

## Short Communication

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### Quenching of organic singlets and triplets by a Ni(II) complex

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The photochemistry and photophysics of coordination compounds has been extensively studied in recent years [1, 2]. In a separate paper [3], we have described energy transfer processes which occur, under gamma radiation, in crystalline clathrates formed by the complex Ni(II)(4-picoline)<sub>4</sub>(NCS)<sub>2</sub>, taken as "host", and various aromatic hydrocarbons, taken as "guests". A mechanism of excitonic nature has proved useful to explain the excitation energy transfer between the host and the guest component; the clathrates were in the solid state, where a physical "association" between donor, and acceptor in the ground state exists, as evidenced by their absorption spectra [4].

The purpose of this short communication is to report the results of preliminary experiments on excitation energy transfers between the same species, *i.e.*, the Ni(II) complex, and the compounds employed as guests, in dilute solution, where it is more difficult that the components may give rise to any chemical or physical form of "association", in their ground states [5].

In particular, these systems were irradiated by u.v. light, and the luminescence of the molecules, employed as guests in the formation of the clathrates, was quenched by the Ni(II) complex.

#### *Biacetyl-Ni(II) (4-picoline)<sub>4</sub>(Cl)<sub>2</sub>*

The emission spectra were measured in deoxygenated water solutions, with a CGA DC/3000/I spectrophotofluorimeter. The exciting light was set at 412 nm, and practically all the incident light was absorbed by biacetyl. The biacetyl concentration was 0.08 M and the Ni(II) complex concentrations were from  $1 \times 10^{-4}$  M up to  $10 \times 10^{-4}$  M, respectively. The Ni(II) complex quenches significantly the biacetyl phosphorescence, without affecting its fluorescence. Using the usual Stern-Volmer equation, the plot of Fig. 1 is obtained, which gives a quenching constant  $k_q = 0.96 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , with a phosphorescence lifetime, for biacetyl, in aqueous solution, of 0.23 ms [6]. This rate for the quenching of biacetyl triplets is considerably smaller than the diffusion-controlled rate. Similar values have been found for other systems, for instance:  $k_q = 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , for biacetyl-tetra-

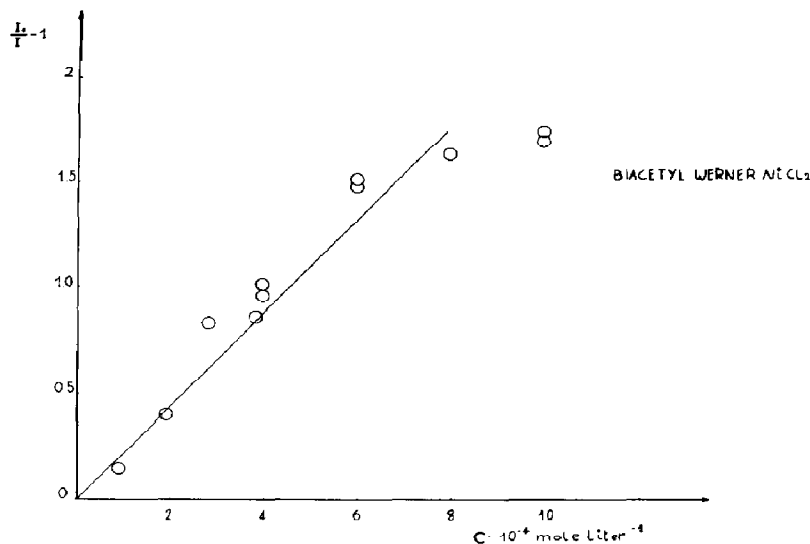


Fig. 1. Quenching Stern-Volmer plot for the system biacetyl-Ni(II) (4-picoline)<sub>4</sub>(Cl)<sub>2</sub>.

chloroplatinate(II);  $k_q = 3.8 \times 10^4 M^{-1} s^{-1}$ , for biacetyl-hexamine cobalt (III);  $k_q = 2.6 \times 10^7 M^{-1} s^{-1}$ , for biacetyl-hexacyanocobaltate(III) [8].

#### *Anthracene-Ni(II) (4-picoline)<sub>4</sub>(NCS)<sub>2</sub>*

The quenching experiments were carried out in deoxygenated methanol solutions of  $0.17 \times 10^{-3} M$  anthracene, with increasing concentrations of Ni(II) complex, from  $1 \times 10^{-3} M$ , up to  $6 \times 10^{-3} M$ . The exciting light was set at 358 nm so that, for the employed Ni(II) complex concentration, the incident light was practically all absorbed by anthracene. The Ni(II) complex quenches the anthracene fluorescence, at room temperature. The Stern-Volmer plot, for its quenching, is shown in Fig. 2. This plot yields a  $k_q = 9.5 \times 10^9 M^{-1} s^{-1}$ , using a lifetime of  $4.5 \times 10^{-9} s$  for singlet anthracene [9].

This rate constant shows that the quenching process during the encounter between the excited donor, and the Ni(II) complex is quite efficient, and practically corresponds to a diffusion-controlled process. Many studies have been carried out which involve anthracene triplets, but very few examples are reported on singlet anthracene, such as for instance, a  $k_q = 8.7 \times 10^9 M^{-1} s^{-1}$ , for the system H<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>-anthracene, in ethanol; also many lanthanide complexes behave in a similar way, with  $k_q$  constants for singlet anthracene higher than for its triplet state [5].

It is rather difficult to assess whether the involved quenching mechanism refers to pure electronic energy transfer; unfortunately, no excited state of the acceptor, (the Ni(II) complex), can be chemically, or physically observed. Even if the luminescence of the Ni(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> ions has been reported [10], no evidence was observed by us for the specific Ni(II) complex employed. The energy diagram of Fig. 3 shows the probable quenching process; the *d-d* energy levels of the Ni(II) complex refer to absorption maxima, so

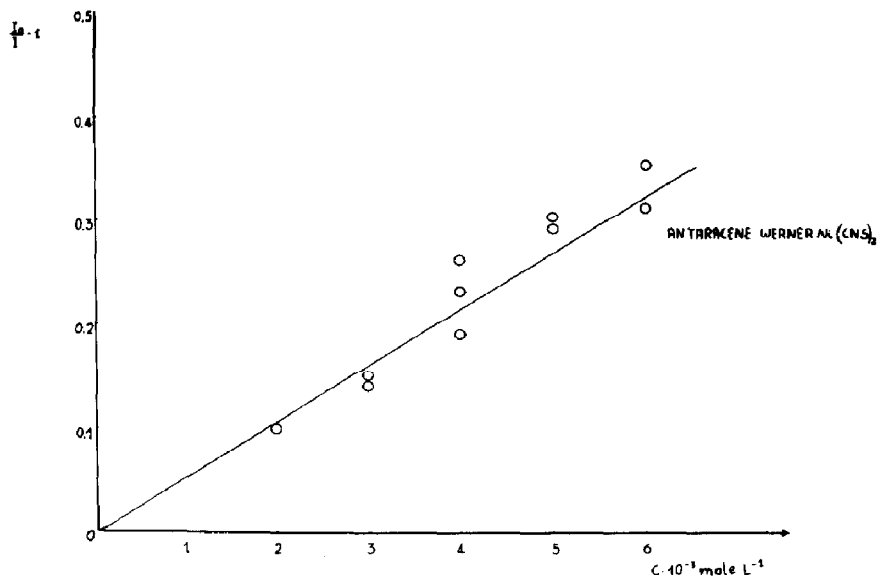


Fig. 2. Quenching Stern-Volmer plot for the system anthracene-Ni(II)(4-picoline)<sub>4</sub>(NCS)<sub>2</sub>.

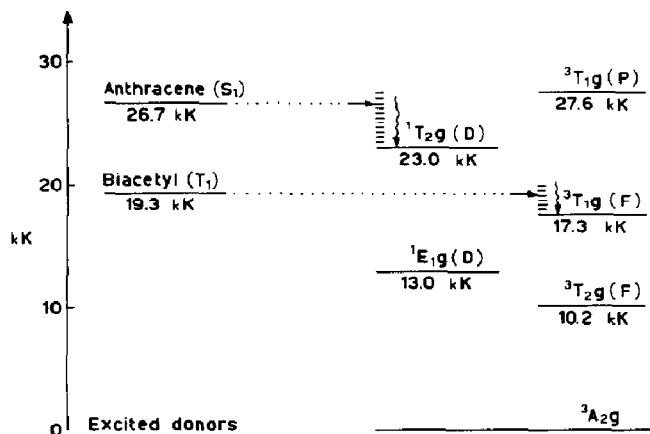


Fig. 3. Diagram of the energy transfers.

that they may not give the right electronic energy difference between excited and ground state, owing to vibrational contribution [7]. As shown by the diagram, two Ni(II) complex excited states seem to be involved in our case; the  ${}^3T_{1g}(F)$  triplet in the triplet biacetyl quenching, and the  ${}^1T_{2g}(D)$  singlet in the singlet anthracene quenching. How these excited states are depopulated, the role, and efficiencies of internal conversions, and/or intersystem crossings remain to be studied. Work is in progress to extend the luminescence quenching experiments to many other aromatic compounds, employed also as guests in the clathrates, in order to get a better understanding of the reactive states of the Ni(II) complex. It seems also very interesting to get experimental evidence whether these clathrate-forming species, when in solution,

at room temperature as well as at 77 K, give rise, at a certain extent, to physical or chemical "association". In this case, both dynamic, and static quenching should occur, affecting, consequently, the slopes of the Stern-Volmer plots [5].

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