

# Steady State and Sub-nanosecond Spectroscopy of the Complex between Metal(II) Maleonitriledithiolates and Methylviologen

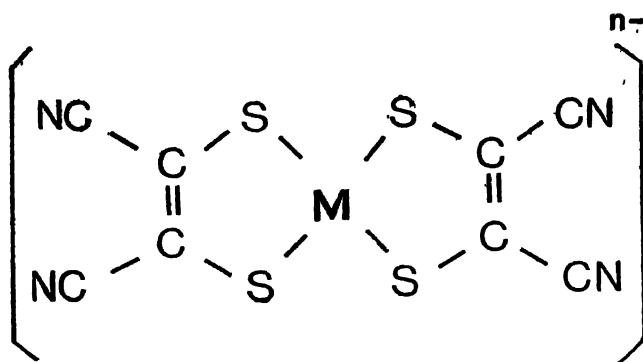
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The photochemically interesting interaction of methylviologen and metal maleonitriledithiolate complexes has been investigated by absorption, emission and transient absorption spectroscopy. Ion-pair charge transfer bands for the  $(MV^{2+})[Pt(mnt)_2]^{2-}$  and  $(MV^{2+})[Ni(mnt)_2]^{2-}$  have been identified in the near-ir. The results presented here suggest that both the complexes mentioned above display weak higher energy state CT absorption bands attributed to weak coupling between the cation and anion. Photoexcitation of either complex in the MLCT region results in electron transfer from the donor *mnt* molecule to the acceptor planar methylviologen molecule producing an excited state. These complexes display room temperature emission which is not observed with conventional alkylammonium cations. The emission and excited state absorption spectra are consistent with a species resembling a reduced dimeric viologen paired with the planar  $M(mnt)_2$ . Picosecond transient absorption spectroscopy indicates an excited state lifetime of  $0.9 \pm 0.2$  ns for the species produced from the platinum complex.

Metal complexes of maleonitriledithiolate (*mnt*)  $[C_2S_2(CN)_2]^{2-}$  (1) are remarkable square-planar compounds which display interesting oxidation-reduction properties. Vogler and Kunkely<sup>1</sup> studied the photo-oxidation of transition metal maleonitriledithiolates in chloroform. This was followed by the work of Patterson and Dooley<sup>2</sup> in mixed solvents of chloroform and acetonitrile. Henning *et al.*<sup>3</sup> obtained hydrogen from water photochemically using photoionisation of  $[Zn(mnt)_2]^{2-}$ . The photoelectrochemistry of the metal complexes was investigated at transparent electrodes<sup>4,5</sup>. The photoexcited state of these complexes displayed sub-nanosecond transients<sup>6</sup>.



M = Ni, Pt

n = 1, 2

(1)

Charge transfer interactions may occur when a suitable electron acceptor is used as a counterion

to the metal complex. Methylviologen (1,1'-dimethyl-4,4'-dipyridinium),  $MV^{2+}$ , has been successfully used as an electron acceptor in many cases. The reduced form is capable of reducing protons to molecular hydrogen in acidic aqueous media. The dianion  $[Pt(mnt)_2]^{2-}$  is thought to be a powerful but short-lived reductant in the photoexcited state<sup>6</sup>. Charge transfer complexes of the Ni and Pt dithiolates are known with radical cations of tetrathiafulvalene<sup>7,8</sup>, tetramethyl-*p*-phenylenediamine (TMPD)<sup>9</sup>, and phenazine<sup>10</sup>. The viologens have been used as electron mediating compounds in a variety of studies. The structure of the salt of nickel maleonitriledithiolate with the methylviologen cation was reported<sup>11</sup>. The interactions of coordination compound ions with counterions may lead to pairing which sometimes display additional electronic absorption bands. These additional bands are known as ion-pair charge transfer (IPCT) transitions<sup>12</sup>. Low energy IPCT bands are of particular photochemical interest with respect to spectral sensitisation of photocatalytic reactions<sup>13</sup>. Here, we report steady state spectral properties and transient absorption spectra of  $M(mnt)_2$  ( $M = Pt, Ni$ ) complexes with methylviologen ( $MV^{2+}$ ). The formation of an ion-pair between these species appears to be a key to the processes.

## Results and Discussion

**Electronic absorption spectra:** The absorption spectra are shown in Fig. 1. The shape of the absorption bands of the  $MV^{2+}$  salt of the nickel complex was slightly broader and red-shifted as compared to the corresponding alkylammonium salt.

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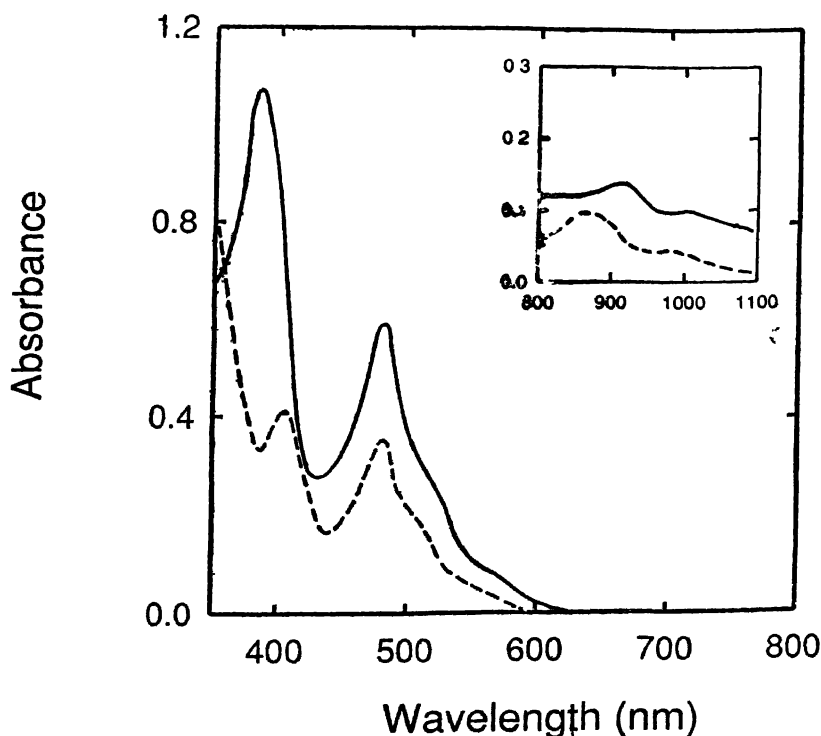


Fig. 1. UV-visible absorption spectra in DMSO ; (—)  $[\text{MV}^{2+}][\text{Ni}(\text{mnt})_2^{2-}]$  and (---)  $[\text{MV}^{2+}][\text{Pt}(\text{mnt})_2^{2-}]$ ; near-infrared spectra in inset.

Bands assigned<sup>5,14</sup> as ligand to metal charge transfer (LMCT)( $L\pi \rightarrow xy$ ) shifted from 378 to 384 nm and those assigned metal to ligand charge transfer (MLCT)( $xz \rightarrow L\pi^*$ ) from 476 to 480 nm<sup>14</sup>. In the platinum complex, the metal to ligand charge transfer band ( $d_{xz} \rightarrow L\pi^*$ ) shifted from 472 to 480 nm. A new shoulder appeared at 388 nm in the Pt spectrum (Fig. 1). This shoulder can be attributed either to the presence of some partially reduced methylviologen type species ( $\lambda_{\text{max}} = 396 \text{ nm}$ ,  $\epsilon = 42000 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>16</sup>, to the appearance of a band associated with an oxidised  $\text{Pt}(\text{mnt})_2^{2-}$  species, or to a higher energy charge transfer band of the type discussed below. If the system is free of impurities, the last option is the most plausible. The visible spectra of  $[\text{MV}^{2+}][\text{Ni}(\text{mnt})_2^{2-}]$  (2) and its tetraethylammonium counterpart were absorbance matched at the peak of the MLCT band (478 nm) where only the dithiolene component of the complex absorbs. A differential absorption spectrum between the alkylammonium  $\text{Ni}(\text{mnt})_2^{2-}$  and the methylviologen salt reveals a spectrum with a broad absorption band at 528 nm ( $\epsilon \approx 90 \text{ M}^{-1} \text{ cm}^{-1}$ ). This band is assigned as a CT band of 2 which is partially masked by the MLCT and  $d-d$  bands of the  $\text{Ni}(\text{mnt})_2^{2-}$ . The extinction coefficients were estimated from the concentration of  $\text{Ni}(\text{mnt})_2^{2-}$  using the absorbance at 478 nm. This assignment is supported by the fact that the position of the band is close to the CT bands observed for  $\text{MV}[\text{Ir}(\text{CO})_2(\text{mnt})_2]_2$ <sup>16</sup> and for  $[\text{MV}][\text{Fe}(\text{CN})_6^{4-}]$ <sup>17</sup> ( $\lambda = 530 \text{ nm}$ ). A broad band appeared in the reflec-

tance spectrum of 2 in the same region<sup>11</sup>. The existence of this ion-pair charge transfer (IPCT) band in the present case is consistent with absorption studies for a series of anionic dithiolene complexes with methylviologen<sup>7,16-20</sup>.

Concentrated solutions of the viologen-mnt complexes displayed a weak but measurable absorbance in the near-ir at 875 ( $\epsilon = 36 \pm 6 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 916 nm ( $\epsilon = 31 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$ ) region for the platinum and nickel complexes respectively. It is quite probable that these are low energy ion-pair charge transfer bands. Intense outer-sphere charge transfer bands have been obtained by Vogler and Kunkely<sup>21</sup> in solutions of square-planar complexes of opposite sign, notably  $\text{Ni}(\text{tim})^{2+}$  ( $\text{tim} = \text{tetramethyl-1,4,8,11-tetraazatetradecatetraene}$ ) and  $\text{M}(\text{mnt})_2^{2-}$  ( $\text{M} = \text{Ni, Pd, Pt}$ )<sup>21</sup>. We note that the series of IPCT bands implied is consistent with observations by Kisch and his associates<sup>18,26</sup>.

**Electronic emission and excitation spectra:** Metal maleonitriledithiolate dianions ( $\text{M} = \text{Ni, Pt}$ ) with alkyl ammonium cations displayed no solution fluorescence when excited in either the LMCT (384 nm) or the MLCT (480 nm) region. The  $\text{MV}^{2+}\text{-M}(\text{mnt})_2$  complexes displayed luminescence which shows that the viologen acceptor cation plays a key role in this complex, and that IPCT excited states processes may be as significant as the appearance of these bands in the ground state spectra. The emission spectrum of  $[\text{MV}^{2+}][\text{Ni}(\text{mnt})_2^{2-}]$  (2) was investigated by exciting

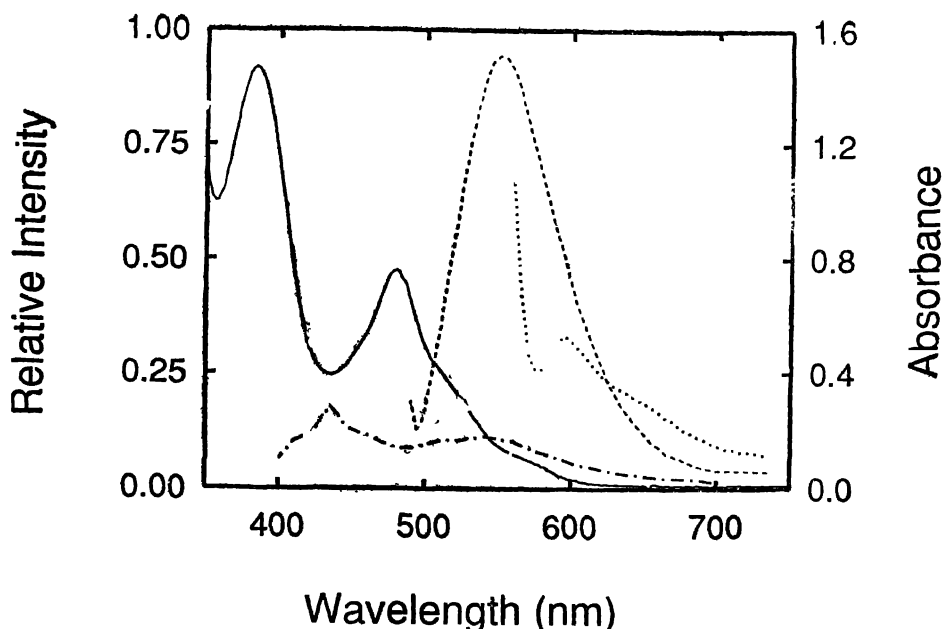
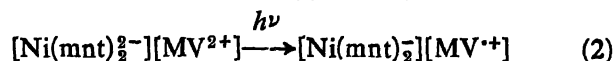


Fig. 2. Room temperature electronic spectra of  $[MV^{2+}] Ni(mnt)_2^{-}$  in DMSO: (—) absorption spectrum and corresponding emission are shown for excitation at (— · —) 384, (---) 480 and (···) 550 nm.

the metal-mnt complex at 480 and 384 nm (Fig. 2). These two wavelengths correspond to regions which are assigned as MLCT and LMCT<sup>7</sup> in the spectrum of the tetraethylammonium salt of  $Ni(mnt)_2^{-}$ . These mnt complex bands are very much intensely absorbing than the overlapping IPCT bands. Strong emission centred at 550 nm was observed for  $\lambda_{ex} = 480$  nm. This luminescence can be associated either with a weak outer-sphere charge transfer absorption band of the complex or an analog of the dimeric viologen radical cation reported by Bird and Kuhn<sup>22</sup> and by Steckhan and Kuwana<sup>23</sup>. Luminescence from intervalence charge transfer bands is quite rare<sup>24</sup>. Since there is transient spectroscopic evidence given below for the extensive formation of  $MV^{+}$  and the oxidised mnt complex the luminescence is most reasonably assigned to the reduced viologen as was the luminescence reported earlier<sup>22,23</sup>. That is, electron transfer forms the products in excited states. We must be cautious that, in this case, a simple dimer of  $MV^{+}$  may not be implicated. Ion-pairing of  $MV^{+}$  with a  $M(mnt)_2^{-}$  species may produce shifts in  $MV^{+}$  luminescence similar to dimerisation. Excitation of **2** at 550 nm, the region of weak charge transfer absorption, produced emission at 595 nm (Fig. 3). An excitation spectrum taken with the emission set at 595 nm revealed a peak at 468 nm which is essentially the MLCT transition region of the  $Ni(mnt)_2^{-}$  portion of the ion-pair. This suggests IPCT states are reached following MLCT absorption as the efficiency of the transient photoredox also requires.

Excitation into the L→M charge transfer band at 384 nm produced weaker and broader luminescence with peaks at 430 and 550 nm. The lumines-

cence is not the same for higher excitation energies. Apparently L→M states are not efficient for photo-induced CT (which supports the assignment to  $MV^{+}$  and  $Ni(mnt)_2^{-}$ ) and LMCT states can relax to the ground state without going via lower MLCT states. Resonance Raman experiments by Clark and Turtle<sup>25</sup> indicated that the  $^1A_g \rightarrow ^1B_{2u}(M \rightarrow L)$  charge transfer transition gives resonance enhancement of both C=C and C≡N vibrations of the mnt ligand. Shorter wavelengths affect C≡N less. This implies that MLCT excitation would lead to a greater delocalisation of charge onto the periphery of the ligand. Photo-induced charge transfer from the mnt to viologen would then be more facile. Observation of resonance enhancement of the  $MV^{2+}$  vibrations on excitation of the MLCT region of  $Ni(mnt)_2^{-}$  will be reported elsewhere<sup>26</sup>. Photoconductivity in the visible and near-infrared region of the nickel dithiolene complexes can be ascribed to the formation of monoanionic dithiolene and partially reduced viologens in the scheme suggested by Meier *et al.*<sup>27</sup>.



The transient absorption spectrum of the Pt compound suggests a similar mechanism to be discussed later.

The room temperature solution fluorescence of **3** is shown in Fig. 5. Fluorescence was observed at  $\lambda_{ex} = 480$  nm while minimal fluorescence was observed when  $\lambda_{ex} = 355$  nm (the wavelength used in the transient spectroscopy). An excitation spectrum of the solution with the emission wavelength set at 572 nm revealed a double peak spectrum with discernable maxima at 430 and 480 nm. Strong emission

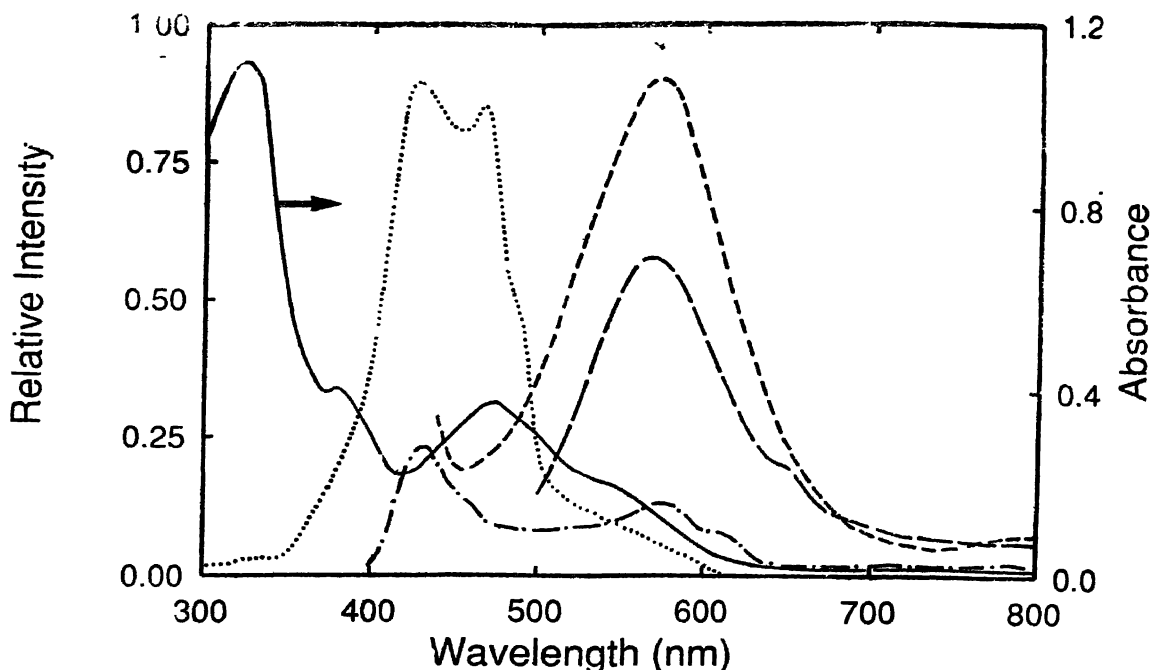


Fig. 3. Room temperature electronic spectra of  $[MV^{2+}][Pt(mnt)_3^{2-}]$  in DMSO: (—) absorption spectrum and corresponding emission are shown for excitation at (---) 430, (---) 480 and (---) 380 nm; excitation spectrum (···) shown for  $\lambda_{emission}$  set at 575 nm.

at 572 nm assigned to a dimeric viologen cation radical species<sup>22,23</sup>, shifted hypsochromically due to ion-pairing with the anionic metal complex. As with the Ni complex, this assignment is attractive. Excitation of the MLCT band at 480 nm ( $d_{xz} \rightarrow L\pi^*$ ) is responsible for some of the emission at 572 nm.

The emission at 572 nm is the fluorescence to be discussed. The 572 nm fluorescence was recorded with excitation wavelengths of 480, 430, 380 and 355 nm. At an excitation of 480 nm, strong emission was observed. A similar result was obtained when the excitation wavelength was changed to 430 nm. Excitation at 380 nm revealed a much broader but weaker fluorescence spectrum characterised by a peak at 430 nm and a broader peak at 572 nm with a shoulder at 620 nm.

**Transient absorption spectroscopy:** The transient spectra for the  $Pt(mnt)_3^{2-}$  complexes of the tetraethylammonium cation and the methylviologen dication were recorded at probe delays of 20, 50, 500 picoseconds, and 1 nanosecond (Figs. 4 and 5 respectively) following excitation with a pulse at 355 nm. The overall shape of the transient spectra differed as cations changed. The transient bleaching of the complex with the tetraethylammonium salt was more pronounced than its viologen counterpart. The spectrum of  $[MV^{2+}][Pt(mnt)_3^{2-}]$  at a probe delay of 5 ns is quite similar to that at a probe delay of 1 ns. It reveals a broad band assigned to reduced associated viologens (530–540 nm)<sup>22,28,28,29</sup> and the monomeric  $MV^{•+}$  (near 618 nm)<sup>18</sup>.

The slight growth in the 450 nm region of Figs. 4 and 5 is attributed to a partial oxidation to give  $Pt(mnt)_2^{\cdot-}$ . The transient spectrum of 3 displays characteristics which are consistent with a viologen-mnt IPCT complex with an excited state lifetime of approximately  $0.9 \pm 0.2$  ns. The corresponding maleonitriledithiolate dianion with a spherical tetrabutylammonium cation (TBA) exhibited a shorter-lived excited state different from that of its methylviologen counterpart. In particular the excited state absorption in the 620–675 nm region for the TBA-mnt complex remains relatively constant for at least 1 ns while considerable decay occurs in the  $MV$ -mnt complex. This decay is illustrative that the pathways of energy dissipation differ between the two complexes as the inert cation is exchanged for an acceptor. The planar methylviologen moiety with a low lying LUMO can participate in charge transfer processes and decay by rapid back electron transfer.

**Conclusion:** The steady state photophysics and transient absorption spectra of ion-pair complexes between metal maleonitriledithiolates ( $M=Ni, Pt$ ) and methylviologen ( $MV^{2+}$ ) were studied in DMSO and DMF solution. Photoinduced electron transfer occurs in the charge transfer complexes obtained from the title maleonitriledithiolate complexes as donors and  $MV^{2+}$  acceptors. A lower energy absorption band in the near-ir was observed for both the complexes and is assigned as an ion-pair charge transfer (IPCT) band. Fluorescence results suggest that lower energy excitation produces strong emission while higher excitation energies yield weaker

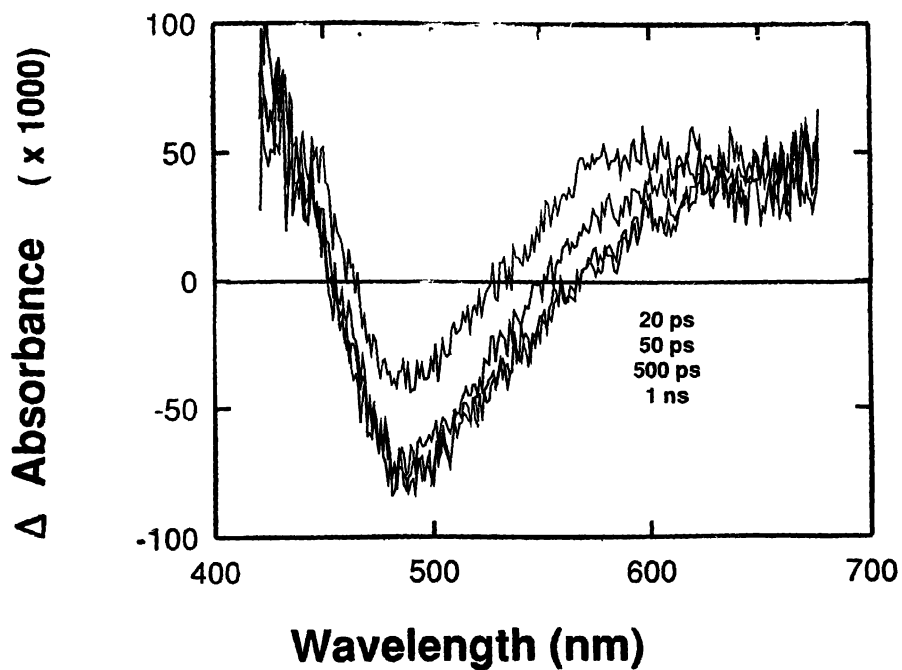


Fig. 4. Transient absorption spectra for  $[(C_6H_5)_4]_2[Pt(mnt)_2]^-$  in DMSO using 355 nm excitation at probe delays of 20, 50, 500 ps, and 1 ns proceeding from top to bottom.

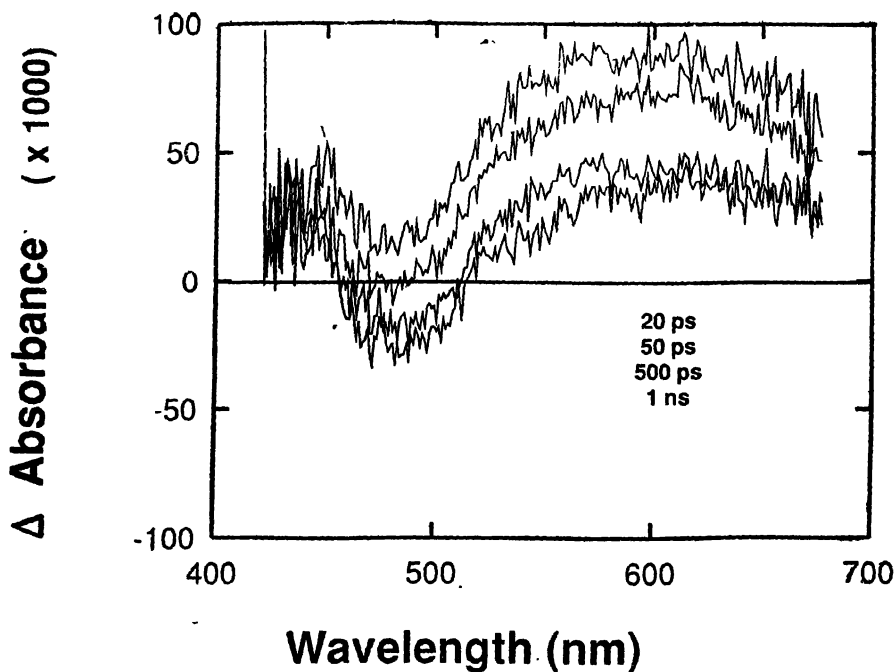


Fig. 5. Transient absorption spectra for  $[MV^{2+}][Pt(mnt)_2]^-$  in DMSO using 355 nm excitation at probe delays of 20, 50, 500 ps, and 1 ns proceeding from top to bottom.

luminescence. There is evidence of further charge transfer absorbance in the 550 nm region for the nickel complex and in the 575 nm region for the platinum complex. Picosecond transient absorption spectroscopy indicates an excited state lifetime of  $0.9 \pm 0.2$  ns for the luminescent species derived from the platinum complex.

### Experimental

Water was deionised and then distilled in glass. Solvents and salts were of reagent grade and used as received unless otherwise specified. Preparation of  $\text{Na}_2\text{mnt}$  was previously described<sup>30</sup>.

$(\text{MV}^{2+})[\text{Ni}(\text{mnt})_2^{2-}]$  (2): The nickel complex was prepared by slight modification of the method of Benson *et al.*<sup>31</sup>.  $\text{Na}_2\text{mnt}$  ( $5.38 \times 10^{-3}$  mol) was dissolved in aqueous methanol (1 : 1 ; 7 ml) and warmed on a hot-plate. To this solution,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  ( $2.45 \times 10^{-3}$  mol) (Anachemia) in water (1.2 ml) was added. The deep red solution was filtered and a solution of methylviologen chloride ( $2.60 \times 10^{-3}$  mol) was added. The precipitate was washed in the same manner as the platinum complex (Found : C, 45.40 ; H, 2.82 ; N, 15.60. Calcd. for : C, 45.73 ; H, 2.69 ; N, 16.00%).

$(\text{MV}^{2+})[\text{Pt}(\text{mnt})_2^{2-}]$  (3): The platinum complex was prepared using a slight modification of the published procedures<sup>31</sup>. To hexachloroplatinate (Aldrich) ( $2.44 \times 10^{-3}$  mol) dissolved in deoxygenated water, was added  $\text{Na}_2\text{mnt}$  ( $5.38 \times 10^{-3}$  mol). The red solution was gently warmed on a hot-plate and treated with an aqueous solution containing methylviologen chloride (Aldrich) ( $2.50 \times 10^{-3}$  mol). The brownish red precipitate was washed several times with water, methanol and acetone. The product was soluble only in DMF (Aldrich, spectrograde) and DMSO (Fischer, spectrograde) (Found : C, 35.01 ; H, 2.20 ; N, 12.58 ; Pt, 18.97. Calcd. for : C, 36.28 ; H, 2.13 ; N, 12.70 ; Pt, 29.49%).

**Electronic spectroscopy:** Uv-visible absorption spectra were obtained using an HP8452A diode array spectrophotometer. Near-ir spectra were taken using a Shimadzu UV-160 spectrophotometer. Fluorescence spectra were obtained using a Perkin-Elmer MPF-44 spectrofluorimeter equipped with a differential corrected spectrum unit. All measurements were performed at ambient temperature.

**Transient absorption spectroscopy:** Picosecond transient absorption spectra were obtained in the Canadian Centre for Picosecond Flash Photolysis located at Concordia University. The system used a Quantel YG 402G neodymium-doped YAG laser. The 1064 nm fundamental yielded 30 ps pulses at a maximum rate of 10 pulses per second. Frequency doubling and tripling of the fundamental using KDP type I and II crystals respectively, produced harmonic frequencies of 532 and 355 nm. The latter frequency was used as a pump beam for excitation in picosecond absorption spectra. Unconverted light (1064 nm) was focused into an aqueous solution of dilute  $\text{H}_3\text{PO}_4$  which produced a white conti-

num from 425 to 675 nm with a pulse width comparable to that of the pump beam. A portion of this white beam was split to the sample to act as the probe beam while the other portion served as a reference beam. The transmitted light from both pump and probe beams were each directed towards their respective sectors of a multichannel silicon enhanced vidicon array. Measurements were taken at probe delays from 20 ps to 5 ns. All data was collected using an EG & G PAR computer and then analysed off-line on a PDP-11 minicomputer.

For each delay period, three 'data sets' were collected and signals averaged. Each data set consisted of one blank shot and three sample shots. Thus, a spectrum for a probe delay of 50 ps was an average of nine sample shots and three blank shots. A transient absorption spectrum is presented as the average difference between the sample and blank. Spectra were normalised for laser intensity. All picosecond absorption spectroscopy was carried out using fresh solutions in 2 mm quartz cell at ambient temperature.

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