

The Near- and Mid-Infrared Spectrum of the Creutz-Taube Ion in Aqueous Solution: An Application of FTIR Spectroelectrochemical Techniques

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Abstract: Near- and mid-infrared studies of the Creutz-Taube ion by spectroelectrochemical techniques have facilitated the characterization of a low wavenumber electronic transition at 2000 cm^{-1} with $\epsilon \approx 300\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ and full width at half height of ca. 1400 cm^{-1} . The infrared spectra of $\{[\text{Ru}(\text{NH}_3)_5\text{pyrazine}]^{n+}, n = 4, 5, \text{ or } 6\}$, have been recorded in solution under identical conditions, the spectrum of the mixed-valence salt ($n = 5$) being shown to be intermediate between those of the oxidized and reduced forms of the complex. Thus, on the vibrational time scale the odd electron is fully delocalized between the two ruthenium centers, a conclusion in keeping with that based on other spectroscopic studies.

The Creutz-Taube (C-T) ion, $\{[\text{Ru}(\text{NH}_3)_5\text{pyrazine}]^{5+}$, holds a unique position in mixed-valence chemistry and has been the focus of many experimental and theoretical studies. The experimental results—infra-red and Raman¹ ESR,^{2,3} and UV-visible^{4,5} spectroscopy, X-ray photoemission,⁶ and X-ray crystallography⁷—can best be interpreted in terms of a delocalized structure, and theoretical studies based on vibronic^{8,9} or electronic^{10,11} coupling models are largely in accord with the experimental results. Electronic transitions for the C-T ion (not present for its 4+ and 6+ analogues) in the infrared and near-infrared spectral regions have been identified at low temperatures using MCD techniques.^{12,13} While the presence of these electronic transitions can be accounted for by both two- and three-center electronic coupling models of the C-T ion (although the assignments for these transitions differ according to the model, viz. $4d_{yz} \rightarrow$ nonbonding and $4d_{x^2-y^2} \rightarrow$ nonbonding for the three-center model,¹⁰ and electric-dipole-allowed transitions between the electronically coupled Ru d-orbitals in the two-center model¹¹), the determination of the band profile and intensity is necessary to provide a more rigorous basis for the comparison of experiment and theory. Attempts to record the low wavenumber electronic bands directly have failed previously on account of interference by the strong absorptions of the solvent and solute. By use of spectroelectrochemical techniques we have been able to identify the near- and mid-infrared spectral changes which accompany oxidation or reduction of the C-T ion and thereby to characterize its low wavenumber electronic and vibrational bands in solution.

Experimental Section

The complex $\{[\text{Ru}(\text{NH}_3)_5\text{pyrazine}]\text{Cl}_5$ was prepared by the literature method⁷ and was shown to be pure by spectroscopic and electrochemical techniques. Electrochemical experiments were carried out with a Me-

trohm E506 potentiostat and Metrohm E612VA scanner. Platinum wires were used as working and counter electrodes in conjunction with a saturated calomel reference electrode (Metrohm 6.0702.100). KCl was used as the supporting electrolyte.

Infrared spectra were recorded with a Bruker IFS 113V Fourier transform interferometer. Near-infrared spectra ($2000\text{--}10\,000\text{ cm}^{-1}$) were collected with a W-lamp source, Si/CaF₂ beamsplitter, and a liquid nitrogen cooled InSb detector, while mid-infrared spectra ($600\text{--}4000\text{ cm}^{-1}$) were obtained with a Glowbar source, Ge/KBr beamsplitter, and a liquid nitrogen cooled MCT detector. The IRRAS cell used for the spectroelectrochemistry has been described elsewhere.¹⁴ The infrared beam passes through the cell window (CaF₂ for the spectral range $1100\text{--}10\,000\text{ cm}^{-1}$, polythene-covered KBr for the spectral range $600\text{--}1100\text{ cm}^{-1}$) and then into a thin layer of solution following which it is reflected back toward the detector from a highly polished disc of platinum metal; this also acts as the working electrode. The thickness of the film could be controlled with a micrometer adjustment. The solvent for each of these measurements was water, ²H₂O being used to characterize the spectra in the regions obscured by strong absorptions arising from stretches, bends, and librational modes of ¹H₂O. All samples were degassed prior to use. Sample concentrations were ca. $1.2 \times 10^{-3}\text{ mol dm}^{-3}$ for the near-infrared and ca. $3.2 \times 10^{-2}\text{ mol dm}^{-3}$ for the mid-infrared studies.

UV-visible spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer.

Results and Discussion

The C-T ion undergoes reversible oxidation (+0.42 V vs SCE) and reduction (−0.03 V vs SCE) processes, the ruthenium atoms having the formal oxidation states (II,II), (II^{1/2},II^{1/2}), and (III,III). The electronic spectrum of the (II^{1/2},II^{1/2}) ion is characterized by the occurrence of a band at 6320 cm^{-1} which is absent from the spectra of both the (II,II) and (III,III) ions. Absorption spectra (reference = empty cell) of the C-T ion at a range of potentials are shown in Figure 1a. In this spectral region the water overtone ($2\nu_{\text{OH}}$, 6940 cm^{-1}) and combination ($\nu_{\text{OH}} + \delta_{\text{HOH}}$, 5160 cm^{-1}) bands are prominent in the spectra, particularly when the potential is such that the C-T ion is predominantly in the (II,II) form. The variation of the concentration of the (II^{1/2},II^{1/2}) ion with applied potential is in accord with the predictions based on the Nernst equation. The C-T ion could be cycled through the (II,II) and (II^{1/2},II^{1/2}) forms without significant decomposition but some occurred on oxidizing the complex to the (III,III) form (ca. 20% in the time taken to electrogenerate the species). By using the spectrum of the complex in the (II,II) form as the reference (since it has no absorption bands in the $6000\text{--}cm^{-1}$ region) the changes in the spectra which result from oxidation can be identified more clearly (Figure 1b). The asymmetry of the $6320\text{--}cm^{-1}$ band, which has been adequately explained by vibronic coupling from a single electronic origin,¹² is apparent in the spectra. The effectiveness of this approach for

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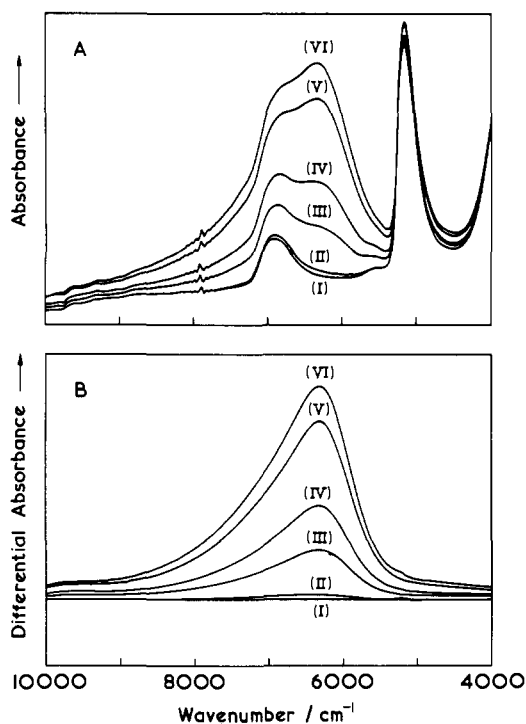


Figure 1. Near-infrared absorption spectra of $\{[\text{Ru}(\text{NH}_3)_5]_2\text{pyrazine}\}^{n+}$, $n = 4$ or 5 /KCl/ H_2O , applied potential = (i) -0.20 , (ii) -0.10 , (iii) $+0.05$, (iv) $+0.07$, (v) $+0.12$, (vi) $+0.20$ V vs SCE: (A) reference = empty cell, (B) reference = spectrum (i), i.e., the (II,II) form of the C-T ion.

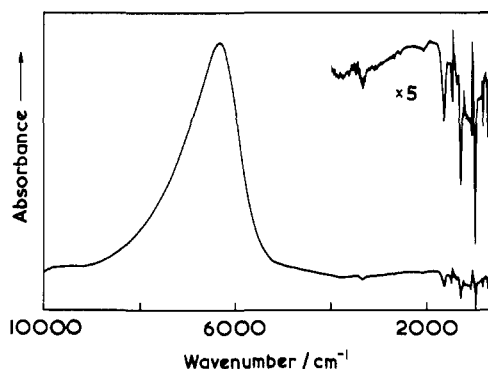


Figure 2. Near- and mid-infrared absorption spectra of $(\text{II}^{1/2}, \text{II}^{1/2})$, reference = spectrum of (II,II), composed from the following scaled spectra: $3500\text{--}10000\text{ cm}^{-1}$, H_2O solvent; $2800\text{--}4000\text{ cm}^{-1}$, $^2\text{H}_2\text{O}$ solvent; $1100\text{--}3100\text{ cm}^{-1}$, H_2O solvent; $700\text{--}1100\text{ cm}^{-1}$, $^2\text{H}_2\text{O}$ solvent.

the subtraction of bands due to strong absorptions of the solvent or the supporting electrolyte is demonstrated by the removal of the water overtone and combination bands from the spectrum (Figure 1b). Spectra recorded in deuteriated solvent give the same bandshapes after appropriate spectral subtraction.

The low extinction coefficients, the interference by vibrational bands, and the strong absorption by the solvent (water) combine to make identification of electronic absorption bands found in the mid-infrared spectral region very difficult. Preliminary infrared studies on aqueous solutions of the C-T ion have suggested the presence of a band at 2000 cm^{-1} through the observation of base line shifts;¹⁵ however, the band profile could not be identified. Low-temperature (1.4 K) MCD spectroscopy of the C-T ion in Nafion films has provided the best previous experimental evidence for the existence of additional low wavenumber electronic transitions, with the identification of bands at ca. 2000 and ca. 4000 cm^{-1} ,^{12,13} however, there would seem to be no possibility of extending such work to the solution state. By the use of relatively concentrated solutions ($>10^{-3}\text{ mol dm}^{-3}$) in deuteriated and

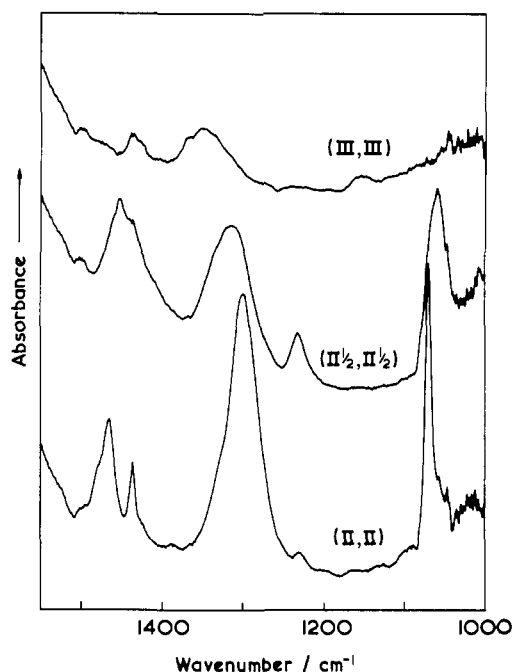


Figure 3. Mid-infrared absorption spectra of $\{[\text{Ru}(\text{NH}_3)_5]_2\text{pyrazine}\}^{n+}$, $n = 4, 5, \text{ or } 6$, reference = empty cell, H_2O solvent.

Table I. Wavenumber (cm^{-1}) and Band Assignments for the C-T Ion in H_2O or D_2O ^a

assignment	II/II	II ^{1/2} /II ^{1/2}	III/III
?	(829 m)	(831 w)	(845 w)
ν_{12}	1069 s	(1069 s)	(1058 m)
ν_{18b}	(1086 w)	1078 sh w	
ν_{9b}			1157 w
?		1232 m	
δ_{HNH}	1298 vs	(992 s)	1319 br s (1002 m)
ν_{19b}	1435 m	(1434 m)	1437 sh
ν_{19a}	1464 s	1451 s	1437 m
?	1482 sh	1499 w	1500 w

^a Values in parentheses were obtained from deuteriated solutions. Nomenclature for the pyrazine modes follows ref 16. vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

nondeuteriated solvents it has now been possible to record high quality absorbance spectra of the C-T ion over the range $700\text{--}10000\text{ cm}^{-1}$ (Figure 2). The spectrum is necessarily a composite of scaled spectra recorded with deuteriated and nondeuteriated solvents and with appropriate combinations of infrared transmitting windows, beamsplitter, and detector. Scaling was accomplished by normalizing the absorbance in regions where there is good spectral overlap. Since it is the absorbance difference between the (II,II) and $(\text{II}^{1/2}, \text{II}^{1/2})$ species which is plotted, wavenumber shifts of vibrational bands will give rise to differential features, while intensity changes will give rise to positive or negative peaks. A broad band at ca. 2000 cm^{-1} is clearly evident in these spectra despite the presence on the low wavenumber side of strong differential features which arise through the shifts of vibrational bands on oxidation of the (II,II) complex. By comparing the spectra in this region as a function of applied potential, using both $^1\text{H}_2\text{O}$ and $^2\text{H}_2\text{O}$ as solvent, it has been possible both to confirm the presence of the band as well as to obtain a good estimate of its intensity and bandshape. Thus the 2000-cm^{-1} band has a full width at half height (FWHH) of ca. 1400 cm^{-1} and intensity ca. 5% of that of the 6320-cm^{-1} band. The weak feature observed at 4000 cm^{-1} in the MCD work¹² is not evident in these spectra; however, there is a suggestion of a band underlying the 6320-cm^{-1} band at $4500\text{--}5000\text{ cm}^{-1}$ which has an intensity and FWHH similar to that of the 2000-cm^{-1} band.

The changes in the vibrational spectra clearly reveal the delocalized character of the C-T ion, at least on the vibrational time

scale. Infrared spectra (reference = empty cell) of the (II,II), (II^{1/2},II^{1/2}), and (III,III) ions over the range 1050–1550 cm⁻¹ are shown in Figure 3. The spectrum of the (II^{1/2},II^{1/2}) ion is clearly intermediate between those of the (II,II) and (III,III) ions. Listings of band wavenumbers are given in Table I together with tentative assignments based upon wavenumber shifts, or lack thereof, on deuteration of the solvent and comparison of the observed spectra with that expected from a previous normal coordinate analysis of pyrazine.¹⁶ As the (II,II) ion is oxidized the bands which arise from the δ_{HNH} mode move to higher wavenumber and lose intensity. These changes are consistent with there being stronger hydrogen bonding between the coordinated ammonia and solvent molecules in the oxidized forms of the complex. Since the pyrazine hydrogen atoms do not exchange under these conditions, deuteration of the solvent leaves the pyrazine bands unchanged in wavenumber provided that there is no coupling between the pyrazine and amine vibrations in either the deuteriated or the nondeuteriated samples. The bands which arise from the ring stretching vibrations (ν_{19a} , ν_{19b} , and ν_{12}) lose intensity and move to lower wavenumber as the C-T ion is oxidized. Our failure to observe the band arising from the ν_{12} mode of the (III,III) ion is likely to be due partly to some decomposition of the complex in solution and partly to strong solvent absorption below 1050 cm⁻¹. The sensitivity of the pyrazine modes to oxidation or reduction of the C-T ion reflects the involvement of pyrazine-based orbitals in the frontier molecular orbitals of the ion.

Conclusion

By the use of spectroelectrochemical techniques it has been possible to observe a weak electronic band of the C-T ion at 2000 cm⁻¹ ($\epsilon \approx 300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) in aqueous solution at room temperature. This band has only ca. 5% the intensity of the 6320-cm⁻¹ band. The FWHH's of the 2000- and 6320-cm⁻¹ bands are similar with each being ca. 1400 cm⁻¹. There is some evidence that an additional electronic band occurs in the 4500–5000-cm⁻¹ region. The two-center electronic coupling model¹¹ predicts statically allowed transitions of the C-T ion to occur at 1834 and 3167 cm⁻¹ with relative intensities of 29% and 2%, respectively, of that of the strong band calculated at 6170 cm⁻¹ (observed at 6320 cm⁻¹). While our results confirm the existence of a band close to 1834 cm⁻¹, there are serious discrepancies between the observed and predicted intensity¹¹ of that feature. Previous at-

tempts to identify clearly the 1834-cm⁻¹ band (predicted ϵ of ca. 2000 dm³ mol⁻¹ cm⁻¹) have failed, it thus being presumed that the band has an unusually large FWHH.^{11,13} The suggestion can now be ruled out, and attention must therefore be refocused on the assumptions which were made in order to calculate the band intensities. The three-center electronic coupling model¹⁰ is comparatively inaccurate at the low wavenumber end of the spectrum, the low-wavenumber bands being predicted to occur at 2300 and 1500 cm⁻¹ with uncertainties of ca. 1000 cm⁻¹. Therefore our results do not enable us to distinguish between the two- and three-center electronic coupling models based on their ability to describe the low wavenumber electronic structure of the C-T ion. However the fact that we have obtained reliable data on the wavenumber, intensity, and bandshape of low-wavenumber electronic bands should now stimulate interest in performing more accurate calculations in this region of the spectrum.

The mid-infrared solution spectra of the (II,II), (II^{1/2},II^{1/2}), and (III,III) ions are distinct, with the spectrum of the (II^{1/2},II^{1/2}) ion being intermediate between those of the (II,II) and (III,III) ions. This observation is wholly consistent with the formulation of the C-T ion as (II^{1/2},II^{1/2}), within the vibrational time scale, i.e., the odd electron is delocalized over the two ruthenium centers. These results confirm and complement those obtained in a previous low wavenumber study of the C-T ion; assignments for the NH₃ rocking and M-NH₃ stretching modes have been made.¹⁷ Earlier suggestions that the near coincidence of bands in the infrared and Raman spectra of the C-T ion in the solid state may indicate that it is "valence trapped"¹ (since coincidences in the infrared and Raman spectra preclude the species from having a center of symmetry) are not in keeping with the present conclusions based upon solution spectra. Possible alternative explanations of the earlier solid-state results are that either some bands are accidentally coincident or the two ruthenium atoms are crystallographically nonequivalent but with this nonequivalence not leading to valence trapping on the vibrational timescale.

As made evident by the present study, the applicability of spectroelectrochemical techniques to the study of low-wavenumber electronic transitions of mixed-valence complexes is likely to be of considerable value and with many applications.

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