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Sub-nanosecond Transients in the Spectra of Bismaleonitriledithiolate Complexes of Ni(II) and Pt(II): Observation of Oxidative Quenching

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We have recently described the photoelectrochemistry of $M(mnt)_2^{2-}$ (M = Ni, Pd, Pt; mnt = $S_2C_2(CN)_2^{2-}$) at optically transparent electrodes of tin oxide on glass with the complexes dissolved in acetonitrile [1]. Interpretation of the photocurrents in terms of a model presuming current determining competition between diffusion of the excited state to the electrode and relaxation to the ground state suggested that the redox reactive states were short lived. (Pd complexes were unreactive.) We now report the transient spectra of the Ni, Pd, and Pt complexes following excitation with the 3 mj, 30 ps half width, 355 nm pulse from the Nd/YAG mode locked laser in the Canadian Centre for Picosecond Laser Flash Photolysis [2]. The results confirm the existence of excited states with lifetimes in the projected range. In addition, a signal of the Pt complex is quenched by added water, and this can be associated with oxidation of the Pt complex.

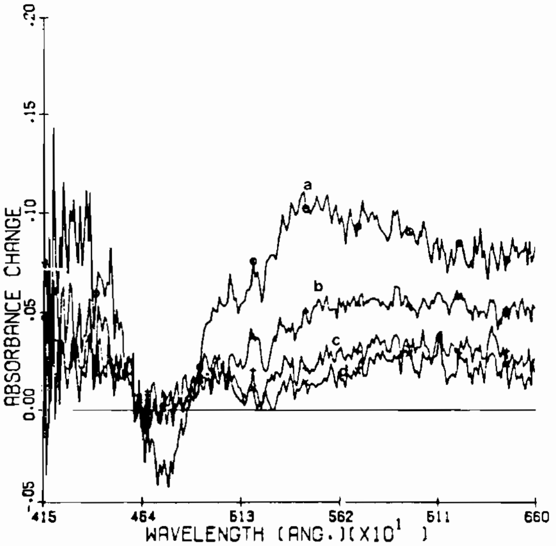

Fig. 1. Transient absorption spectra of $Ni(mnt)_2^{2-}$. Delay times reading from top to bottom of excess absorption near 550 nm and bottom to top at bleach near 472 nm: 20, 50, 100, 200 ps.

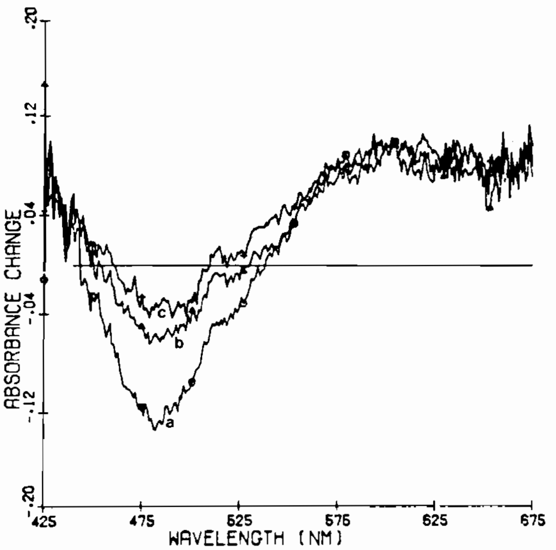

Fig. 2. Transient bleaching of $Pt(mnt)_2^{2-}$. Reading from bottom up curves, delay times are: 500 ps, 5, 10 ns.

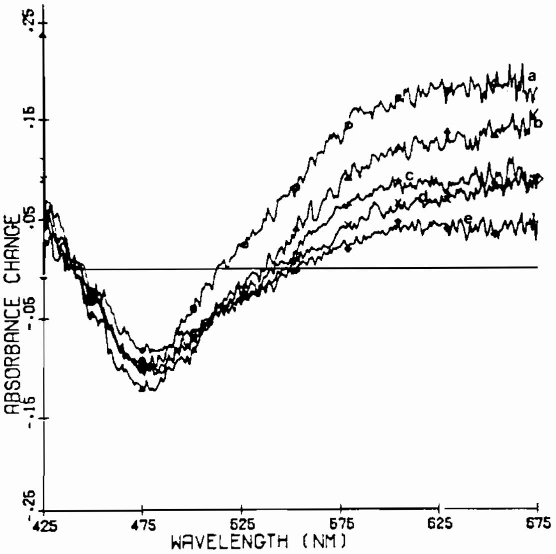

Fig. 3. $Pt(mnt)_2^{2-}$ transient absorbance quenching by water. Reading from top, delay times are: 50 ps, 1, 3, 5, 10 ns.

Figures 1, 2, and 3 show absorbance change spectra recorded using a continuum pulse produced by superbroadening of the Nd fundamental in D_2O. The Ni and Pt complexes in acetonitrile are represented by Figs. 1 and 2, and the Pt complex behaviour in acetonitrile with 30% (volume) water is represented in Fig. 3. The first two spectra (in CH_3CN) exhibit spectra for probe pulse delays between

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20 ps and 1 ns. The sample with water present shows spectra to 10 ns (the long time limit of the apparatus). No transients were observed for the Pd complex between 20 ps and 10 ns. Similarly, the effect of water on the Ni complex spectra was small. It will become relevant below to note that the oxidized monoanionic complex of Pt yields no transients under our conditions.

We consider first the spectra in neat acetonitrile. In both cases, a bleaching is observed near 475 nm. This corresponds well to the main ground state absorption band in the visible region indicating depletion of the ground state. In both cases there is a broad excited state absorption to the red of the negative bleaching peak. In the case of the Ni complex, both the bleaching and the excited state absorption have decayed to small values by a delay time of 200 ps. Longer delay spectra than those shown here do reveal that a small but measurable excited state absorbance in the red does persist to 10 ns. In the case of the Pt complex, all processes are slower. However, the decay of the bleaching signal is not accompanied by decrease of the excited state absorbance to the red before 10 ns.

Although it is not the point of this communication to present a definitive assignment for these transients, it may be noted that a consistent interpretation would assume that the initially populated state partitions rapidly between a low lying singlet and triplet. The triplet yield is larger for Pt and the singlet decay time has reached about 5 ns in comparison to about 50 ps in the Ni case. The most interesting feature is that shown in Fig. 3. Water quenches the Pt 'triplet'; its lifetime is reduced to ~3 ns from a value >10. As well, the bleaching of the ground state absorbance is reduced. This is a hint of another feature. All of the mnt anionic complexes exhibit very limited solubility in water or aqueous solvent mixtures. After addition of even small amounts of water, precipitation of the complex is observed within 24 h and it is almost certain that the transient spectra are recorded for colloidal suspensions rather than true solution although there is only a modest increase in light scattering which imposes no significant limitation on the sensitivity of absorption spectroscopy.

Two continuous irradiation experiments have allowed us to assign the water quenching as an oxidative process with reduction of the solvent. First, CW irradiation of the Pt complex in deaerated aqueous media for several hours leads to the change of the visible spectrum [1] from that characteristic of the 2– ion to that of the oxidized 1– ion (growth of a band at 855 nm and shift of the 472 nm maximum to 450 nm). Second, an electrode prepared with tin oxide coated with a quaternized polyvinylpyridine anion exchange film may be loaded with the dianionic Pt complex from an acetonitrile solution. When this electrode is mounted in a conventional three electrode potentiostatic arrangement in contact with an aqueous electrolyte and irradiated, the effect of light is to lead to the shift of the cathodic solvent reduction wave in the cyclic voltammogram in the anodic direction. This change is accompanied by development of the absorption band of the 1– complex in the film.

References

1 L. Persaud and C. H. Langford, *Inorg. Chem.*, in press.
2 N. Serpone and D. K. Sharma, to be published.