ELECTRONIC AND RESONANCE RAMAN SPECTRA OF THE DICHLORO-BIS(2,6 DIMETHYL PYRAZINE)BIS(TRIPHENYL PHOSPHINE) RUTHENIUM(II) COMPLEX

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Abstract: Excitation at the visible absorption bands of the dichlorobis(2,6 dimethyl pyrazine)bis(triphenyl phosphine)ruthenium(II) complex leads to a selective enhancement of the pyrazine Raman peaks, consistent with the occurrence of three metal-to-ligand charge-transfer transitions.

This work deals with the electronic spectra and the resonance Raman behaviour of the dichlorobis(triphenyl phosphine)ruthenium(II) complex with the 2,6 dimethyl pyrazine ligand. Ruthenium triphenyl phosphine complexes have been employed in a variety of chemical and catalytical reactions.[1,2] The dichlorotris(triphenyl phosphine)ruthenium(II) complex, for instance, is a very selective hydrogenation catalyst under mild conditions, but of surprisingly wide applicability at high temperatures.[1] The introduction of pyrazine ligands in the complexes gives rise to new chromophore groups, providing interesting probes for spectroscopic and mechanistic studies.

Experimental Section

The $[RuCl_2(PPh_3)_2(dmpz)_2]$ complex (dmpz = 2,6 dimethyl pyrazine) was synthesized according to the procedure described by Gilbert and Wilkinson[3] for the pyridine analogue. Anal. Calcd for $RuCl_2P_2C_{48}H_{46}N_4$: C, 63.15; N, 6.13; H, 5.04. Found: C, 62.2; N, 5.93; H, 5.1. The electronic spectra were recorded on a Hewlett Packard model 8451A diode-array spectrophotometer, using solid samples suspended in fluorolube. Resonance Raman spectra were recorded on a Jarrell-Ash instrument, using Spectra Physics argon and krypton ion lasers. The samples were prepared in compressed pellets (1:100) with a supporting medium of sodium sulfate, and placed in a spinning cell. The intensities were measured as peak heights relative to the sulfate Raman band at 994 cm^{-1}.

Results and Discussion

The electronic spectrum of $[RuCl_2(PPh_3)_2(dmpz)_2]$ is shown in Figure 1.A. The absorption bands below 350 nm are also observed in the $RuCl_2(PPh_3)_3$ complex, arising mainly from the internal $\pi \rightarrow \pi^*$ transitions in the aromatic groups. The two strong transitions in the visible region (408, 513 nm) are characteristic of the N-heterocyclic complex, and are consistent with charge-transfer transitions from ruthenium(II) d_π to pyrazine p_π orbitals, analogous to those previously reported in

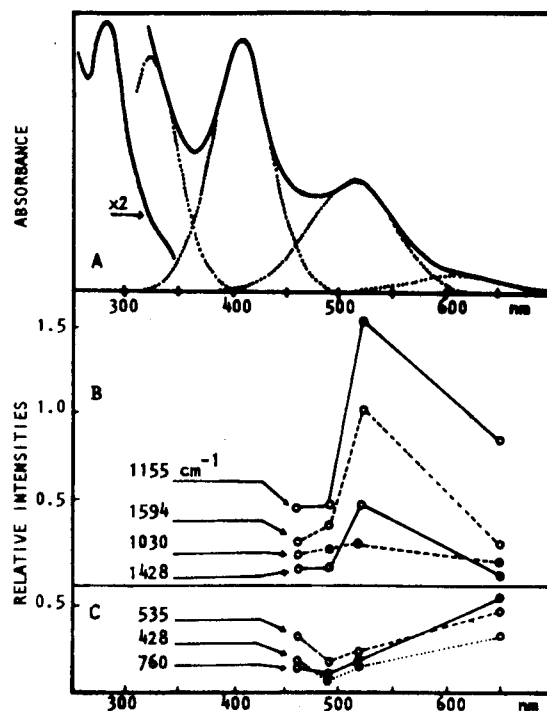Fig.1. Electronic spectrum of $[RuCl_2(PPh_3)_2(dmpz)_2]$ (A) and resonance Raman profiles (B-C) for the vibrational bands of the dmpz ligands.(— Gaussian analysis)

the literature for related complexes.[4,5] A third, low energy weak absorption band has also been detected by means of Gaussian analysis, as shown in Figure 1.A.

The structure of the $[RuCl_2(PPh_3)_2(py)_2]$ complex (py = pyridine) has been reported to be similar to that of the 1,10 phenanthroline complex, with the pyridine ligands in cis C_{2v} configuration.[1] An analogous structure is expected for the pyrazine complex. According to the model proposed by Day and Sanders[6] for this type of complex, the occupied metal d_π orbitals transform as b_1 (d_{xz}), a_2 (d_{xy}) and b_2 (d_{yz}). The lowest unoccupied π^* orbitals of the N-heterocyclic ligands transform as b_1 (ψ) and a_2 (χ). It has been shown that the interactions between d_{xz} - ψ and d_{xy} - χ, provide the major contribution to the transition moment integrals via the resonance terms.[6] Therefore, based on orbital symmetry arguments, the two strong charge-transfer bands can be assigned to the $d_{xz} \rightarrow \psi$ (CT1) and $d_{xy} \rightarrow \chi$ (CT2) electronic transitions. The $d_{yz} \rightarrow \chi$ transition is also symmetry allowed; however, the orbitals involved are practically orthogonal and the transition is expected to be less intense, being probably responsible for the weak absorption band (CT3) observed around 610 nm.

Typical Raman spectra obtained at several excitation wavelengths, are illustrated in Figure 2 for the 2,6 - dimethyl pyrazine complex. Practically all the observed peaks belong to the N-heterocyclic ligand, following a good correlation with the vibrational spectra of 2, 6-

dimethyl pyridine (dmpy) and $K_3[IrCl_5pyrazine]$, which have been previously assigned in the literature.[7,8] The peaks at 1594 and 1424 cm^{-1} correlate with the a_1 ring stretching mode of dmpy at 1591 and 1414 cm^{-1}, respectively. The several peaks in the region of 1155-1030 cm^{-1} correspond to the composite CC, CN and ring-H in plane deformation vibrations of a_1 symmetry, also observed in the dmpy ligand. The peaks at 760 and 535 cm^{-1} seem to be related to the CH and CC deformation modes of b_2 symmetry in the pyrazine complex.[8] The peaks at 428 and 270 cm^{-1} correlate with the X-sensitive deformation and torsion vibrational modes of substituted pyridine ligands, of b_2 and a_2 symmetry, respectively.[7] The peak at 428 cm^{-1} may also be due to a Ru-N stretching vibration, since, in ruthenium(II) ammines[9], it has been detected in the range of 400-423 cm^{-1}.

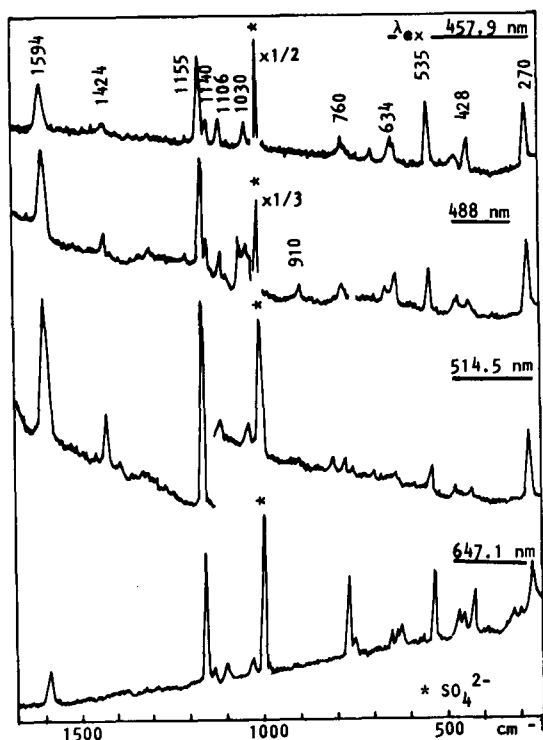The resonance Raman excitation profiles shown in Figure 1.B-C are consistent with three charge-transfer excited states involving the Ru-pyrazine chromophore, in agreement with the electronic spectra. The vibrational modes which exhibited selective enhancement at the strong absorption band at 513 nm belong to the totally symmetric representation. In contrast, the vibrational peaks at 760, 535 and 428 cm^{-1} which were enhanced at the weak electronic band (610 nm) are associated with deformation modes of b_2 symmetry in the pyrazine ligand. The enhancement of non-totally symmetric vibrations can be explained in terms of changes of symmetry in the excited state, or by vibronic coupling involving two excited states, as expressed by the B term in the theoretical formalism of the resonance Raman effect.[10] In the present case, the second hypothesis is more plausible, due to the existence of three overlapping excited states.

References

1. Jardine, F. H.; Progr. Inorg. Chem. (1984) 31, 265.

2. James, B. R.; Inorg. Chim. Acta Rev. (1970) 1, 73.

3. Gilbert, J. D.; Wilkinson, G.; J. Chem. Soc. (A) (1969) 1750.

4. Ford, P.; Rudd D. F. P.; Gaunder, R.; Taube, H.; J. Am. Chem. Soc. (1968) 90, 1187.

5. Zwickel, A. M.; Creutz, C.; Inorg. Chem. (1971) 10, 2395.

6. Day, P.; Sanders, N.; J. Chem. Soc. (A) (1967) 1536.

7. Green, J. S.; Harrison, D. J.; Kynaston, W.; Paisley; Spectrochim. Acta (1970) 26A, 2139.

8. Zarembowitch, J.; Bokobza-Sebagh, L.; Spectrochim. Acta (1976) 32A, 605.

9. Deak, A.; Templeton, J. L.; Inorg. Chem. (1980) 19, 1075.

10. Clark, R. J. H.; Dines, T. J.; Angew. Chem. Int. Ed. Engl. (1986) 25, 131.

Fig. 2. Resonance Raman spectra of $[RuCl_2(PPh_3)_2(dmpz)_2]$ obtained at several excitation wavelengths.