

TIME-RESOLVED INFRARED SPECTROSCOPY OF BINUCLEAR RHENIUM (I) POLYPYRIDYL COMPLEXES IN SOLUTION

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A series of four binuclear rhenium (I) complexes of the general form $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{BL}$, where BL is a polypyridyl bridging ligand, have been studied using ultrafast time-resolved UV/visible (TRVIS) and infrared (TRIR) spectroscopies. Visible excitation produces a metal-to-ligand charge-transfer (MLCT) excited state. Kinetic measurements show that the lifetime of this MLCT state varies between 100 and 1900 ps, depending on the structure of the bridging ligand. TRIR difference spectra show that each complex forms a similar MLCT state which has mixed valence character.

Keywords: Time-resolved infrared spectroscopy; time-resolved UV/visible spectroscopy; ultrafast; metal-to-ligand charge transfer; excited states; rhenium (I) polypyridyl complexes

INTRODUCTION

Steady-state studies have shown that each of the complexes $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{BL}$ (BL = BL1, BL2, BL4, or dpq), as shown in Figure 1, has a strong visible absorption band at 500–600 nm which has been assigned to a MLCT transition [1]. The aim of this work was to use

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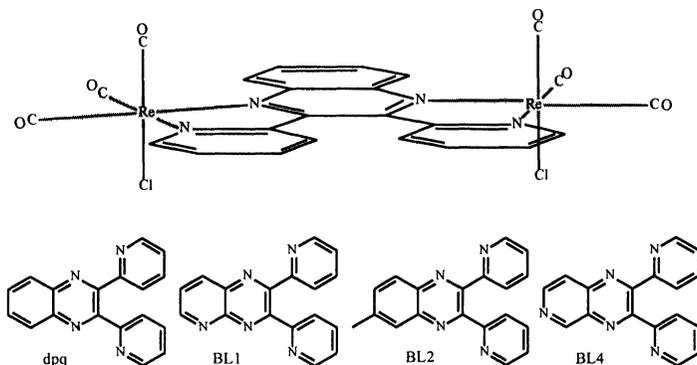


FIGURE 1 Structures of the $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{BL}$ complexes.

ultrafast TRVIS and TRIR to study the structure and dynamics of the MLCT state for each complex.

EXPERIMENTAL

The ultrafast laser apparatus has been described previously [2]. The complexes were studied in dichloromethane solution, and 200 fs pulses at 604 nm were used for photolysis.

RESULTS AND DISCUSSION

The TRVIS difference spectrum was found to be similar for each complex. The TRVIS kinetics showed that the lifetimes of the MLCT states vary between ca. 100 and 1900 ps, depending on the identity of the bridging ligand and increasing in the order $\text{BL1} < \text{BL4} < \text{dpq} < \text{BL2}$.

The kinetics observed by TRIR were found to be similar to those observed by TRVIS spectroscopy. In addition to decay of the excited state to the ground state, the TRIR kinetics also showed clearly the presence of a fast component of ca. 5 ps, as illustrated in Figure 2, which may be assigned to vibrational relaxation in the excited state. TRIR difference spectra recorded in the $\nu(\text{CO})$ region showed excited state absorption to both higher and lower wavenumbers than the

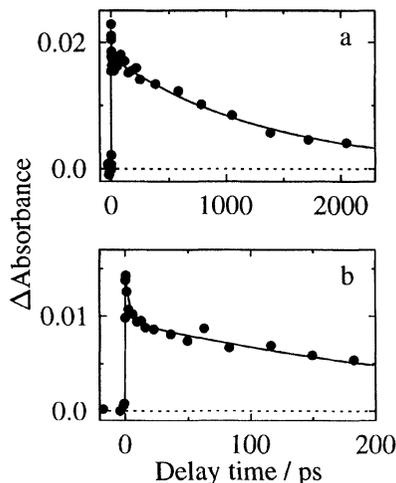


FIGURE 2 TRIR kinetics observed on 604 nm photolysis of (a) $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{dpq}$, measured at 1971 cm^{-1} and fitted to a bi-exponential function with lifetimes of 5 and 1350 ps, and (b) $[\text{Re}(\text{CO})_3\text{Cl}]_2\text{BL4}$, measured at 1889 cm^{-1} and fitted to a bi-exponential function with lifetimes of 5 and 300 ps.

ground-state absorption bands. This may be interpreted as the formation of an asymmetric, mixed-valence MLCT state. The magnitudes of the up-shifts and down-shifts, relative to the ground state absorption bands, were found to be similar for each complex, suggesting that the structures of the excited states also are similar.

CONCLUSIONS

Each of the four binuclear rhenium (I) polypyridyl complexes studied here forms a short-lived MLCT state following visible photolysis. TRIR spectra show that the structures of the MLCT states are similar, with oxidation of one metal centre and reduction of the bridging ligand. The lifetime of the MLCT state is found to be strongly dependent on the structure of the bridging ligand in the complex.

Acknowledgements

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