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A Resonance Raman Investigation on the CT Spectra and Photochromism of the Binuclear Complex $(NH_3)_5Ru^{II}(\mu\text{-pyrazine})Cu^{II}$

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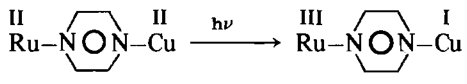
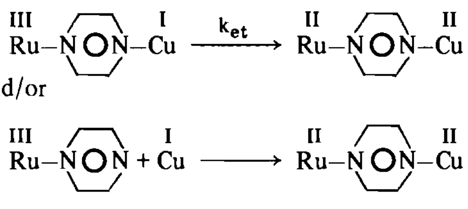
Electron transfer photochromism was recently demonstrated by Durante and Ford [1] for the binuclear complex [2] $(NH_3)_5Ru^{II}(\mu\text{-pz})Cu^{II}$ (pz = pyrazine) in aqueous solution. This complex, as well as the protonated complex $(NH_3)_5RupzH^{3+}$, were reported to be photochemically stable to continuous photolysis ($\phi \sim 10^{-4}$). Both the complexes exhibit a visible spectrum dominated by an intense MLCT absorption band (λ_{max} 508 nm and 529 nm, respectively) which is bathochromically shifted in comparison to the less photochemically stable $(NH_3)_5Ru(\mu\text{-pz})Ni^{II}$ (λ_{max} 493 nm) and $(NH_3)_5Rupz^{2+}$ (λ_{max} 472 nm, $\phi \sim 10^{-3}$) complexes. Apparently, the trends on the bathochromic shifts of the MLCT band are paralleled by a photochemical stabilization of the ruthenium(II)–pyrazine complexes.

Flash photolysis [1, 3] of the $(NH_3)_5Ru^{II}(\mu\text{-pz})Cu^{II}$ complex produces efficient transient bleaching of the MLCT absorption at 508 nm ($\phi \sim 0.2$) [1] followed by regeneration of the starting material. Because the Ru(III)–pyrazine complex is practically colorless [1, 4], the transient bleaching was assigned to a photostimulated electron transfer process,



(1)

followed by regeneration of the initial complex, according to the redox reactions,



(2)

Since the visible absorption spectra of Ru(II)–pyrazine complexes are attributable to metal-to-pyrazine charge transfer [4], resonance enhancement [5] of the Raman bands of the pyrazine ligand is expected. For the Ru(III)–pyrazine complexes which do not display intense absorption, the Raman spectra are not resonance enhanced. Therefore, a decrease in the intensities of the Raman bands of $(NH_3)_5Ru^{II}(\mu\text{-pz})Cu^{II}$ should be associated to the photostimulated electron transfer process previously described [1].

Resonance Raman spectra (Jarrell-Ash, Model 25-300 Spectrometer) in the range of 200–1700 cm^{-1} are shown in Fig. 1. The ν_1 symmetric stretching band of the sulfate ion (0.33 *M*) was used as internal reference in aqueous solution. The spectra 1.a and 1.b were recorded with a spinning cell (*ca.* 1500 rpm) at 488 nm and 514 nm, respectively, using argon ion laser excitation. The samples were prepared under argon atmosphere, with excess of copper(II) sulfate (0.33 *M*) to assure the complete formation of the binuclear complex from the $(NH_3)_5Rupz^{2+}$ ion (8×10^{-5} *M*). All the bands are polarized, belonging exclusively [6] to the Ru–pyrazine moiety in the complexes. A tentative assignment, by comparison with the Raman frequencies of free pyrazine [7] is the following: 1605 cm^{-1} (ring stretch), 1234 cm^{-1} (in plane C–H def.), 1088 cm^{-1} (in plane C–H def.), 1016 cm^{-1} (ring stretch), 687 cm^{-1} (in plane ring def.) and 318 cm^{-1} (Ru–N stretch).

Resonance enhancement is somewhat stronger at 514.5 than at 488 nm, for its proximity to the maximum wavelength of the MLCT absorption band (508 nm). Polarization measurements indicated that only the totally symmetric vibrations of pyrazine are enhanced in the binuclear complex. According to Albrecht and Hutley [5], when a vibrational interaction with a single excited electronic state is involved, only the totally symmetric vibrations should be enhanced. In the case of vibronic mixing of two excited states, the enhancement should occur with any symmetry mode which is contained in the direct product of the representations of the two electronic states.

Under C_{2v} symmetry, the highest occupied $d\pi$ orbitals of ruthenium(II) transform as $b_1(d_{xz})$, $a_2(d_{xy})$ and $b_2(d_{yz})$. The two lowest unoccupied π^* orbitals of pyrazine transform as b_2 and a_2. Transitions to the $a_2(\pi^*)$ orbital have been excluded [4] in a number of ruthenium(II)–N-heterocycles, based on the fact that this orbital has a node through the *para* position. This is supported by dramatic substituent effects observed at the *para* position on the charge transfer bands of the complexes [4], which cannot be explained if $a_2(\pi^*)$ orbitals are involved. Also, a higher $b_2(\pi^*)$ orbital has not been considered for energetic reasons [4]. Neglecting the $A_1 \rightarrow A_2$ transitions which are not allowed in the C_{2v} point group, Ford *et al.* [4] proposed that two transitions, from the A_1, $[b_1^2(d_{xz})a_2^2(d_{xy})b_2^2(d_{yz})]$ ground state to the A_1, $[b_1^2(d_{xz})a_2^2(d_{xy})b_2(d_{yz})b_2(\pi^*)]$ and $B_1\,[b_1^2(d_{xz})a_2(d_{xy})b_2^2(d_{yz})b_2(\pi^*)]$ excited states, can be responsible for the visible charge transfer band in the complexes.

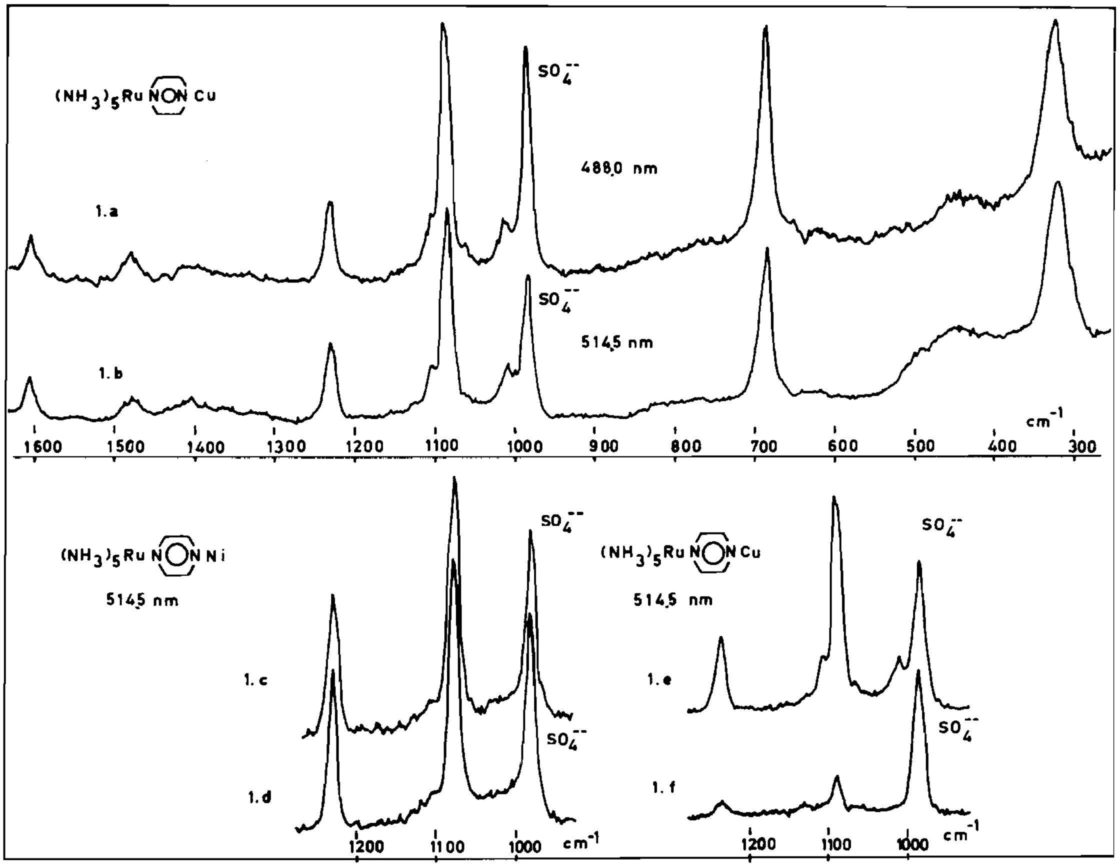


Figure 1. Resonance Raman Spectra of aqueous solutions of $(NH_3)_5Ru^{II}(\mu\text{-pz})M^{II}$ (8×10^{-5} *M*), containing a large excess of dissolved MSO_4 (0.33 *M*). Spectra 1.a and 1.b were recorded under similar conditions, with a spinning cell, but using two different wavelengths of excitation. Spectra 1.c and 1.d, as well as, 1.e and 1.f, were recorded with the cell spinning or stopped, respectively.

Vibronic mixing of the two excited states would enhance only the b_1 modes. Therefore, the fact that solely the totally symmetric vibrations have been enhanced in our Raman spectra can be taken as evidence that a single excited state is involved in the MLCT transition. For symmetry reasons, transition from $b_2(d_{yz})$ to $b_2(\pi^*)$ should be preferred over $a_2(d_{xy})$ to $b_2(\pi^*)$, since in the former the orbitals are directly pointed to a maximum overlap [8]. A similar use of resonance Raman spectra was very recently reported for tris(diimine) complexes of iron(II) [9].

Spectra 1.c and 1.d, recorded respectively with the cell spinning and stopped, refer to the analogous $(NH_3)_5Ru^{II}(\mu\text{-pz})Ni^{II}$ complex. They are presented for comparison purposes. Despite some photochemical decomposition, as observed by a slight decrease of the Raman bands with time, the alternating spectra obtained with the cell moving or stopped, were essentially equivalent.

For the $(NH_3)_5Ru^{II}(\mu\text{-pz})Cu^{II}$ complex, disappearance of the resonance Raman bands is observed when the cell is stopped. This is illustrated in Figure 1 (spectra 1.e and 1.f). Despite these remarkable changes in the intensities of the Raman bands, the alternating spectra in the 1300–900 cm^{-1} range, recorded many times with the cell spinning or stopped, resulted highly reproducible. This indicates that any irreversible photochemical process, if not negligible, cannot account for the behavior reported here. Therefore, we presume that the reversible changes on the intensities of the Raman bands arise mainly from the electron transfer photochromism previously reported by Durante and Ford.

Under the conditions employed, with the cell fixed, the photostimulated electron transfer process (eq. 1) can become almost saturated, forming Ru(III)–pyrazine products which do not exhibit resonance Raman effect. The back-reaction (eq. 2) which was reported [1] to occur with a k_{obsd} of 7.8×10^3 s^{-1} at 25 °C, [Cu(II)] = 0.33 *M* and [Ru] = 1.4×10^{-5} *M*, is too slow to compete efficiently with the photostimulation process. Nevertheless, diffusion through the area exposed to the laser beam may be responsible for a gradual, but slow renewal of the sample in that region, contributing to some residual intensities of the Raman peaks.

When the cell is spinning, the back-reaction can regenerate the starting materials during the rotation period of *ca.* 0.04 sec. This explains why the saturation behavior has not been observed with the spinning cell. Perhaps, by using ultra-fast devices, the speed of rotation could be increased to such a limit (*ca.* 10^5–10^6 rpm in the present case) that, exceeding the rates of the back-reactions, saturation should be attained again.

Acknowledgments

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References

1 V. A. Durante and P. C. Ford, *J. Am. Chem. Soc., 97,* 6898 (1975).
2 M. S. Pereira and J. M. Malin, *Inorg. Chem., 13,* 386 (1974).
3 H. E. Toma and C. Creutz, unpublished results obtained at the Brookhaven National Lab., New York.
4 P. C. Ford, D. F. Rudd, R. Gaunder and H. Taube, *J. Am. Chem. Soc., 90,* 1187 (1968).
5 A. C. Albrecht and M. C. Hutley, *J. Chem. Phys., 55,* 4438 (1971); and R. J. H. Clark, in "Adv. Infrared and Raman Spectr.", Vol. 1, Chapter 4, Clark and Hester Edit., Heyden & Son (1975).
6 T. C. Strekas and T. G. Spiro, *Inorg. Chem., 15,* 974 (1976).
7 R. Lord, A. Marston and F. Miller, *Spectrochim. Acta, 9,* 113 (1957); J. D. Simmons and K. K. Innes, *J. Mol. Spectrosc., 14,* 190 (1967).
8 P. Day and N. Sanders, *J. Chem. Soc.,* 1536 (1967).
9 R. J. H. Clark, P. C. Turtle, D. P. Strommen, B. Streusand, J. Kincaid and K. Nakamoto, *Inorg. Chem., 16,* 84 (1977).