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Picosecond time-resolved infrared spectroscopic investigation of excited state dynamics in a Pt^{II} diimine chromophore

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This is the first report describing the use of picosecond time-resolved infrared (TRIR) spectroscopy to probe a d^8 metal chromophore, Pt(4,4′-(CO$_2$Et)$_2$-2,2′-bpy)Cl$_2$: monitoring changes in the ν(CO) vibrations allows for an assignment of the lowest excited state to an MLCT with an 8.7 ps lifetime.

The photochemistry and photophysics of metal-to-ligand charge transfer (MLCT) excited states of transition metal complexes are of considerable interest, particularly in view of their wide range of applications in photocatalysis, photochemical molecular devices, solar energy conversion and probes for DNA.[1] The elucidation of the nature and dynamics of the lowest excited state is of particular importance for transition metal complexes since these possess a manifold of low-lying excited states of different origin.

Fast time-resolved infrared spectroscopy (TRIR), a combination of UV flash photolysis and fast IR detection, has proved to be an effective probe of the nature of the excited states of coordination compounds.[2] This is especially true for complexes bearing ligands such as CO or CN, since these groups act as direct IR probes of the electron density at the metal centre. Peripheral IR reporter groups such as carboxylic acids and esters on substituted diimine ligands have also been used[3] to indirectly probe charge transfer processes using both ns- and ps-TRIR. To date, the majority of TRIR studies on the nature of the lowest excited states of inorganic chromophores have focussed[2] on d^6 metal complexes, *e.g.* Re^I, Ru^{II} and Os^{II}, possessing MLCT, sigma-bond-to-ligand charge transfer, XLCT or π–π* lowest excited states. However, there have been relatively few TRIR studies of the excited states of d^8 chromophores.[4] This is surprising given that the d^8 chromophores have been used as DNA intercalators[5] and building blocks in polynuclear transition metal systems designed for electron/energy transfer.[6,7] There is a range of Pt^{II} diimine thiolate,[7] acetylenide[7,8] and cyanide[9] complexes which show emission in solution. However, the majority of Pt^{II} excited states are too short-lived for ns-emission and ns-TRIR to be convenient methods for the elucidation of their dynamics and therefore analysis requires faster spectroscopic timescales. In this paper we have used picosecond TRIR to probe the nature of the lowest excited state of Pt^{II}(4,4′-(CO$_2$Et)$_2$-2,2′-bpy)Cl$_2$† (**1**) by following changes in the electronic density on the CO reporters of the diimine ligand. The lowest excited state of the methyl analogue of **1** has previously been assigned[10] as MLCT on the basis of absorption spectroscopy and electrochemistry.

The ground state IR spectrum of **1** in CH$_2$Cl$_2$ at room temperature displays a strong ν(CO) band at 1733 cm^{-1} [Fig. 1(a)]. Picosecond TRIR spectra‡ were recorded at several pump-probe delays, between 500 fs and 200 ps, after excitation into the lowest electronic absorption band. Fig. 1(b) shows representative spectra at four of these time delays.

There is an instantaneous bleaching of the parent absorption together with the formation of new ν(CO) bands at *ca.* 1707 cm^{-1}. Within 100 ps, the bleach and transients have recovered back to the baseline. There is a single exponential recovery of the parent absorption. However, the decay of the transient bands is accompanied by a small shift to higher wavenumber. This movement is assigned to early relaxation processes (cooling or solvation) associated with the decay of 'hot' vibrational modes initially formed upon excitation.

The production of 'hot' excited states and their effect on the infrared spectrum is well established and has been discussed in detail.[11] The negative shift of the ν(CO) band that is observed upon irradiation in CH$_2$Cl$_2$ is very close to the shifts observed previously upon formation of the ^{3}MLCT state in Ru^{II} [12,13] and Re^I [14] complexes with diimine ligands bearing two ester or two amide groups. This implies that in **1** the ester groups of the diimine ligand are coupled with the electronic transition, reflecting an increase of electronic density on the ester groups upon excitation, which is consistent with an MLCT assignment for this excited state. The shift observed upon formation of the MLCT excited state of **1** is smaller than the −46 cm^{-1} reported for [Ru(bpy)$_2$(4-(CO$_2$Et)-4′-CH$_3$-2,2′-bpy)]$^{2+}$ [12] in which the bpy ligand bears only one ester group. This suggests that the electronic density in the MLCT excited state of **1** is delocalised over both of the pyridine rings in the bpy-ester ligand within the first 500 fs after excitation, as has been reported for the Ru complex with ester-[12,13] and amido-bearing[13] diimine ligands.

It should be noted that changing the metal from Re^I to Ru^{II} or Pt^{II} does not significantly influence the shift in the ν(CO) band position in the lowest excited state. This is illustrated by *fac*-[Re^{II}(4,4′-(CO$_2$Et)$_2$-2,2′-bpy$^{-\bullet}$)(CO)$_3$(4-Etpy)]$^{+*}$, [Ru^{III}(bpy)$_2$-(4,4′-(CO$_2$Et)$_2$-2,2′-bpy$^{-\bullet}$)]$^{2+*}$ and the MLCT excited state of **1**

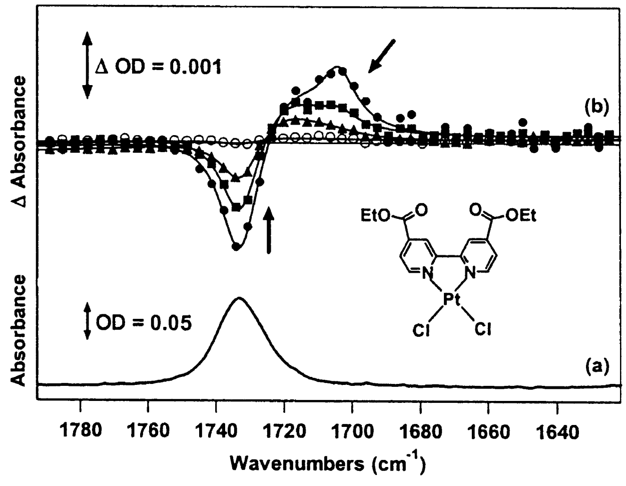

Fig. 1 (a) Ground state FTIR spectrum of **1** in CH$_2$Cl$_2$. (b) TRIR spectra obtained at (●) 1.5 ps, (■) 4 ps, (▲) 11 ps and (○) 50 ps following 400 nm (*ca.* 150 fs FWHM, 14 μJ per pulse) photolysis of this solution. Solid lines represent curve-fitted spectra and arrows indicate movement of the bands with increasing time delay following excitation.

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which all show similar changes in ν(CO) band position of the ester groups on promotion to the MLCT excited state. This is because the LUMO is predominantly localised on the diimine part with only a small contribution from the metal. This observation is consistent with the EPR assignment of the SOMO in $[Pt(4,4'-(CO_2Me)_2-2,2'-bpy)Cl_2]^{-\cdot}$ as being mostly π* diimine-based with a 12% metal orbital contribution.[10] The nature of the HOMO in Pt(diimine)Cl_2 complexes has been discussed elsewhere.[15] Analysis of electronic absorption spectra and Extended Hückel calculations suggests the presence of a manifold of at least four metal-centred HOMOs, thus making an alternative XLCT assignment of the excited state unlikely.

The kinetic traces obtained using multi-Lorentzian curve fitting of the spectra at each time delay are shown in Fig. 2. The transient ν(CO) band was modelled as the sum of two Lorentzian components: one at higher wavenumber corresponding to the vibrationally 'cooled' state of the MLCT excited state, and one at lower wavenumber corresponding to the initially formed vibrationally 'hot' excited state. Contributions from higher vibrational states were neglected in this approximation. Fitting the spectra whilst fixing the positions and widths of the two transients and the bleach, allowed their areas to be determined at each time delay.

The rate of vibrational cooling of the MLCT excited state of **1** was calculated by measuring the change in the ratio of 'hot/(hot + cool)' transient band areas *versus* time. These data, shown in Fig. 2(a), fit well to a single exponential decay with a lifetime of 2.3 ± 0.3 ps. The lifetime of vibrational cooling has been reported[16] to be *ca.* 5 ps for $[Ru^{III}(4,4'\text{-dimethyl-}2,2'\text{-bpy}^{-\cdot})_3]^{2+*}$ and *ca.* 2 ps for $[Ru^{III}(4,4'\text{-diphenyl-}2,2'\text{-bpy}^{-\cdot})_3]^{2+*}$ in CD_3CN. The 2.3 ps lifetime obtained in the present study is in reasonable agreement with the above-mentioned values for Ru complexes. Fig. 2(b) shows the rate of ground state recovery, which fits to a single exponential to give a lifetime of the MLCT excited state of 8.7 ± 0.8 ps. This short lifetime is consistent with the excited state of **1** being non-emissive in fluid solution at room temperature. Fig. 2(c) plots the sum of the areas of the 'hot and cool' transients with time. The kinetics for the decay of the excited state are found to correspond to the recovery of the ground state. This is illustrated in Fig 2(c) which shows that an exponential decay with an 8.7 ps time constant (solid line) provides a good fit to the data.

In light of recent investigations performed on the rate of intersystem crossing in transition metal complexes,[16,17] we tentatively assign the observed picosecond dynamics to processes occurring in the ^{3}MLCT state of **1**. Clearly, more investigations are required into the factors that determine the rate of intersystem crossing in Pt^{II} chromophores for an unambiguous assignment to be possible.

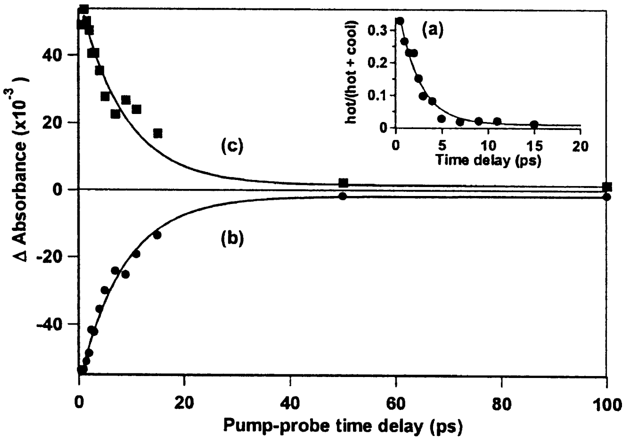

Fig. 2 (a) The ratio of 'hot/(hot + cool)' transient band areas *versus* time delay and kinetic traces obtained from (b) the area of the parent bleach and (c) the sum of the areas of the curve-fitted transient bands following 400 nm photolysis of **1** in CH_2Cl_2. Points, experimental data; lines, exponential fits.

In conclusion, we have shown that picosecond TRIR spectroscopy allows the lifetimes of short-lived excited states of Pt^{II} complexes to be easily determined by the introduction of peripheral IR reporters. The excited state dynamics of **1** in the picosecond time domain are composed of vibrational cooling (2.3 ps) and back electron transfer (8.7 ps) in the MLCT state.

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Notes and references

† **1** was prepared from K_2PtCl_4 and $4,4'-(CO_2Et)_2-2,2'$-bpy in H_2O at 75 °C; purified by column chromatography on silica, $CH_2Cl_2:CH_3CN$ 20:1; characterised by ^{1}H NMR, UV/Vis, elemental analysis, FAB MS.

‡ The ps-TRIR experiments were carried out at the Central Laser Facility of the Rutherford Appleton Laboratory. Briefly, part of the output from a 1 kHz, 800 nm, 150 fs, 2 mJ Ti:Sapphire oscillator/regenerative amplifier was used to pump a white light continuum seeded BBO OPA. The signal and idler produced by this OPA were difference frequency mixed in a type I $AgGaS_2$ crystal to generate tuneable mid-infrared pulses (*ca.* 150 cm^{-1} FWHM, 1 μJ). Second harmonic generation of the residual 800 nm light provided 400 nm pulses, which were used to excite the sample. Changes in infrared absorption were recorded by normalising the outputs from a pair of 64-element HgCdTe linear array detectors on a shot-by-shot basis.

1 M. Gratzel and B. O'Regan, *Nature*, 1998, **353**, 737; K. E. Erkilla, D. T. Odom and J. K. Barton, *Chem. Rev.*, 1999, **99**, 2777; R. Ballardini, V. Balzani, A. Credi, M. T. Gandolfi and M. Venturi, *Acc. Chem. Res.*, 2001, **34**, 445; J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995.
2 M. W. George and J. J. Turner, *Coord. Chem. Rev.*, 1998, **177**, 201.
3 T. A. Heimer and E. J. Heilweil, *J. Phys. Chem. B*, 1997, **101**, 10 990; G. D. Smith, K. A. Maxwell, J. M. DeSimone, T. J. Meyer and R. A. Palmer, *Inorg. Chem.*, 2000, **39**, 893; S. I. Khan, A. E. Beilstein, G. D. Smith, M. Sykora and M. W. Grinstaff, *Inorg. Chem.*, 1999, **38**, 2411.
4 C. E. Whittle, J. A. Weinstein, M. W. George and K. S. Schanze, *Inorg. Chem.*, 2001, **40**, 4053; G. D. Smith, M. S. Hutson, Y. Lu, M. T. Tierney, M. W. Grinstaff and R. A. Palmer, *Appl. Spectrosc.*, 2001, **55**, 637.
5 M. Cusumano, M. L. Di Pietro, A. Giannetto and F. Romano, *Inorg. Chem.*, 2000, **39**, 50; C. S. Peyratout, T. K. Aldridge, D. K. Crites and D. R. McMillin, *Inorg. Chem.*, 1995, **34**, 4484; K. W. Jennette, J. T. Gill, J. A. Sadownick and S. J. Lippard, *J. Am. Chem. Soc.*, 1976, **98**, 6159.
6 A. Harriman and R. Ziessel, *Coord. Chem. Rev.*, 1998, **171**, 331; A. Harriman and R. Ziessel, *Chem. Commun.*, 1996, 1707.
7 M. Hissler, J. E. McGarrah, W. B. Connick, D. K. Geiger, S. D. Cummings and R. Eisenberg, *Coord. Chem. Rev.*, 2000, **208**, 115.
8 C. W. Chan, L. K. Cheng and C. M. Che, *Coord. Chem. Rev.*, 1994, **132**, 87.
9 C. N. Pettijohn, E. B. Jochnowitz, B. Chuong, J. K. Nagle and A. Vogler, *Coord. Chem. Rev.*, 1998, **171**, 85.
10 E. J. L. McInnes, R. D. Farley, C. C. Rowlands, A. J. Welch, L. Rovatti and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1999, 4203.
11 T. P. Dougherty and E. J. Heilweil, *Chem. Phys. Lett.*, 1994, **227**, 19; P. Hamm, S. M. Ohline and W. Zinth, *J. Chem. Phys.*, 1997, **106**, 519; S. Marks, P. A. Cornelius and C. B. Harris, *J. Chem. Phys.*, 1980, **73**, 3069.
12 P. Y. Chen, K. M. Omberg, D. A. Kavaliunas, J. A. Treadway, R. A. Palmer and T. J. Meyer, *Inorg. Chem.*, 1997, **36**, 954.
13 K. M. Omberg, G. D. Smith, D. A. Kavaliunas, P. Y. Chen, J. A. Treadway, J. R. Schoonover, R. A. Palmer and T. J. Meyer, *Inorg. Chem.*, 1999, **38**, 951.
14 P. Y. Chen, R. A. Palmer and T. J. Meyer, *J. Phys. Chem. A*, 1998, **102**, 3042.
15 W. B. Connick, V. M. Miskowski, V. H. Houlding and H. B. Gray, *Inorg. Chem.*, 2000, **39**, 2585; J. A. Zuleta, J. M. Bevilacqua, D. M. Proserpio, P. D. Harvey and R. Eisenberg, *Inorg. Chem.*, 1992, **31**, 2396.
16 N. H. Damrauer and J. K. McCusker, *J. Phys. Chem. A*, 1999, **103**, 8440.
17 A. T. Yeh, C. V. Shank and J. K. McCusker, *Science*, 2000, **289**, 935; J. E. Monat and J. K. McCusker, *J. Am. Chem. Soc.*, 2000, **122**, 4092.