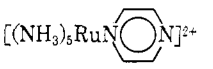
A Direct Approach to Measuring the Franck–Condon Barrier to Electron Transfer between Metal Ions

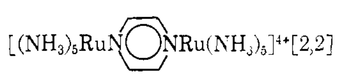
Sir:

The ion **1** has been described[1] and has a band maximum at 472 mμ attributable to the charge-transfer absorption $t_{2g} \rightarrow \pi^*$.



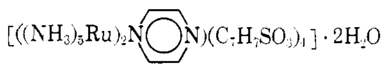
1

When $(NH_3)_5RuOH_2^{2+}$ is added to a solution containing the pyrazine complex, a band develops with a maximum at 547 mμ. Job's method[2] has been applied to the system, yielding proof that the new species contains two ruthenium atoms for each pyrazine, consistent with formulation **2**[3] for the complex.



2

A tosylate salt (**3**) isolated from the solution gave the following analysis. *Anal.* Calcd for **3**: C, 32.8; H, 5.63; N, 14.3; S, 10.9. Found: C, 33.0; H, 5.68; N, 14.1; S, 11.4.



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Microanalyses were performed by Stanford Microanalytical Laboratory.

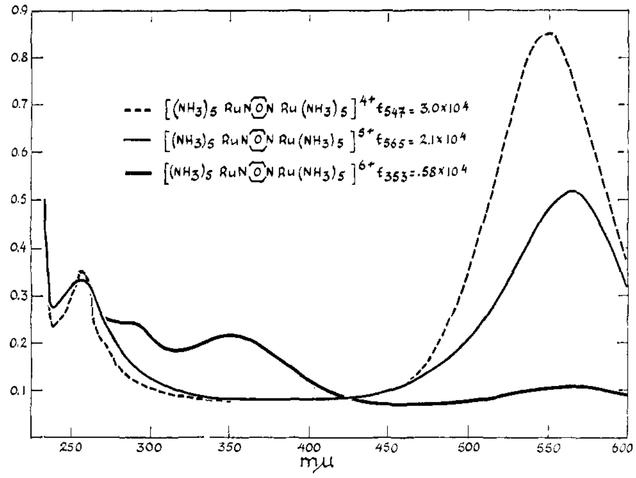
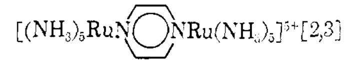


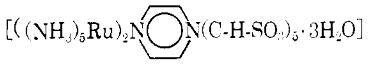
Figure 1. Visible–ultraviolet spectra of [2,2], [2,3], and [3,3] in 0.05 N $HClO_4$. (Absorbance around 560 mμ for [3,3] is probably due to residual [2,3] in the solution; photoreduction of [3,3] takes place readily.) $\epsilon_{[2,2]}$ and $\epsilon_{[2,3]}$ are measured in the range 2–3 × 10^{-5} M, path length 1 cm. $\epsilon_{[3,3]}$ is measured at 8 × 10^{-5} M, 1-cm path length.

We have studied the oxidation of [2,2] and have been particularly interested in the possibility of oxidizing it by a one-electron change to generate **4**. We find that potentiometric titration of [2,2] by Ce(IV) takes place in two well-defined steps, one end point corresponding to the formation of [2,3] and further oxidation producing [3,3]. Both steps are reversible; the formal oxidation reduction potentials (Latimer convention) for the [2,2]–[2,3] and [2,3]–[3,3] couples are −0.40 and −0.76 V at 25° and $[Cl^-] = 0.10$.



4

From a solution of [2,3] prepared by silver ion oxidation of [2,2] we isolated the tosylate salt **5** which gave the following analysis. *Anal.* Calcd for **5**: C, 34.4; Ru, 14.8; N, 12.3; S, 11.7; H, 5.5. Found: C, 34.3; Ru, 14.4; N, 12.4; S, 11.8; H, 5.4.



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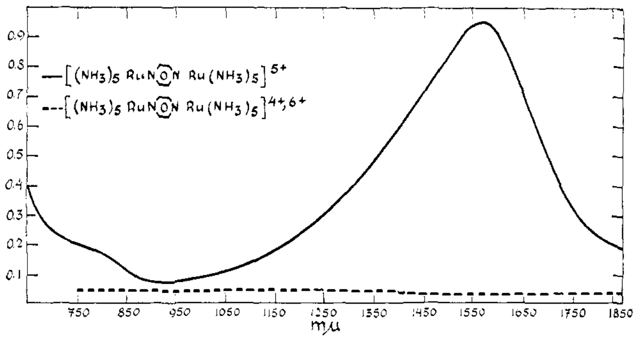

Figure 2. Near-infrared spectrum of [2,3] in D_2O: concentration of [2,3] = 1.5 × 10^{-4} M; 1-cm path length. (Dashed line is actually the blank, but accurately indicates the spectra of [2,2] and [2,3] in this range above 750 mμ at this concentration level.)

As expected, [3,3] does not show the strong absorption in the visible region characteristic of the Ru(II)–py combination. At first examination, the absorption spectrum of [2,3] proved disappointing. In the visible region one band is observed (see Figure 1) with a maximum (λ 565 mμ) only slightly shifted from that of the [2,2] species, and thus is attributable to the $t_{2g} \rightarrow \pi^*$ transition. But on extending the investigation to the near-infrared, another absorption is observed (λ_{max} 1570 mμ). Because of the width and intensity of this absorption (see Figure 2), we ascribe it also to an electron-transfer transition rather than to an overtone of a vibrational mode. This assignment is supported by the fact that neither [2,2] nor [3,3] shows absorption at long wavelengths having characteristics similar to those described for [2,3].

We attribute the absorption in the long wavelength region to the transition [2,3] → [3,2]*. Even though the *composition* of the first-coordination spheres of the ruthenium atoms in [2,3] is the same, energy is required for the transition because the 3+ and 2+ ions in the final state will be in environments appropriate to 2+ and 3+ ions, respectively. In this interpretation, the energy of the transition is a direct measure of the Franck–Condon[4] barrier to electron transfer—not the energy barrier separating the ground state from the activated complex for spontaneous electron transfer, but

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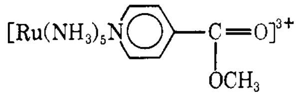
[1] P. Ford, D. F. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

[2] M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964, p 282.

[3] This complex was prepared originally at Stanford University by Dr. P. Ford.

[4] (a) Attributed to J. Franck by W. F. Libby, Abstracts, Physical and Inorganic Section, 115th National Meeting of the American Chemical Society, San Francisco, Calif., March 27–April 1, 1949; (b) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

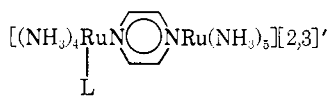
an energy approximately[5] four times that. The factor 4 can arise from the quadratic dependence of the energy on the extent of distortion of the ion's first coordination sphere.[6] Marcus has estimated[7] this distortion to contribute approximately 8 kcal to $\Delta F^{\ddagger}$ for self-exchange in the $Fe(H_2O)_6^{2+}$–$Fe(H_2O)_6^{3+}$ and $Co(H_2O)_6^{2+}$–$Co(H_2O)_6^{3+}$ systems. An energy cost somewhat less than this would be expected for the present system involving as it does only changes in the t_{2g} energy levels. If the energy barrier measured by the infrared transition is interpreted as being four times $\Delta F^{\ddagger}$ for internal electron transfer, a self-exchange rate of 3×10^9 sec^{-1} is calculated for [2,3]. This seems reasonable in comparison to a second-order rate constant of 10^6 M^{-1} sec^{-1} measured[8] for electron transfer between **1** and **6** (this value



6

has been corrected for the effect[9] of $\Delta F°$). When allowance is made for the energy required to bring the reactants together, the second-order rate constant referred to would convert to a considerably greater first-order constant for electron transfer within the collision complex.

Observations made with unsymmetrical species of type **7** in D_2O solutions strongly support our interpretation of the long wavelength band. First we prepared **8**



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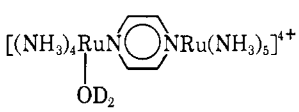

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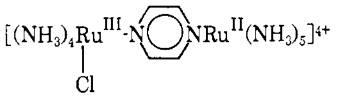
by adding *cis*-$(NH_3)_4Ru(OD_2)_2^{2+}$ to a solution of **1**. When the association reaction was complete as judged by the absorption spectrum in the visible region, $S_2O_8^{2-}$ was added as oxidant to prepare [2,3]′, L = D_2O. The long wavelength band is shifted only slightly in this complex, the maximum appearing at 1530 mμ. The shift is much more pronounced, however, in complexes prepared by substituting other ligands for D_2O. A complex where L = pyrazine was prepared by making a solution of [2,2]′, L = D_2O, 1 M in pyrazine, allowing the reaction to go to completion to give [2,2]′, L = pyrazine, and then adding $S_2O_8^{2-}$ as oxidant to give [2,3]′, L = pyrazine. In this solution, the new band appeared at 1160 mμ. A *cis*-chloro dimer was prepared by oxidizing [2,2]′, L = D_2O, in 2 M sodium chloride. Presumably the first product of the oxidation is the [2,3] aquo dimer which then equilibrates with the medium. This transformation can actually be observed in the near-infrared spectra. At first, two maxima are evident. One, at 1530 mμ, attributed to the *cis*-aquo dimer, disappears over 0.5 hr to give a single maximum centered at 1450 mμ, attributable to



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It is notable that the shift observed for the near-infrared band when ammonia is replaced by chloride (0.1 V) or by pyrazine (0.3 V) parallels the difficulty of electron transfer as measured in equilibrium processes. This trend is expected on the basis of our interpretation of the long wavelength band. In [2,3]′, L = Cl^-, it is more difficult to reduce Ru(III) bound to chloride than to ammonia. In [2,3]′, L = pyrazine, the presence of a back-bonding ligand makes the oxidation of Ru(II) more difficult than for the pentaammine.

The interpretation advanced for the long wavelength band in the [2,3] species depends on the supposition that the two Ru atoms in the species are not equivalent though, as already acknowledged, electron transfer is expected to be rapid. To the extent that the interpretation is successful in explaining the observations, it supports the basic assumption. The assumption finds added support in the observation that the $t_{2g} \rightarrow \pi^*$ transition in [2,3] differs in energy only slightly from that in [2,2]. Apparently much stronger coupling is needed than is provided by the π-orbital system of the pyrazine bridging group to bring the Ru atoms into equivalent configurations. As measured by the rates for spontaneous electron transfer, the energies required to bring Ru(II) and Ru(III) into equivalent configurations decreases as NH_3 is replaced by back-bonding ligands,[8,10,11] and with more back-bonding ligands in the coordination sphere, the two atoms in the +5 ion may be equivalent. Work is in progress in an effort to prepare an ion analogous to [2,3] from the nucleus $Ru(bipy)_2(H_2O)_2$.

Warning. Perchlorate salts of ruthenium ammines are hazardous and should be handled only in milligram quantities unless elaborate precautions appropriate to manipulating sensitive and explosive materials are taken.

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(5) "Approximately" for the reason, among others, that the distortion called for in the spontaneous electron transfer may differ in symmetry from that which results from radiation-induced electron transfer.

(6) (a) P. George and J. S. Griffith, "The Enzymes," Vol. 1, P. D. Boyer, *et al.*, Ed., Academic Press, New York, N. Y., 1959, p 347; (b) R. A. Marcus, *Discussions Faraday Soc.*, **29**, 21 (1960); (c) N. S. Hush, *Progr. Inorg. Chem.*, **8**, 391 (1967).

(7) R. A. Marcus, *Trans. N. Y. Acad. Sci.*, **19**, 423 (1957).

(8) R. G. Gaunder, unpublished observations.

(9) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

(10) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(11) J. C. Solenberger, Ph.D. Thesis, Washington University, St. Louis, Mo., June 1969.

Carol Creutz, Henry Taube
Department of Chemistry
Stanford University, Stanford, California 94305

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A Method for Determining the Chiralities of Optically Active Glycols

Sir:

The chirality of glycols can be determined from the sign of the strong $\pi \rightarrow \pi^*$ Cotton effect of its dibenzoate