# Electronic, Infrared, and Resonance-Raman Spectroscopic Study of Pyridine Complexes of Ruthenium-(II) and -(III)

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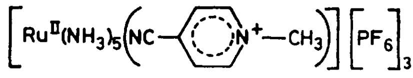
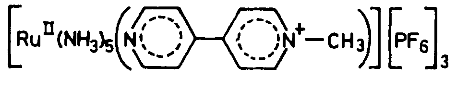
The electronic, i.r., Raman, and resonance-Raman spectra of the complexes $[Ru^{II}(NH_3)_5L][PF_6]_3$ (L = 4-cyano-1-methylpyridinium or 1-methyl-4,4′-bipyridinium) and $[Ru^{III}(NH_3)_5L]Cl_3$ (L = 4-dimethylaminopyridine) have been studied. Excitation within the contour of the strong (ε *ca.* 15 000 dm³ mol⁻¹ cm⁻¹) band at 545—640 nm in the electronic spectra of the ruthenium(II) complexes leads to resonance enhancement of many $a_1$ bands (all with depolarisation ratio $\frac{1}{3}$) of the pyridine ring in each case. The resonant transition is thus deduced to be a *z*-polarised, pyridine $(\pi^*)\leftarrow$Ru $(d_\pi)$ transition, in agreement with a previous conclusion. The most plausible assignment for the resonant transition is $b_2\ (\pi^*)\leftarrow b_2\ (d_{yz})$.

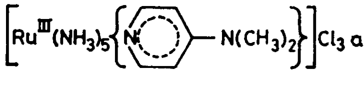
THERE has recently been much interest in bridged dimeric species of the type $[L_5Ru^{II}L'M^{III}L_5]$, where L can be cyanide, 2,2′-bipyridine, or ammonia and L′ can be pyrazine, 4,4′-bipyridine, *trans*-1,2-bis(4-pyridyl)ethene, or a suitably substituted pyridine.[1-5] Low-energy electronic transitions in the visible and near-i.r. regions have been observed in the electronic spectra of these mixed-valence complexes and assigned to intervalence charge-transfer (c.t.) transitions. The metal atoms are thought to interact *via* their $d_\pi$ orbitals with the $\pi^*$ orbitals of the bridging ligand.

Monomeric ruthenium-(II) and -(III) complexes involving both ammonia and substituted pyridines as ligands have also been prepared and studied.[6] Varying the substituent pattern of the pyridine ring changes the wavenumber of the c.t. band and the photochemical reactivity of these complexes.[7,8] In this work some deeply coloured monomeric species of ruthenium-(II) and -(III) bonded to pyridine rings are examined using Raman, resonance-Raman (r.R.), i.r., and electronic spectroscopy. It was hoped to gain some insight into the nature of the electronic transitions in these complexes by plotting excitation profiles of the Raman bands enhanced near resonance.

The complexes studied and reported upon in this paper are shown below.


abbreviated as $[Ru(NH_3)_5(cmpy)][PF_6]_3$


abbreviated as $[Ru(NH_3)_5(mbipy)][PF_6]_3$


abbreviated as $[Ru(NH_3)_5(dmapy)]Cl_3$

EXPERIMENTAL

*Preparation of Samples.*—The ruthenium complexes were prepared by J. C. Curtiss and T. J. Meyer (University of North Carolina) by standard procedures.

*Instrumental Details.*—The Raman spectra were recorded using a Spex 1401 spectrometer in conjunction with Coherent Radiation model 52 Ar⁺ and 500 Kr⁺ lasers. The scattered radiation was collected at 90° and focused by an *f*/0.95 lens onto the entrance slit of the monochromator, after having been passed through a polarisation scrambler. The 0.75-m Czerny–Turner monochromator was fitted with two Bausch and Lomb gratings (1 200 line mm⁻¹) blazed at 500 nm. The method of detection was photon counting using a cooled, grade 1, R.C.A. C31034 phototube (linear display). For all excitation wavelengths, extraneous emission lines were removed by use of a Claassen filter and beam expander. The spectra were calibrated by reference to the emission lines of neon which were superimposed directly onto the spectra during recording. In order to minimise thermal and photochemical decomposition of the samples, low laser powers (⩽50 mW) were used, and the beam was line focused with a cylindrical lens.

Band intensities were measured relative to an internal standard (the $a_1$ mode of potassium sulphate) and then corrected for the spectral response of the instrument. All Raman spectra of complexes in the solid state were recorded at liquid-nitrogen temperatures, each complex being dispersed in a potassium sulphate disc mounted on a cold-finger. Solution measurements were made at room temperature using the spinning-cell technique.

Electronic spectra of the solids dispersed in potassium chloride discs, and of the solutions in methyl cyanide or water, were recorded using a Cary 14 spectrometer. Infrared spectra were obtained with a Perkin-Elmer 225 spectrometer.

RESULTS

*Infrared Spectra.*—The i.r. band wavenumbers of the complexes are listed in Tables 1—3, together with assign-

TABLE 1

Assignments and intensities of bands observed in the i.r. spectrum of $[Ru(NH_3)_5(cmpy)][PF_6]_3$

| Wavenumber/cm$^{-1}$ | Assignment | |
|---|---|---|
| 275mw | $\nu$(M–NH$_3$) metal–ammonia str. | |
| 498m | $\nu$(M–NC) | |
| 522w | Not assigned | |
| 558s | $\delta$(FPF), $\nu_4(t_{1u})$ bend | |
| 736w | $\nu$6a | $a_1$ |
| 780mw (sh) | $\rho$(NH$_3$) rock | |
| 840vs | $\nu$(P–F), $\nu_3(t_{1u})$ str. | |
| 860vs (sh) | | |
| 1 055w | $\nu$12 ring str. | $a_1$ |
| 1 180m | $\nu$18a in-plane C–H bend | $a_1$ |
| 1 205m | $\nu$9a in-plane C–H bend | $a_1$ |
| 1 245m | $\nu$3 in-plane C–H bend | $b_2$ |
| 1 275m | $\delta$(NH$_3$) symmetric bend | |
| 1 370w | $\nu$14 ring str. | $b_2$ |
| 1 410w | Not assigned | |
| 1 465w | $\nu$19b ring str. | $b_2$ |
| 1 515m | $\nu$19a ring str. | $a_1$ |
| 1 550w | $\nu$8b asymmetric py ring str. | $b_2$ |
| 1 630s | $\nu$8a ring str. | $a_1$ |
| 1 660s (sh) | Not assigned | |
| 2 175vs | $\nu$(C≡N) cyanide str. | |
| 3 000m (sh) | $\nu$(C–H) pyridine str. | |
| 3 170s (sh) | $\nu$(N–H) ammonia str. | |
| 3 290s | $\nu$(C–H) methyl str. | |

TABLE 2

Assignments and intensities of bands observed in the i.r. spectrum of $[Ru(NH_3)_5(mbipy)][PF_6]_3$

| Wavenumber/cm$^{-1}$ | Assignment | |
|---|---|---|
| 265m | $\delta$(N–M–N) metal–ammonia bend | |
| 358w | $\nu$(M–NH$_3$) metal–ammonia str. | |
| 480w | Not assigned | |
| 558s | $\delta$(FPF), $\nu_4(t_{1u})$ bend | |
| 716m | Not assigned | |
| 788m | $\rho$(NH$_3$) rock | |
| 840s | $\nu$(P–F), $\nu_3(t_{1u})$ str. | |
| 860m (sh) | | |
| 1 000s | $\nu$1 symmetric ring str. | $a_1$ |
| 1 035w | Not assigned | |
| 1 055w | $\nu$12 ring str. | $a_1$ |
| 1 195s | $\nu$18a in-plane C–H bend | $a_1$ |
| 1 245m | $\nu$9a in-plane C–H bend | $a_1$ |
| 1 275s | $\delta$(NH$_3$) symmetric bend | |
| 1 300m (sh) | Not assigned | $a_1$ |
| 1 340w | Not assigned | |
| 1 420m | $\nu$14 ring str. | $b_2$ |
| 1 485m | $\nu$19b ring str. | $b_2$ |
| 1 525m | $\nu$19a ring str. | $a_1$ |
| 1 590s | $\nu$8a ring str. | $a_1$ |
| 1 635s | $\nu$8a ring str. | $a_1$ |
| 1 660m (sh) | Not assigned | |
| 3 020m | $\nu$(C–H) pyridine str. | |
| 3 160s | $\nu$(N–H) ammonia str. | |
| 3 240s | $\nu$(C–H) methyl str. | |

TABLE 3

Assignments and intensities of bands observed in the i.r. spectrum of $[Ru(NH_3)_5(dmapy)]Cl_3$

| Wavenumber/cm$^{-1}$ | Assignment | |
|---|---|---|
| 532w | $\nu$(M–NH$_3$) metal–ammonia str. | |
| 816s | $\rho$(NH$_3$) rock | |
| 830s (sh) | | |
| 1 015s | $\nu$1 symmetric str. | $a_1$ |
| 1 055m | $\nu$12 ring str. | $a_1$ |
| 1 120vw | Not assigned | |
| 1 190w | $\nu$15 in-plane C–H bend | $b_2$ |
| 1 240s | $\nu$9a in-plane C–H bend | $a_1$ |
| 1 295m (sh) | $\delta$(NH$_3$) symmetric bend | |
| 1 320s | | |
| 1 355w | Not assigned | |
| 1 390m | $\nu$14 ring str. | $b_2$ |
| 1 545m | $\nu$19a ring str. | $a_1$ |
| 1 620s | $\nu$8a ring str. | $a_1$ |
| 1 660m (sh) | Not assigned | |
| 3 060s | $\nu$(C–H) pyridine str. | |
| 3 200s | $\nu$(N–H) ammonia str. | |
| 3 370s | $\nu$(C–H) methyl str. | |

ments and relative intensities. The assignments were made by comparison with those of related substituted pyridines. Thus the spectrum of $[Ru(NH_3)_5(cmpy)][PF_6]_3$ was compared to those of 4-deuterio-,[9] 4-chloro-,[10] 4-bromo-,[10] and 4-cyano-pyridine[11,12] and pyridinium hydrochloride,[13] that of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ to those of 4,4′-bipyridine dihydrochloride and various metallopyridines,[14] and that of $[Ru(NH_3)_5(dmapy)]Cl_3$ to those of metallopyridines[14] and 4-aminopyridine.[15]

The spectra of all three complexes showed bands at about 1 630 cm$^{-1}$ with a shoulder at 1 660 cm$^{-1}$. This band is assigned to a pyridine ring-stretching vibration rather than to the asymmetric bending mode of ammonia, $\delta_{asym}(NH_3)$, which lies typically[16] between 1 585 and 1 610 cm$^{-1}$ for $[M(NH_3)_6]^{2+}$ and between 1 585 and 1 630 cm$^{-1}$ for $[M(NH_3)_6]^{3+}$; the band at 1 630 cm$^{-1}$ was considered to be too sharp and at too high a wavenumber to be attributable to this ammonia mode. The pyridine-band assignments have been designated, as usual, by analogy with those for benzene.[13]

The bands between 1 600 and 1 000 cm$^{-1}$ observed in the i.r. spectra of all three complexes were assigned to various pyridine-ring stretching and substituent-bending modes. However, bands at 1 275 cm$^{-1}$ which occur in the spectra of both the cmpy and mbipy complexes, and one at 1 320 cm$^{-1}$ which occurs in the spectrum of the former, cannot be assigned to any pyridine modes, but they do lie at approximately the correct wavenumber for the symmetric bending mode of the ammonia ligand, $\delta_{sym}(NH_3)$. This mode occurs at 1 220 cm$^{-1}$ for $[Ru(NH_3)_6]^{2+}$ and 1 368 cm$^{-1}$ for $[Ru(NH_3)_6]^{3+}$.[16] The value of 1 275 cm$^{-1}$ for $\delta_{sym}(NH_3)$ in the ruthenium(II) complexes under study is rather high, but in both cases the Ru$^{II}$ is attached to a powerful electron-withdrawing substituent, the *N*-methylpyridine group, which should reduce the electron density on the Ru$^{II}$ atom and so give it ruthenium(III) character.

The symmetric ring-stretching vibrations of the mbipy and dmapy complexes occur at 1 000 and 1 015 cm$^{-1}$, respectively, but no corresponding mode could be identified in the spectrum of the cmpy complex.

The strong bands observed at 840 and 558 cm$^{-1}$ are assigned to the $\nu_3(t_{1u})$ and $\nu_4(t_{1u})$ fundamentals of the counter ion $[PF_6]^-$ [17,18] in the two ruthenium(II) complexes. Shoulders on the $\nu_3$ band of each complex at 780 cm$^{-1}$ are assigned to the ammonia rocking mode, $\rho(NH_3)$, observed[16] at 770 cm$^{-1}$ in the i.r. spectrum of $[Ru(NH_3)_6]^{2+}$. For $[Ru(NH_3)_5(dmapy)]Cl_3$ the ammonia rocking mode gives rise to a broad band at about 820 cm$^{-1}$ and is consistent with the value (788 cm$^{-1}$) reported by Griffith[19] for $[Ru(NH_3)_6]Cl_3$. A band at 532 cm$^{-1}$ in the spectrum of the dmapy complex is assigned to the Ru–NH$_3$ stretching mode, *cf.* the corresponding band between 490 and 460 cm$^{-1}$ in the spectrum of $[Ru(NH_3)_5Cl]^{2+}$.[20]

The very strong band at 2 175 cm$^{-1}$ in the i.r. spectrum of $[Ru(NH_3)_5(cmpy)][PF_6]_3$, assigned to the cyanide stretch, occurs at substantially lower wavenumber than that reported elsewhere (2 240 cm$^{-1}$)[11,12] for free 4-cyanopyridine. This observation implies that there is some weakening of the CN bond, probably caused by back donation from the ruthenium(II) centre into the π* antibonding orbital of the cyanide ion. Similar observations have been reported by Clarke and Ford [21] for benzonitrile and acetonitrile complexes of penta-ammineruthenium(II). Such back bonding would also strengthen the metal–isocyanide bond, and so the band at 498 cm$^{-1}$ is assigned to ν(Ru–NC) in agreement with other work.[22] Finally for the cmpy complex the band at 275 cm$^{-1}$ is assigned to the metal–ammonia stretching mode, which occurs between 240 and 370 cm$^{-1}$ in $[M(NH_3)_6]^{2+}$ species.[23]

In the spectrum of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ the weak band at 358 cm$^{-1}$ is assigned to the metal–ammonia stretching mode. The ruthenium(II) ion is directly attached to a strong electron-withdrawing group, and would be expected to have some ruthenium(III) character; thus ν(M–NH$_3$) should occur at a higher wavenumber than otherwise expected {for $[M(NH_3)_6]^{3+}$, ν(M–N) occurs between 400 and 530 cm$^{-1}$}. For the same reason the band at 265 cm$^{-1}$ in the spectrum of the mbipy complex is assigned to the metal–ammonia bending vibration. The wavenumber of this vibration lies between 165 and 215 cm$^{-1}$ for $[M(NH_3)_6]^{2+}$ ions and between 240 and 330 cm$^{-1}$ for $[M(NH_3)_6]^{3+}$ ions.[23]

TABLE 4

Electronic absorption maxima ($\lambda_{max.}$/nm) and associated absorption coefficients ($\epsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) for the complexes studied

| Electronic absorption | $[Ru(NH_3)_5(cmpy)]^{2+}$ | | $[Ru(NH_3)_5(mbipy)]^{3+}$ | | $[Ru(NH_3)_5(dmapy)]^{3+}$ | | |
|---|---|---|---|---|---|---|---|
| $\lambda_{max.}$ (solid state) | 545 | 275 | 640 | 280 | 570 | 350 | 280 |
| (aqueous solution) | 545 | 260 | 585 | 265 | 580 | 340 | 260 |
| $\epsilon_{max.}$ (aqueous solution) | 1.4 × 10$^4$ | 1.3 × 10$^4$ | 1.2 × 10$^4$ | 1.5 × 10$^4$ | 2.2 × 10$^3$ | 3.4 × 10$^3$ | 6.4 × 10$^3$ |
| $\lambda_{max.}$ ($CH_3CN$ solution) | 545 | 260 | 590 | 265 | | | |
| $\epsilon_{max.}$ ($CH_3CN$ solution) | 1.6 × 10$^4$ | 1.4 × 10$^4$ | 1.4 × 10$^4$ | 1.5 × 10$^4$ | | | |

*Electronic Spectra.*—The data obtained from solid-state and solution electronic spectra are shown in Table 4. The cmpy complex shows only a small shift (*ca.* 5 nm) in its absorption maximum from solution to the solid state, and so it would appear that the ammonia ligands are not substituted by either methyl cyanide or water. The same conclusion is also deduced from the electronic spectra of the dmapy complex. However, the absorption maximum observed at 640 nm in the solid-state spectrum of the mbipy complex moves to 595 nm in water and to 600 nm in methyl cyanide; this suggests considerable interaction of the solvent with the solute molecules in this case.

It has been found [6] that the wavenumber of the charge-transfer (c.t.) band for $[Ru^{II}(NH_3)_5(py)][ClO_4]_2$ (py = pyridine) is solvent dependent. Thus, in water the complex has an absorption maximum at 407 nm, whilst in dimethyl sulphoxide this shifts to 447 nm. However, no correlation between the shift in the c.t. maximum and the dielectric constant was found. A substantial bathochromic shift in the absorption maximum was also reported [6] when electron-withdrawing substituents were placed at the *para* position of the ring. Thus, in $[Ru(NH_3)_5(mbipy)][PF_6]_3$, the hypsochromic shift could be explained by electron donation from the solvent to the positively charged nitrogen atom of the pyridine ring.

The absorption coefficients of *ca.* 10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$, the full width half-maxima of *ca.* 5 000 cm$^{-1}$, and the solvent dependence of the electronic absorption maxima of the mbipy and cmpy complexes are characteristic of c.t. bands. As there are no unfilled low-lying metal orbitals to accept an electron, the electronic absorption band seen in the visible region for both of these ruthenium(II) complexes probably arises from a metal-to-ligand c.t. transition.

The narrower, solvent-independent, lower-intensity band in the visible spectrum of $[Ru(NH_3)_5(dmapy)]Cl_3$ at 580 nm may be either due to a $d \leftarrow d$ transition essentially localised on the metal atom or to a ligand-to-metal c.t.

The strong absorption band at 260 nm seen in all the compounds is probably due to a $\pi^* \leftarrow \pi$ transition in the pyridine ring; it compares well with the value of 244 nm for the corresponding band in free pyridine.

*Raman Spectra.*—Only a solution Raman spectrum of $[Ru(NH_3)_5(dmapy)]Cl_3$ (Figure 1) is included, as attempts to obtain a solid-state spectrum using low laser power produced only a poor spectrum. Decomposition of the

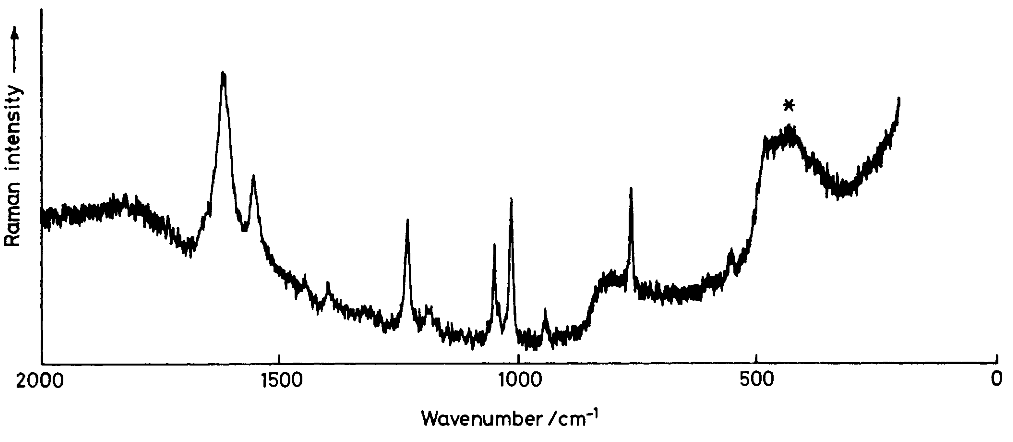


FIGURE 1 Resonance-Raman spectrum of $[Ru(NH_3)_5(dmapy)]Cl_3$ in aqueous solution at 295 K. Excitation radiation: 17 599 cm$^{-1}$ (568.2 nm), 50 mW. The asterisk indicates a band due to glass

sample occurred when a tightly focused beam of greater power was used.

The mbipy complex was found to be photosensitive at room temperature in MeCN solution; after exposure to 568.2-nm $Kr^+$ radiation at a power of 100 mW for 10 min, the electronic band maximum had been reduced by 20% and moved from 590 to 580 nm. After irradiation for 40 min the band intensity had been reduced by 40% and the absorption maximum shifted to 540 nm. Irradiation for another 2 h caused no further reduction in intensity or shift of the absorption maximum. For this reason, depolarisation-ratio measurements of the bands of this compound were made as quickly as possible and are thus somewhat less accurate than those made for the cmpy and dmapy complexes. Solution wavenumber measurements were made as quickly as possible because of the rapid sample decomposition, and so are less accurate ($\pm 2$ $cm^{-1}$) than other similar measurements.

A list of the Raman bands observed in the solid state and solution (in parentheses) are given in Tables 5—7. Solid-state spectra of the cmpy and mbipy complexes are shown in Figures 2 and 3 respectively.

All three complexes belong to the $C_{2v}$ point group and so all vibrations except the $a_2$ type are both i.r. and Raman active; $a_2$-type vibrations are Raman active only.

Depolarisation ratios ($p$) were measured to find the symmetry species of the modes responsible for the more intense bands in the solution spectra of the complexes. The measurements were made, in all cases, as close to rigorous resonance conditions as possible, using 568.2-nm $Kr^+$ radiation. A value for $p$ of $0.30 \pm 0.03$ was found for all bands measured for the cmpy and dmapy complexes. The bands of the former were at 276, 498, 733, 1 182, 1 206, and 1 630 $cm^{-1}$ and for the latter were at 768, 1 020, 1 055, 1 237, 1 559, and 1 621 $cm^{-1}$. For the mbipy complex all the bands measured had $p \approx 0.28 \pm 0.04$; they occurred at 350, 584, 731, 1 006, 1 196, 1 233, 1 305, 1 531, and 1 641 $cm^{-1}$. From this value of $p \approx \frac{1}{3}$ it can be inferred that, not only do these bands arise from totally symmetric vibrations, but also the resonant electronic transition is between non-degenerate states.[24] All the totally symmetric ring modes of pyridine are shown in Figure 4.[25] Many combination bands involving in particular the $a_1$ ring modes depicted in

TABLE 5

Assignments, intensities, and full widths at half-maxima (f.w.h.m.) of bands observed in the Raman spectra of $[Ru(NH_3)_5(cmpy)][PF_6]_3$

| | Wavenumber [a]/$cm^{-1}$ | f.w.h.m./$cm^{-1}$ | Rel. peak height | Assignment | |
|---|---|---|---|---|---|
| | 188 (186) | 17 | 11 | δ(NMN) ammonia bend | |
| | 235 | 20 | 2 | Not assigned | |
| p | 278 (276) | 14 | 24 | ν(M–$NH_3$) metal–ammonia str. | $a_1$ |
| | 412 (420) | (sh) | 6 | Not assigned | |
| | 447 (454) | (sh) | 11 | Not assigned | |
| p | 494 (498) | 11 | 70 | ν(M–NC) metal–isocyanide str. | $a_1$ |
| | 529 (526) | (sh) | 4 | Not assigned | |
| p | 562 | 9 | 21 | ν6a/ν(N–$CH_3$) | $a_1$ |
| | 683 | 20 | 1 | Not assigned | |
| | 712 | (sh) | 3 | Not assigned | |
| p | 730 (733) | 11 | 33 (50) | ν6a/ν(N–$CH_3$) | $a_1$ |
| | 774 | 30 | 5 | ρ($NH_3$) rock | |
| | 865 | *ca.* 40 | 30 | | |
| | 884 | | 15 | | |
| | 939 | 18 | 5 | Not assigned | |
| | 1 000 (998) | | 3 | ν1 symmetric str. | $a_1$ |
| | 1 058 (1 048) | 16 | 5 | Not assigned | |
| p | 1 181 (1 182) | 13 | 46 | ν12 ring str. | $a_1$ |
| p | 1 209 (1 206) | 13 | 100 | ν9a in-plane C–H bend | $a_1$ |
| | 1 229 (1 233) | | 5 | Not assigned | |
| | 1 277 (1 266) | 35 | 4 | δ($NH_3$) symmetric bend | |
| | 1 367 (1 374) | 27 | 3 | ν14 ring str. | $b_2$ |
| | 1 430 (1 420) | 17 | 4 | Not assigned | |
| | 1 457 (1 456) | 9 | 3 | ν19b ring str. | $b_2$ |
| p | 1 515 (1 510) | 9 | 8 | ν19a ring str. | $a_1$ |
| p | 1 629 (1 627) | 30 (sh) | 57 | ν8a ring str. | $a_1$ |
| p | 1 637 (1 637) | | 43 | | |
| | 1 706 (1 704) | 17 | 12 | ν9a + ν(M–NC) | |
| | 1 745 | | 3 | ν12 + 562 | |
| | 1 772 | 9 | 3 | ν9a + 562 | |
| | 1 907 | 19 | 4 | ν6a + ν12 [b] | |
| | 1 940 | 11 | 5 | ν6a + ν9a | |
| | 2 049 | | 5 | ν12 + ρ($NH_3$) | |
| | 2 076 | | 7 | ν9a + ρ($NH_3$) | |
| | 2 128 | 24 | 8 | ν(CN) or ν8a + ν(M–$NH_3$) | |
| | 2 184 | 32 | 8 | ν(CN) | |
| | 2 360 | 24 | 5 | 2ν12 [c] | |
| | 2 389 | 16 | 7 | ν12 + ν9a | |
| | 2 419 | 16 | 7 | 2ν9a | |
| | 2 504 | 47 | 5 | ν8a + ρ($NH_3$) | |
| | 2 560 | 32 | 3 | 2δ($NH_3$) | |
| | 2 808 | 16 | 4 | ν8a + ν12 [d] | |
| | 2 839 | 24 | 6 | ν(C–H) pyridine | |
| | 3 265 | | 4 | ν(N–H) ammonia | |
| | 3 298 | | 2 | ν(C–H) methyl | |

[a] Numbers in parentheses refer to solution measurements; p = polarised. [b] Possibly coupled to ν8a + ν(M–$NH_3$) (1 907 $cm^{-1}$) [c] Possibly coupled to ν8a + ν6a (2 360 $cm^{-1}$). [d] Possibly coupled to ν8a + ν9a (2 839 $cm^{-1}$).

TABLE 6

Assignments, intensities, and full widths at half-maxima of bands observed in the Raman spectra of $[Ru(NH_3)_5(mbipy)][PF_6]_3$

| | Wavenumber/cm$^{-1}$ | | f.w.h.m./cm$^{-1}$ | Rel. peak height | Assignment | |
|---|---|---|---|---|---|---|
| | 217 | (219) | 10 | 9 | $\nu$(M–py) metal-pyridine str. | |
| p | 356 | (350) | 13 | 36 | $\nu(M-NH_3)$ metal–ammonia str. | $a_1$ |
| | 404 | (402) | 13 (sh) | 5 | Not assigned | |
| | 435 | (435) | (sh) | 8 | Not assigned | |
| | 454 | | (sh) | 9 | Not assigned | |
| | 561 | | 10 | 14 | Not assigned | |
| p | 589 | (584) | 8 | 29 | $\nu6a/\nu(N-CH_3)$ | $a_1$ |
| | 714 | | (sh) | 4 | Not assigned | |
| p | 734 | (731) | 11 | 20 | $\nu6a/\nu(N-CH_3)$ | $a_1$ |
| | 742 | (748) | (sh) | 7 | Not assigned | |
| | 827 | | *ca.* 30 | 16 | $\rho(NH_3)$ rock | |
| | 864 | | | 27 | | |
| p | 1 007 | (1 006) | 12 | 22 | $\nu1$ ring str. | $a_1$ |
| | 1 047 | (1 047) | (sh) | 7 | $\nu12$ ring str. | $a_1$ |
| | 1 061 | (1 059) | (sh) | 9 | Not assigned | |
| | 1 147 | | 5 | 4 | Not assigned | |
| | 1 177 | | | 3 | Not assigned | |
| p | 1 198 | (1 196) | 9 | 57 | $\nu18a$ in-plane C–H bend | $a_1$ |
| | 1 223 | (1 233) | | 19 | $\nu9a$ in-plane C–H bend | $a_1$ |
| p | 1 240 | | | 42 | | |
| p | 1 303 | (1 304) | 11 | 49 | | |
| | 1 424 | | 17 | 4 | $\nu14$ ring str. | $b_2$ |
| | 1 489 | (1 491) | 9 | 12 | $\nu19a$ ring str. | $a_1$ |
| p | 1 530 | (1 531) | 15 | 21 | | |
| p | 1 600 | (1 601) | 15 | 100 | $\nu8a$ ring str. | $a_1$ |
| p | 1 642 | (1 641) | 11 | 54 | | |
| | 1 656 | (1 651) | (sh) | 23 | | |
| | 2 100 | | 160 | 2 | $2\nu12$ | $a_1$ |
| | 2 480 | | 120 | 3 | $2\nu9a$ | $a_1$ |
| | 2 840 | | 120 | 2 | $\nu$(C–H) pyridine | |

TABLE 7

Assignments, intensities, and full widths at half-maxima of bands observed in the aqueous solution Raman spectrum of $[Ru(NH_3)_5(dmapy)]Cl_3$

| | Wavenumber/cm$^{-1}$ | f.w.h.m./cm$^{-1}$ | Rel. peak height | Assignment | |
|---|---|---|---|---|---|
| p | 560 | 8 | 12 | $\nu6a/\nu(N-CH_3)$ | $a_1$ |
| p | 768 | 6 | 49 | $\nu6a/\nu(N-CH_3)$ | $a_1$ |
| | 822 | 60 | 20 | $\rho(NH_3)$ | |
| | 949 | 8 | 12 | Not assigned | |
| p | 1 020 | 8 | 78 | $\nu1$ ring str. | $a_1$ |
| p | 1 055 | 9 | 46 | $\nu12$ ring str. | $a_1$ |
| | 1 191 | 20 | 15 | $\nu15$ in-plane C–H bend | $a_1$ |
| p | 1 237 | 11 | 56 | $\nu9a$ in-plane C–H bend | $a_1$ |
| | 1 319 | 16 | 5 | $\delta(NH_3)$ symmetric bend | |
| | 1 375 | 10 | 6 | Not assigned | |
| | 1 402 | 8 | 13 | Not assigned | |
| | 1 447 | 11 | 11 | $\nu8b$ ring str. | $b_2$ |
| p | 1 559 | | 49 | $\nu19a$ ring str. | $a_1$ |
| p | 1 621 | 36 | 100 | $\nu8a$ ring str. | $a_1$ |

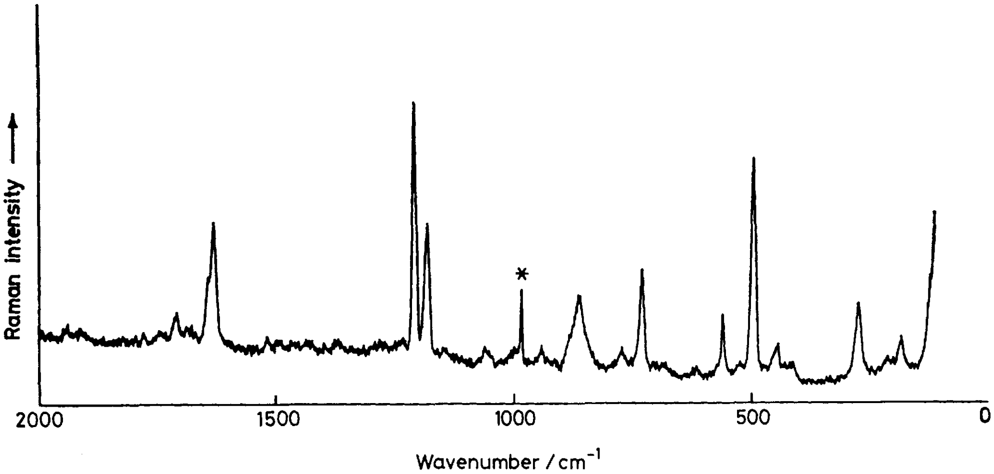


FIGURE 2 Resonance-Raman spectrum of $[Ru(NH_3)_5(cmpy)][PF_6]_3$ in a potassium sulphate disc at 80 K. The asterisk indicates a band due to sulphate. Other details as in Figure 1

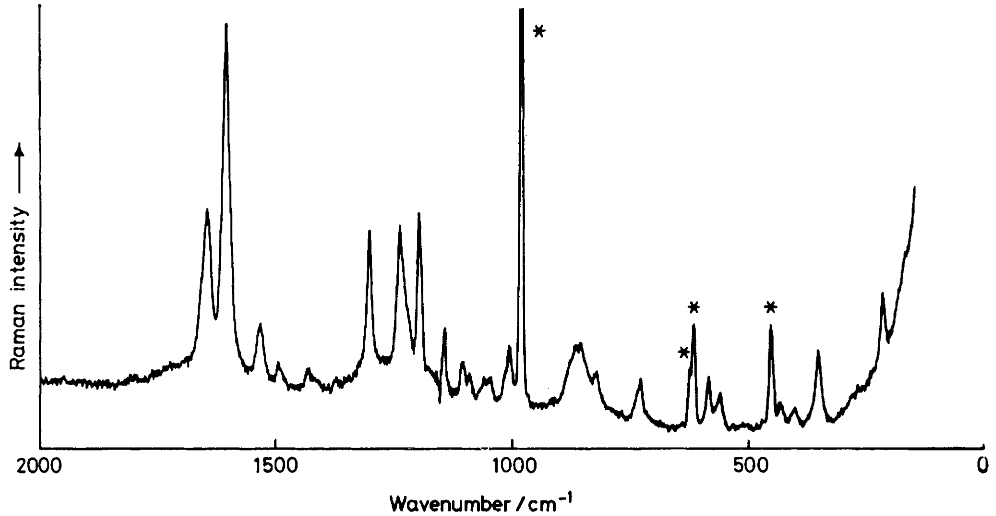


FIGURE 3 Resonance-Raman spectrum of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ in a potassium sulphate disc at 80 K. Details as in Figure 2

Figure 4 are clearly seen in the r.R. spectra and their assignments are included in Tables 5 and 6. The $b_2$modes were assigned on the basis of group frequency arguments.

An unequivocal assignment of the broad strong bands at 860—880 cm$^{-1}$ observed in the solid-state spectra of cmpy and mbipy, but not in that of the dmapy, complexes was not possible. These bands appear only weakly in the solution spectra of the first two complexes but reappear with undiminished intensity in the spectra of complexes which have been recovered from solution. This reappearance tends to rule out a reaction between solute and solvent, *e.g.* replacement of $NH_3$ by $CH_3CN$. The band could be assigned to either $\rho(NH_3)$ of the complex or $\nu_4$(P–F) $t_{1u}$ of the counter ion $[PF_6]^-$. The i.r. spectrum of the dmapy complex contains a band at 820 cm$^{-1}$ which may be assigned to $\rho(NH_3)$ for a ruthenium(III) penta-ammine. Large formal charges on the ruthenium atom will strengthen the Ru–N bond and weaken the N–H bond; it would, therefore, be expected that the wavenumber of $\rho(NH_3)$ for Ru$^{II}$ would be greater than that for Ru$^{III}$. However, attempts by various workers to show this experimentally have been equivocal.[23]

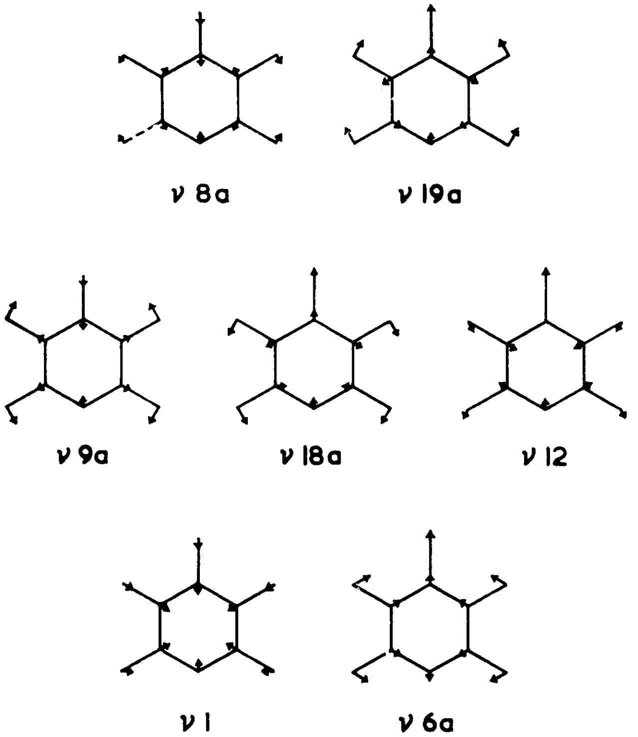


FIGURE 4 Totally symmetric ring co-ordinates of pyridine

Assigning the band at 860—880 cm$^{-1}$ to $\nu_4$(P–F) $t_{1u}$ of the counter ion $[PF_6]^-$, a band which should be i.r. active only, would be highly suspect because the $a_{1g}$ totally symmetric stretching mode (745 cm$^{-1}$), which ought to be the most intense band in the Raman spectrum, does not appear. Furthermore the band at 860—880 cm$^{-1}$ not only shows considerable resonance enhancement but also gives combination bands with bands assigned to the totally symmetric modes of pyridine; again this would be unlikely if the band arose from $\nu_4$(P–F) $t_{1u}$ of $[PF_6]^-$. Thus this band in the Raman spectra of the cmpy and mbipy complexes is assigned to $\rho(NH_3)$.

In an attempt to discover which bands in the spectra of the complexes were due to the ammonia ligands, deuterium substitution was carried out in the following way: $ND_3$ was bubbled through a methyl cyanide solution of the appropriate ruthenium(II) complex and the solution then evaporated to dryness on a vacuum line. Fresh methyl cyanide was then distilled onto the complex and the spectrum then recorded. The ruthenium(III) complex was simply dissolved in deuterium oxide and the spectrum recorded. For the cmpy complex only one band (at 276 cm$^{-1}$) changed position on deuteriation, to 254 cm$^{-1}$. This shift is of similar magnitude to that observed by Campbell *et al.*[26] for several bands of deuteriated ruthenium red, $[Ru_3O_2(NH_3)_{14}]^{6+}$. No bands were observed to shift in the spectrum of the mbipy complex after the attempt at deuteriation, presumably because of the slow rate of deuterium substitution. In the spectrum of the dmapy complex a new broad band at 620 cm$^{-1}$ appeared on deuteriation, accompanied by almost complete loss of the band at 822 cm$^{-1}$. The very weak band at 1 375 cm$^{-1}$ assigned to the symmetric bending mode of ammonia also disappeared. These results are also similar to those obtained for ruthenium red [27] and are in agreement with the proposed assignment.

*Excitation Profiles*.—Excitation profiles were obtained for the most intense Raman bands of both the ruthenium(II) complexes in the solid state at 80 K (Figures 5 and 6), but not for the ruthenium(III) complex because of its weak scattering. In the Raman spectra of the cmpy and mbipy complexes there is a general enhancement of all bands at resonance. For both complexes it is the polarised bands, assigned to the $a_1$-type vibrations of pyridine, that are the most enhanced.

In the r.R. spectrum of $[Ru(NH_3)_5(cmpy)][PF_6]_3$ the band associated with the $Ru^{II}$–NC stretch at 494 $cm^{-1}$ and to a lesser extent that attributable to the $Ru^{II}$–$NH_3$ stretch at 278 $cm^{-1}$ show some enhancement. Similarly in the r.R. spectrum of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ the bands at 217 and 356 $cm^{-1}$, assigned to $Ru^{II}$–py and $Ru^{II}$–$NH_3$ stretching modes, respectively, increase in intensity at resonance. These observations are consistent with an assignment of the resonant electronic transition to a metal-to-ligand charge transfer. In the simplified molecular orbital scheme shown in Figure 7, this is seen to involve a transfer of an electron from a ruthenium(II) $d_\pi$ orbital into the $\pi^*$ antibonding orbital of the pyridine ring. The electronic absorption band could arise from two transitions, $b_2(\pi^*)\leftarrow b_2(d_{yz})$ and $b_2(\pi^*)\leftarrow a_2(d_{xy})$. The transition of an electron to this delocalised antibonding orbital, in the excited state, would cause small changes in the bond strengths of the pyridine ring and its substituents. This would lead to the resonance enhancement of many bands

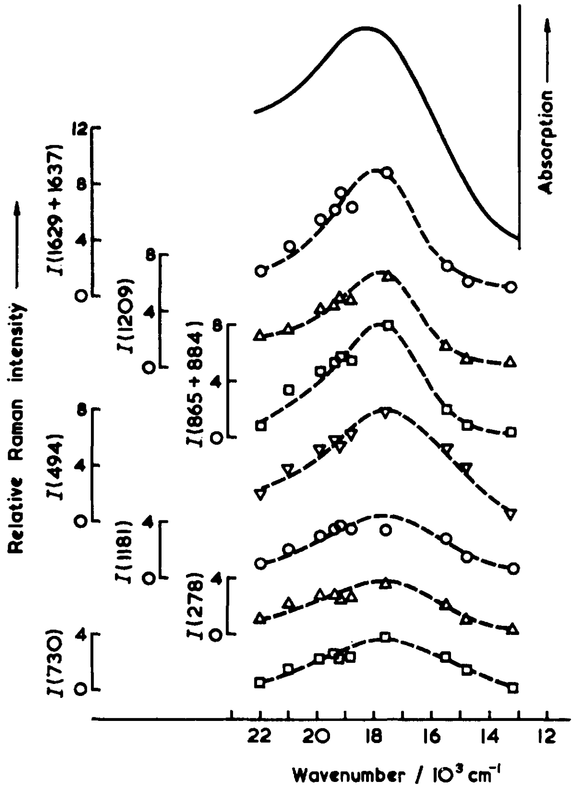


FIGURE 5 Excitation profiles of the strongest Raman bands (at 278, 494, 730, 865 + 884, 1 181, 1 209, and 1 629 + 1 637 $cm^{-1}$) of $[Ru(NH_3)_5(cmpy)][PF_6]_3$ dispersed in a potassium sulphate disc at *ca.* 80 K. The diagram includes a CsCl disc transmission spectrum (——) of the complex at 295 K

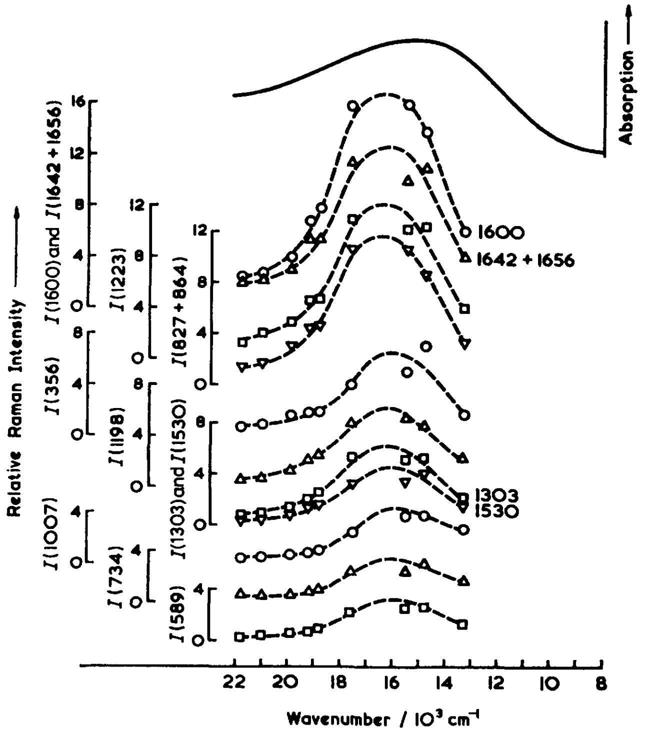


FIGURE 6 Excitation profiles of the strongest Raman bands (at 356, 589, 734, 827 + 864, 1 007, 1 198, 1 223, 1 303, 1 530, 1 600, and 1 642 + 1 656 $cm^{-1}$) of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ dispersed in a potassium sulphate disc at *ca.* 80 K. The diagram includes a CsCl disc transmission spectrum (——) of the complex at *ca.* 295 K

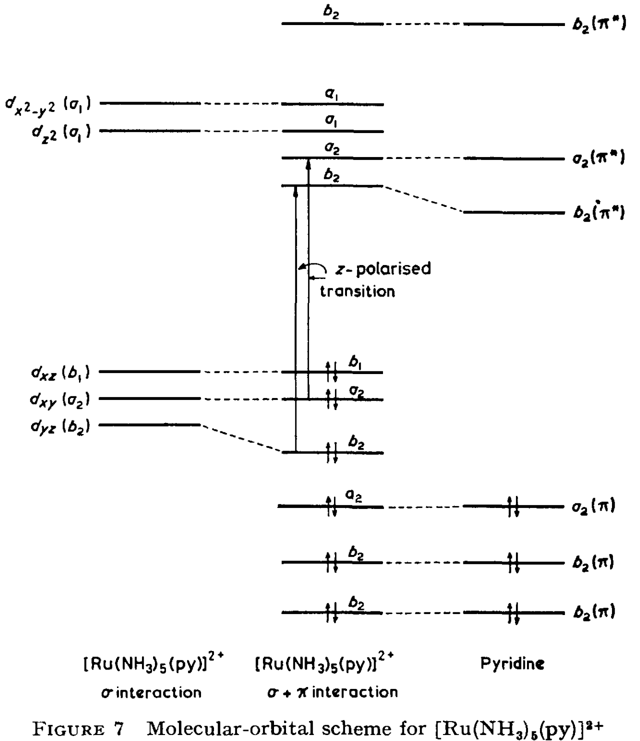


FIGURE 7 Molecular-orbital scheme for $[Ru(NH_3)_5(py)]^{2+}$ (after ref. 6)

but to no overtone or combination-band progressions, *i.e.* it is consistent with the *A*-term scattering mechanism in the small displacement approximation.[27]

## DISCUSSION

Studies of the protonation equilibrium constant of $[Ru(NH_3)_5(pyz)]^{2+}$ (pyz = pyrazine) by Taube and co-workers [6] have shown that this complex ion is nearly two orders of magnitude more basic than unco-ordinated pyrazine. Since the electrostatic effect of co-ordination of pyrazine to the ruthenium(II) centre would be expected to make the free nitrogen atom less basic, it is clear that the metal centre must take part in some special interaction with the ligand which more than compensates for the expected electrostatic effect. It has been proposed [6] that this interaction is back donation of electron density from the filled ruthenium $d_\pi(t_{2g})$ orbitals to the empty $\pi^*$ orbitals on the pyrazine. The present r.R. results substantiate this proposal for the complexes studied, in that if the intense electronic band in the visible spectrum of this complex is correctly assigned as an electric-dipole-allowed transition ligand ($\pi^*$) $\longleftarrow$ Ru$^{II}$ (rather than a metal-based transition), then geometric changes would be expected in many parts of the complex ion, particularly the aromatic ring, on electronic excitation from the ground to the excited state. In consequence, many totally symmetric modes of the complex ion, particularly of the aromatic ring, would be expected to give rise to enhanced bands at resonance.[27] This is exactly the result obtained in the present study, the modes most enhanced being ones attributed to $a_1$ vibrations of the aromatic ring as well as, in the case of $[Ru(NH_3)_5(cmpy)][PF_6]_3$, $\rho(NH_3)$, $\nu(Ru-NC)$, and $\nu(Ru-NH_3)$, and in the case of $[Ru(NH_3)_5(mbipy)][PF_6]_3$ $\rho(NH_3)$ and $\nu(Ru-NH_3)$.

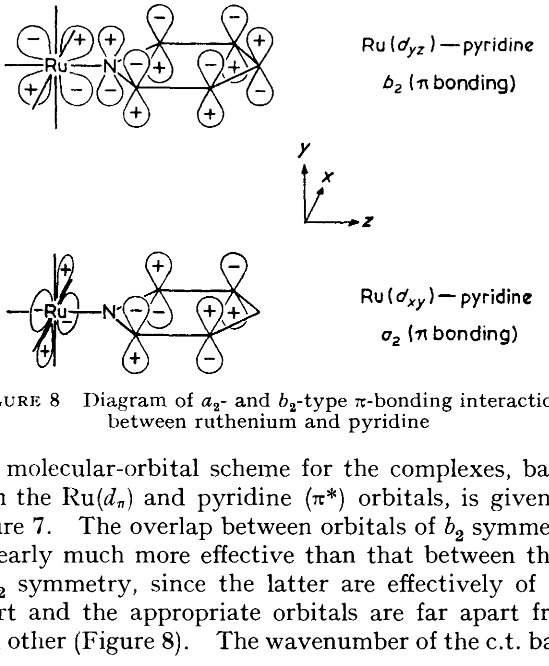


FIGURE 8 Diagram of $a_2$- and $b_2$-type π-bonding interactions between ruthenium and pyridine

A molecular-orbital scheme for the complexes, based upon the Ru($d_\pi$) and pyridine ($\pi^*$) orbitals, is given in Figure 7. The overlap between orbitals of $b_2$ symmetry is clearly much more effective than that between those of $a_2$ symmetry, since the latter are effectively of the δ sort and the appropriate orbitals are far apart from each other (Figure 8). The wavenumber of the c.t. band is sensitive to substituents in the *para* position of the pyridine ring. It is thus unlikely that the $a_2(\pi^*)$ orbital could act as the upper state in the c.t. transition because this orbital has a node at the *para* position. Hence, of the two *z*-polarised transitions indicated in Figure 7, the correct assignment for the c.t. transition in the two ruthenium(II) complexes studied is deduced to be $b_2(\pi^*)\leftarrow b_2(d_{yz})$.

The Raman spectra obtained for $[Ru(NH_3)_5(dmapy)]Cl_3$, even at resonance with the band at 580 nm, were much weaker than those obtained for the cmpy or mbipy complexes, despite the fact that the complex concentrations used were similar. This suggests that the absorption band at 580 nm is not due to a $\pi^*\leftarrow d_\pi$ transition. The Raman spectra of this complex [like that of the ruthenium(II) complexes studied] was dominated by bands assigned to $a_1$ modes. However the assignment of the band at 580 nm remains uncertain.

The authors are indebted to the S.R.C. and the University of London for financial support, and Professor T. J. Meyer and Dr. J. C. Curtiss for a gift of the complexes.

[1/276 *Received*, 18*th February*, 1981]

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