

# Characterization of the Bis( $\beta$ -diimino-tetracyano-pyrrolizinido)–metal(II) Complexes Incorporated in Polymeric Matrices

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**Abstract.** The bis( $\beta$ -diimino-tetracyano-pyrrolizinido)–Cu(II) complex ( $\text{CuL}_2$ ) has been incorporated in polystyrene (0.28% w/w), by evaporating tetrahydrofuran solutions either at room temperature (**a**) or at 100 °C (**b**). From IR and UV–vis measurements and optical microscopy on the resulting films (**a** or **b**, thickness 50  $\mu\text{m}$ ) it is concluded that  $\text{CuL}_2$  is present as a concentrated ( $C \approx 10^{-1}$  M) THF solution in **a** and as small solid particles (diameter  $< 1 \mu\text{m}$ ) in **b**. The difference in colour of the films (dark blue **a**, light blue **b**), due to the different physical state of  $\text{CuL}_2$  in the matrix, is expected, and has been preliminarily shown using similar films based on  $\text{NiL}_2$ , to be useful for sensing organic vapours in the atmosphere.

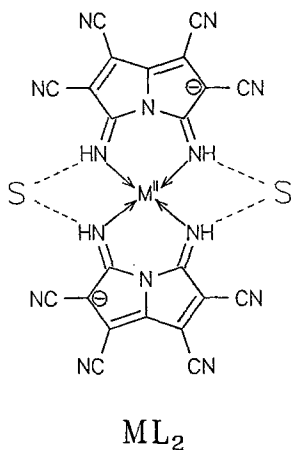
**Key words:** Pyrrolizinido complexes, dyes, sensors, organic solvents.

## 1. Introduction

The bis(1,2,6,7-tetracyano-3,5-diimino-3,5-dihydropyrrolizinido)–metal (II) complexes ( $\text{ML}_2$ ), which some of us synthesized for the first time [1], are interesting as they represent an important new, very intense dye class, whose optical spectra are extraordinarily similar to those of the corresponding metal-phthalocyanines (MPc) [2]. In most cases,  $\text{ML}_2$  species are much more soluble than MPc in donor solvents and, in the solid state, in contrast to MPc, they always contain some crystallization solvent (S), usually laterally adducted to the imino groups in the molecular plane via hydrogen bonds. Interestingly, the crystallization solvent can be conveniently discriminated by examining the IR  $\nu_{\text{N-H}}$  bands, whose shape, intensity and energy depend markedly on S [3].

Recently, we began a research program to address possible uses of  $\text{ML}_2$  species as functional dyes for technological applications. For this purpose we are currently investigating their chemico-physical properties, when incorporated in polymeric matrices, because we believe that this is the only promising route to the exploitation of such materials, after the unsuccessful efforts to deposit them by vacuum subli-

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Scheme 1.

mation due to their inherent thermal instability at high temperature ( $>200\text{ }^\circ\text{C}$ ) [4]. On the other hand, the incorporation of dye molecules in polymers is a widely used method for their practical applications, as they might display useful properties not observed in solution, apart from a general enhanced thermal, chemical, and photo stability in the matrix [5].

In this paper we describe the properties of the  $CuL_2$  complex in polystyrene (PS). Information was obtained from IR and UV-vis spectral studies on the composite, thick,  $CuL_2/PS$  films. A possible use of such a system for sensing organic vapours is envisaged.

## 2. Experimental

### 2.1. MATERIALS

Polystyrene (beads, MW 280 000) was used as received from Fluka. Tetrahydrofuran (THF) was refluxed over sodium-benzophenone ketyl and freshly distilled under  $N_2$  before use.  $CuL_2 \cdot 2THF$  was prepared following our procedure [1].

#### 2.1.1. Preparation of $CuL_2/PS$ samples

A mixture of  $CuL_2 \cdot 2THF$  (0.5 mg, 0.0007 mmole) and PS (180 mg) was dissolved in THF (4 mL) under  $N_2$ . The clear, homogeneous, blue solution was placed in a leveled Petri dish (diameter 5 cm) and then evaporated to dryness under a stream of ultrapure dinitrogen (upp  $N_2$  over activated  $SiO_2/CrO$ ) at room temperature. The residue, a blue film **a**, was easily peeled off and used directly in the subsequent measurements. The composition of the film **a** was:  $PS/CuL_2/THF = 96.64/0.27/3.09\%$  (w/w); the THF content was determined by TGA measurements. Another film **b**, the same as **a** but solvent-free and lighter in colour, was obtained after evaporation

to dryness by heating of the initial solution at 50 °C for 30 min and then at 100 °C for a further 30 min. Both films, **a** and **b**, were of similar thickness: of the order of 50  $\mu\text{m}$ . Films, prepared by following the same procedure as above but without  $\text{CuL}_2$ , were also made.

## 2.2. INSTRUMENTATION

Thermal gravimetric analyses (TGA) were performed with a Du Pont 950 apparatus. A Cary 5 instrument was used to record optical spectra. A Nikon microphot-FX microscope with a resolution of 1  $\mu\text{m}$  at the largest magnification ( $10 \times 100$ ) was used for the visual observations.

### 2.2.1. Infrared absorption spectroscopy

The IR spectra of the films were measured by using a Digilab 40A FT-IR spectrometer with dynamic alignment. The selected spectral resolution was  $4 \text{ cm}^{-1}$ . The transmission spectra of the samples were obtained from the ratio of a 'single beam' spectrum of the sample, e.g. a polystyrene film with incorporated  $\text{CuL}_2$ , and the one from a reference film, e.g. a pure polystyrene film of the same thickness as the sample film. By a careful selection of the reference film almost complete compensation of the polymer infrared spectrum was obtained. Apart from the modulation due to the interference effect related to the thickness of the films, the minima in the transmission spectra were then only due to the guest chemical species present in the host matrix.

Finally, the spectra were subjected to data reduction, removal of the remaining polystyrene features and smoothing, by using a GRAMS/386 software product by Galactic.

IR solution ( $\text{CuL}_2$  in THF) spectra were also recorded by the same method.

## 3. Results and Discussion

### 3.1. PROPERTIES OF THE SAMPLE **a**

Figure 1 presents the IR transmission spectra of samples **a** and **b**, obtained by following the complete procedure described in the previous section. Let us first focus our attention on spectrum **a**. To interpret this spectrum we made other measurements

As already indicated, we prepared two pure (with no  $\text{CuL}_2$ ) polystyrene films, one, **A**, condensed at room temperature as in the case of sample **a**, the second, **B**, condensed at 100 °C as in the case of sample **b**. Figure 2 shows the IR transmission spectrum of film **A**, obtained by using as reference film **B**; such a spectrum is almost coincident with the IR spectrum of neat THF [6].

TGA measurements show the presence of 3.09% (w/w) of THF in the films condensed at room temperature, **a** and **A**, resulting from the weight loss by heating

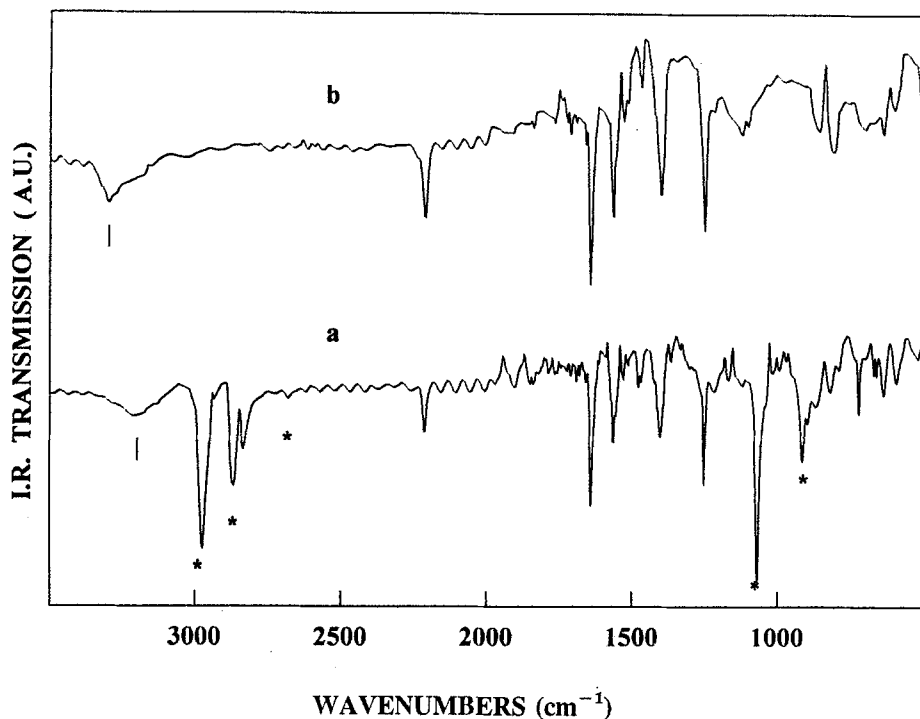


Fig. 1. Infrared transmission spectra of sample **a** (a polystyrene film with  $\text{CuL}_2$  inclusion condensed from THF solution at room temperature) and of sample **b** (a similar film but condensed at  $100^\circ\text{C}$ ). The symbol (\*) indicates the THF main peaks, while the vertical bar indicates the N—H stretching vibration of the  $\text{CuL}_2$  molecules in the films. A pure polystyrene film condensed at  $100^\circ\text{C}$  was used as a 'reference spectrum' (see text).

the films from  $50$ – $120^\circ\text{C}$ , while THF is absent in the films condensed at  $100^\circ\text{C}$ , as expected because of both the lower boiling point of the solvent ( $80^\circ\text{C}$ ) and the absence of any attractive interaction between the solvent and the matrix other than van der Waals interactions.

Visual inspection, by optical microscopy, reveals the presence of small droplets (maximum diameter  $50\ \mu\text{m}$ ) in films **a** and **A**. Consequently, spectrum **a** in Figure 1 is interpreted as originating from droplets of a concentrated THF/ $\text{CuL}_2$  solution ( $C \approx 10^{-1}\ \text{M}$ ), dispersed in polystyrene. Specifically, the symbol (\*) indicates the main bands attributable to THF (compare also with Figure 2), while the other bands in the transmission spectrum are mostly due to the  $\text{CuL}_2$  complex. Incidentally, it is particularly interesting to note that  $\text{CuL}_2$  is much more soluble in THF in the matrix than in THF alone (solubility of  $\text{CuL}_2$  in THF, *ca.*  $1.5 \times 10^{-3}\ \text{M}$ ). Confirmation of the above interpretation comes from the data presented in Figure 3, where the concentration normalized transmission spectra in the UV–vis range for sample **a**, curve **a**, and a THF/ $\text{CuL}_2$  solution, curve **c**, are presented. The two curves show

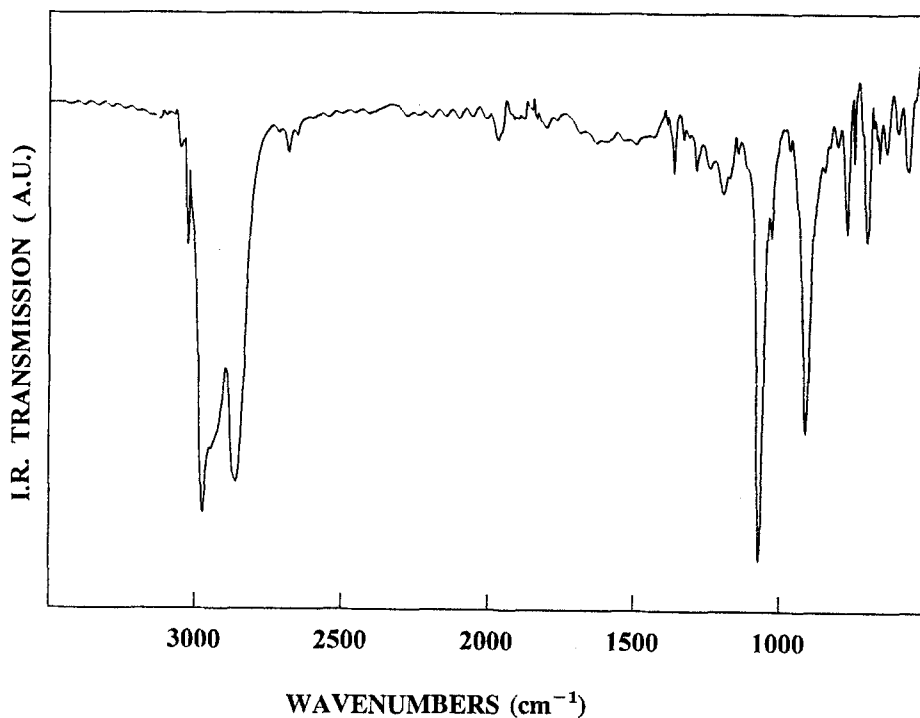


Fig. 2. Infrared transmission spectrum of a pure polystyrene film condensed from THF solution at room temperature. The reference spectrum was one from a similar sample condensed at 100 °C.

a remarkable similarity both in shape and intensity, supporting the interpretation already discussed.

### 3.2. PROPERTIES OF THE SAMPLE **b**

As already reported, no THF is present in a film of sample **b**. In fact, the IR transmission spectrum of sample **b**, curve **b** in Figure 1, does not show any feature of the THF solvent. Also, the observation by optical microscopy, in the limit of the instrumental resolution at the largest magnification, does not give any evidence of liquid droplets or spots in that film. The transmission spectrum of sample **b** is then mainly interpreted as the spectrum of a heterogeneous composite of  $\text{CuL}_2$  particles in polystyrene. It has not yet been possible to measure the diameter of such particles. At present, we can only say that it is certainly less than  $1 \mu\text{m}$ , i.e. the maximum resolution of the optical microscope. Interestingly, by comparing the IR spectra of the  $\text{CuL}_2$  molecules in films **a** and **b**, the only appreciable difference observed is in the high frequency region. In sample **b**, the blue-shift and the persistent broadening of the band assignable to the N—H stretching vibration at  $3300 \text{ cm}^{-1}$  ( $3200 \text{ cm}^{-1}$  in sample **a**) is proof of a change in the local environment around

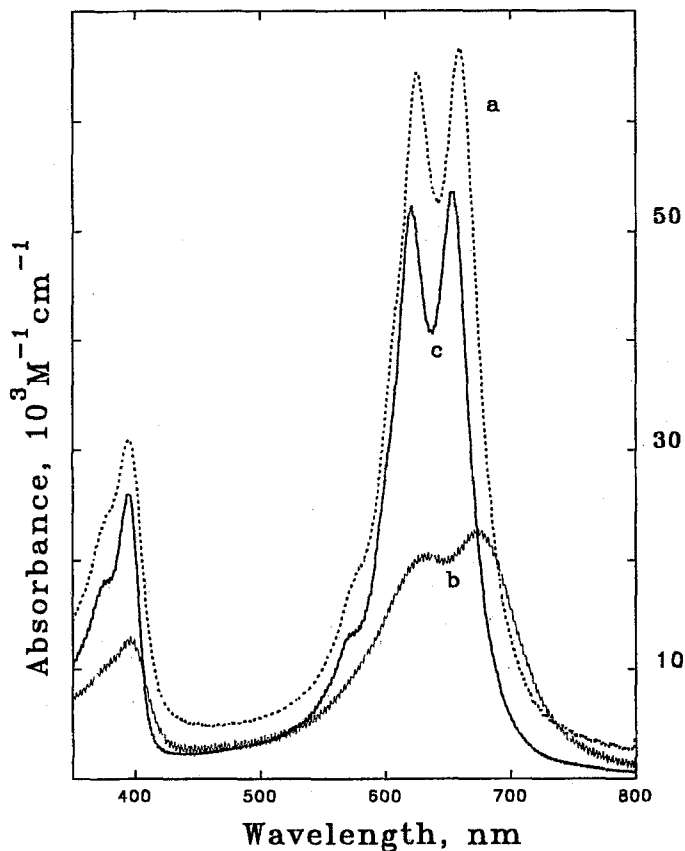


Fig. 3. Optical spectra of film **a** (curve **a**), film **b** (curve **b**) and  $\text{CuL}_2$  in THF (curve **c**). Concentration for **a** (or **b**) and **c** was  $4.6 \times 10^{-3}$  M and  $4.53 \times 10^{-5}$  M, respectively. Pathlength was  $50 \times 10^{-4}$  cm and 1 cm for the films and the solution, respectively.

the  $\text{CuL}_2$  molecules, going from a situation characterized by hydrogen bonds with the solvent molecules (sample **a**) to a different arrangement, where only weaker intermolecular hydrogen bonds ( $\text{N—H—NC}$ ) are likely to occur. We note that the  $\text{N—H}$  stretching IR band, which, in sample **a** coincides in shape and frequency with the one from  $\text{CuL}_2$  in THF solution, is different in sample **b** from the case of  $\text{CuL}_2 \cdot 2\text{THF}$  in nujol mull ( $\nu_{\text{N—H}}$ : 3165, 3258  $\text{cm}^{-1}$ ) [7], thus confirming the absence of THF coordinated to the  $\text{CuL}_2$  molecule in this sample. The transmission spectrum in the UV–vis range of sample **b**, curve **b** in Figure 3, also supports the hypothesis of  $\text{CuL}_2$  particles dispersed in the polymer, by showing the broadening and the red-shift of the 600–700 nm bands, features that both characterize the phase change from solution to solid of  $\text{ML}_2$  complexes [8]. Accordingly, the colour fading (from **a** to **b**, see Figure 3) is simply due to a change of the physical state of  $\text{CuL}_2$  units.

We end this section by noting that film **a**, baked for 30 min at 100 °C, once cooled, behaves as the sample **b**, discussed already.

#### 4. Conclusions

On the basis of our findings, it is clear that  $\text{CuL}_2$  can be incorporated in polystyrene in two ways: either as droplets of THF solution (**a**) or as solid particles (**b**). We expect that sample **b** can be used as an optical sensor for organic vapours (e.g. THF) in the atmosphere, provided that a suitable plasticizer is added to polystyrene in order to increase its permeability to the flow of the molecules to be detected. As a matter of fact,  $\text{CuL}_2$  is so finely dispersed in **b** and so soluble in THF in the matrix, that it could readily dissolve when in contact with the solvent vapour, thus causing an appreciable increase of light absorption at 658 nm (wavelength corresponding to the maximum of absorbance, see Figure 3). Such a mechanism might also explain the results of related experiments, carried out on a similar composite film (polymer/plasticizer/ $\text{ML}_2$ ) at the Mitsubishi Kasei Corporation in Yokohama: a thin film of phenoxy resin/polyethylene-teraphthalate/ $\text{NiL}_2$ , cast at 100 °C on an aluminium support, is colorless, becomes blue after  $\approx 60$  s of exposure to THF vapour and fades again on heating with no apparent degradation over several cycles [9].

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