

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