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Resonance Raman Spectra of Ru(bipyridine)$_3$(ClO$_4$)$_2$ and Ru(bipyrazine)$_3$(PF$_6$)$_2$ in Relation to the Phosphorescence Lifetimes

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Quite recently, Crutchley and Lever have shown that Ru(bpz)$_3^{2+}$ (bpz = bipyrazine) is a better photocatalyst than is Ru(bipy)$_3^{2+}$ (bipy = bipyridine) for the photodissociation of H_2O [1]. MV^{2+} (MV = methyl viologen) is reduced by the bipyrazine complex to MV$^+$ with a quantum yield $\phi_{MV^+} = 0.77$, whereas $\phi_{MV^+} = 0.19$ for the corresponding bipyridine complex.

This differing behaviour may be caused by the slightly longer lifetime of the lowest triplet metal to ligand charge transfer state (^{3}MLCT) of Ru(bpz)$_3^{2+}$ (τ = 1.04 μs) with respect to Ru(bipy)$_3^{2+}$ (τ = 0.685 μs). One of the factors which influences the life time of such a MLCT state is its charge transfer character, and information about this character can be obtained from the resonance Raman (rR) spectrum [2].

We report here the rR spectra of both complexes.

The absorption spectra (Fig. 1) show a shift to higher energy of the lowest MLCT band going from the bipyridine to the bipyrazine complex. This means that the effect which the lowering of energy of the π^* level [3] will have on the position of the MLCT band is more than compensated by the stabilization of the metal d orbitals as a result of the much weaker σ donor strength of the bipyrazine ligand [4]. The MLCT band of both complexions has the same structure as observed for Fe(bipy)$_3^{2+}$. For this latter complex, the higher energy shoulder will therefore belong to a vibronic transition [5]. This assignment is confirmed by the rR spectra (see below).

The rR spectra, shown in Fig. 2, have been taken for solutions with the same optical density using the 981 cm^{-1} band of the sulfate ion as a reference band. These spectra, which were excited close to the maximum of the MLCT band, are dominated by bands arising from the skeletal stretching vibrations of the ligand (1000–1600 cm^{-1}). This indicates that the MLCT state is extensively delocalized over the ligand. These ligand modes are much more intensive than the metal–ligand stretching vibration (at about 340 cm^{-1}). Thus, the metal–ligand bonds are hardly affected by the MLCT transition and this is in accordance with the conclusion of Rillema *et al.* [6] that Ru(bipy)$_3^{2+}$ and *Ru(bipy)$_3^{2+}$ have similar structures. Apparently, the loss of π-backbonding by the MLCT transition is practically compensated for by the increase of σ-donation from the ligands. The spectrum of Ru(bipy)$_3^{2+}$ excited at the high energy side of the MLCT band (insert Fig. 2) shows an increase of rR intensity for the 1605 cm^{-1} band with respect to the bands at 1559 and 1487 cm^{-1} respectively.

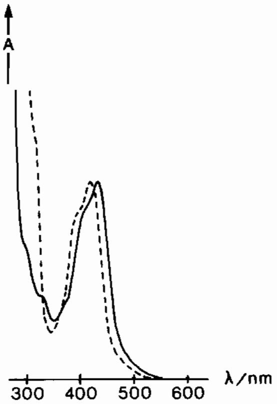

Fig. 1. MLCT bands of Ru(bipy)$_3$(ClO$_4$)$_2$ (——; ϵ_{450} = 14.7 × 10^3 dm^3 mol^{-1} cm^{-1}) and Ru(bpz)$_3$(PF$_6$)$_2$ (------; ϵ_{440} = 13.8 × 10^3 dm^3 mol^{-1} cm^{-1}).

This confirms the assignment of the high-energy shoulder to a vibronic transition involving the fundamental at 1605 cm^{-1}.

Apart from the expected frequency shifts, the rR spectra of both complexes are very much alike. The main difference is the lower relative intensities of the ligand stretching modes in the case of Ru(bpz)$_3^{2+}$. This means that the bonds of the bipyrazine ligands are less affected by the MLCT transition than are those of the bipyridine ligands. Less charge will therefore be transferred to these ligands during the MLCT transition. Furthermore, a decrease of rR intensity for the ligand stretching modes means a decrease of the Franck-Condon (F.C.) factors of these vibrations for the MLCT transition with which the exciting laserline is in resonance. Assuming that the singlet and triplet MLCT states mainly arise from the same singly excited configuration, a similar decrease of F.C. factors is expected for the transition between the ^{3}MLCT and electronic ground state. Since the

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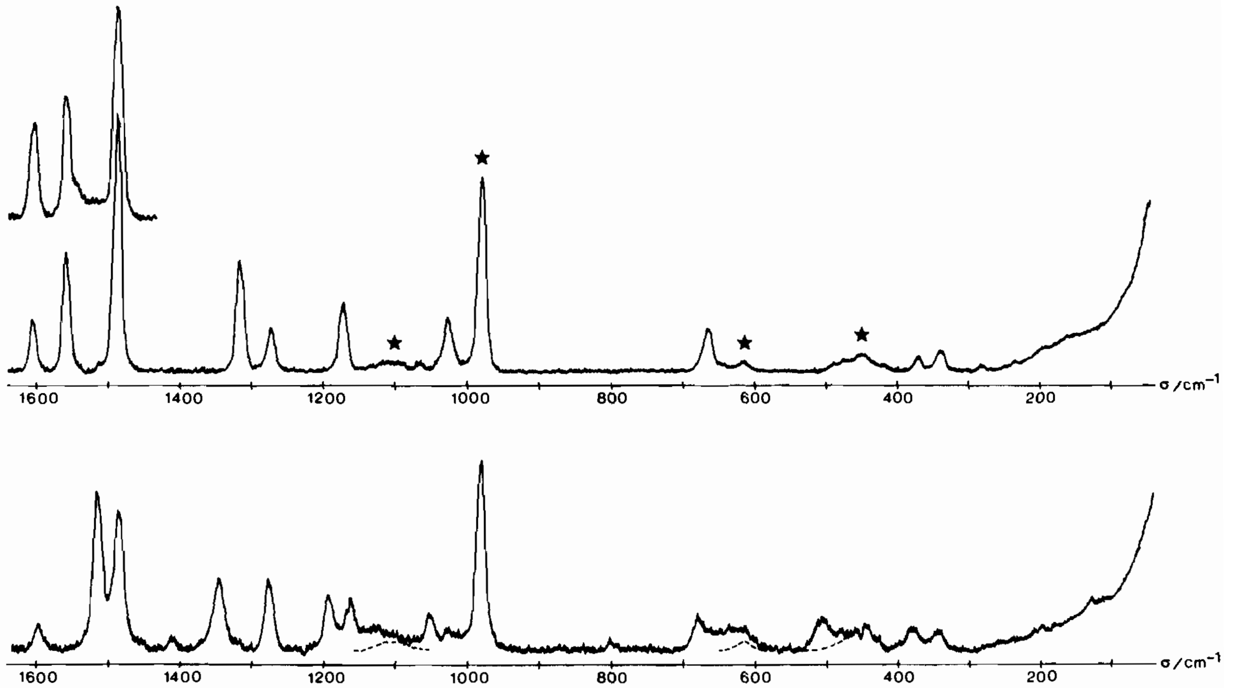

Fig. 2. Resonance Raman spectra of solutions of $Ru(bipy)_3(ClO_4)_2$ (above) and $Ru(bpz)_3(PF_6)_2$ (below) in water, excited with λ = 457.9 nm and λ = 440.0 nm, respectively. Insert: excitation of $Ru(bipy)_3(ClO_4)_2$ with λ = 430.0 nm. Bands indicated with an asterisk belong to the sulfate ion.

vibronic and spin-orbit coupling will hardly differ for these complexes, differences in the non-radiative decay constants of the ^{3}MLCT state will mainly be determined by differences in the F.C. factors. A decrease of these F.C. factors is expected to cause an increase of the lifetime of the ^{3}MLCT state. The rR intensities of the high frequency ligand stretching modes are therefore expected to be related to the lifetime of the ^{3}MLCT state. Indeed, a decrease of these intensities going from the bipyridine to the bipyrazine complex appears to be accompanied by an increase of lifetime of the ^{3}MLCT state from 0.685 to 1.04 μs [1]. This conclusion is supported by the observation that the high-frequency C–H stretching modes, which do not show a rR effect, also do not contribute to the lifetime of the ^{3}MLCT state. Going from $Ru(bipy)_3^{2+}$ to $Ru(bipy\text{-}d_8)_3^{2+}$ the phosphorescence lifetime hardly changes [7]. Further work on this relationship between rR intensities and lifetimes of MLCT states is in progress.

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