



Vapochromism of a Pyrrolizinato-nickel(II) Complex Incorporated in Polyvinylbutyral. An Optochemical Detecting System for Alcohols in Air

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Abstract. The bis(1,2,6,7-tetracyano-3,5-dihydro-3,5-diiminopyrrolizinido)nickel(II) complex (NiL_2 , $\text{L} = \text{C}_{11}\text{H}_2\text{N}_7^-$) has been incorporated as dispersed monomer in polyvinylbutyral (PVB) at a fairly high concentration (0.021 M). NiL_2/PVB spin coated thin films (thickness, $\sim 2 \mu\text{m}$) on glass and silicon and evaporated free standing thicker films (thickness, $\sim 50 \mu\text{m}$) have been studied by means of absorption or reflectivity visible as well as infrared spectroscopy. The light-blue NiL_2/PVB film fades slightly on heating (for 7 min at 90°C) and remains as such after cooling to room temperature. The optical spectrum of the thermally activated NiL_2/PVB system, in contact with organic solvent vapors at room temperature, changes with time evolving towards the initial spectrum before the thermal treatment. The system is therefore amenable for sensing organic solvents in air. Several ordinary solvents have been tested. After 12 min exposure to air saturated with vapor a steady-state absorbance signal at the most sensitive wavelength (661 nm) is reached for any tested solvent. The system is most sensitive to alcohols. Response cycles are reported for methanol as solvent.

Key words: sensors, thin-films, pyrrolizinato-complexes, tetracyanoethylene.

1. Introduction

Recently, we began to study the bispyrrolizinato- and monopyrrolizinato-metal(II) complexes (Chart 1, ML_2 and $>\text{ML}$, respectively) as functional materials for the construction of optical chemical sensors.

The possibility of a successful exploitation of these species in such application is based on some of their favourable properties: ML_2 complexes are intense dyes, they interact with various molecules undergoing distinct color changes and can be incorporated easily at a fairly high concentration in either organic or inorganic polymeric matrices. Our recent contributions to this subject concerned CuL_2 in polystyrene (CuL_2/PS) [1] or in crosslinked polyvinylformal (PVF) [2] and $>\text{HgL}$ in hybrid silica [3]. Presently, we are studying NiL_2 incorporated in organic polymers. The interest in this species with this aim in mind is based on its peculiar thermochromism in solution, which we previously investigated [4]. Among the ML_2 complexes, NiL_2 solely undergoes a reversible color change in solution as

Chart 1

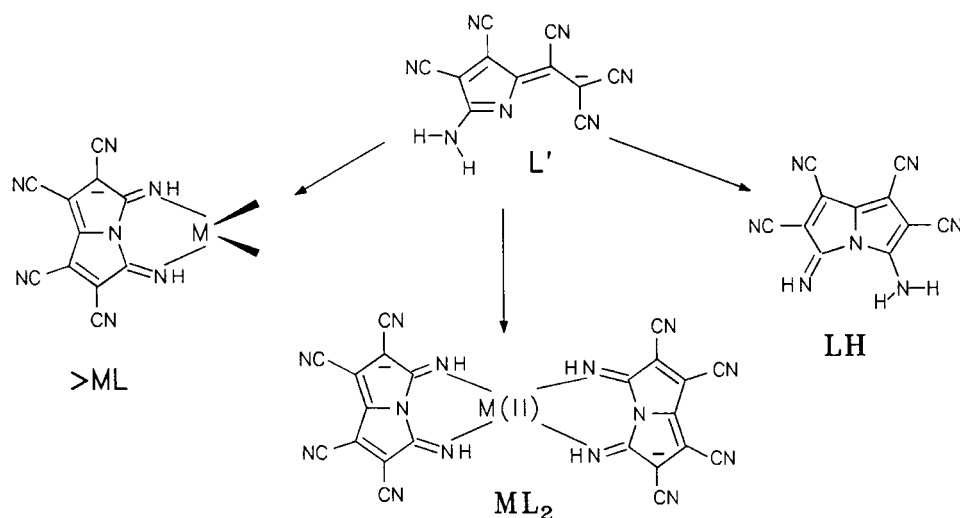


Chart 1.

the temperature rises. Temperature dependent optical spectra are reported in Fig. 1. Apparently, NiL_2 behaves differently on heating when incorporated in a polymeric matrix. In particular, the system NiL_2/PVB (PVB, polyvinylbutyral) shows a non-reversible thermochromism. In turn it exhibits an interesting “vapochromism” [5] after thermal activation, of potential utility for sensing alcohols in air, as reported in the current paper.

2. Experimental

2.1. MATERIALS

$NiL_2 \cdot 2\text{acetone}$ was prepared according to our procedures [6]. PVB (powder, Mw 36000, d 1.083, T_g 51 °C) and the other polymers used (PS, PMMA, ETC) were purchased from Aldrich. All the solvents were of analytical-reagent grade.

2.2. PREPARATION OF THE COMPOSITES

In a typical experiment, a solution (0.5 mL) of $NiL_2 \cdot 2\text{acetone}$ (3.7 mg, 0.0058 mmol) and PVB (0.3 g) in THF/MeOH (3/1, 4 mL) was spin coated (for 30 s at 150 r.p.m. and then for 10 s at 5000 r.p.m.) on a glass plate ($2.5 \times 2.5 \times 0.08$ cm) or on a silicon slide (0.5 mm thick and mirror-like polished on both sides) in a Convac spinner model 1001. Light blue films (1.35 mg, $\sim 2 \mu\text{m}$ thick) were obtained with optical absorption maxima at $\lambda_{\text{max}} = 661$ and 664 nm, for the film on

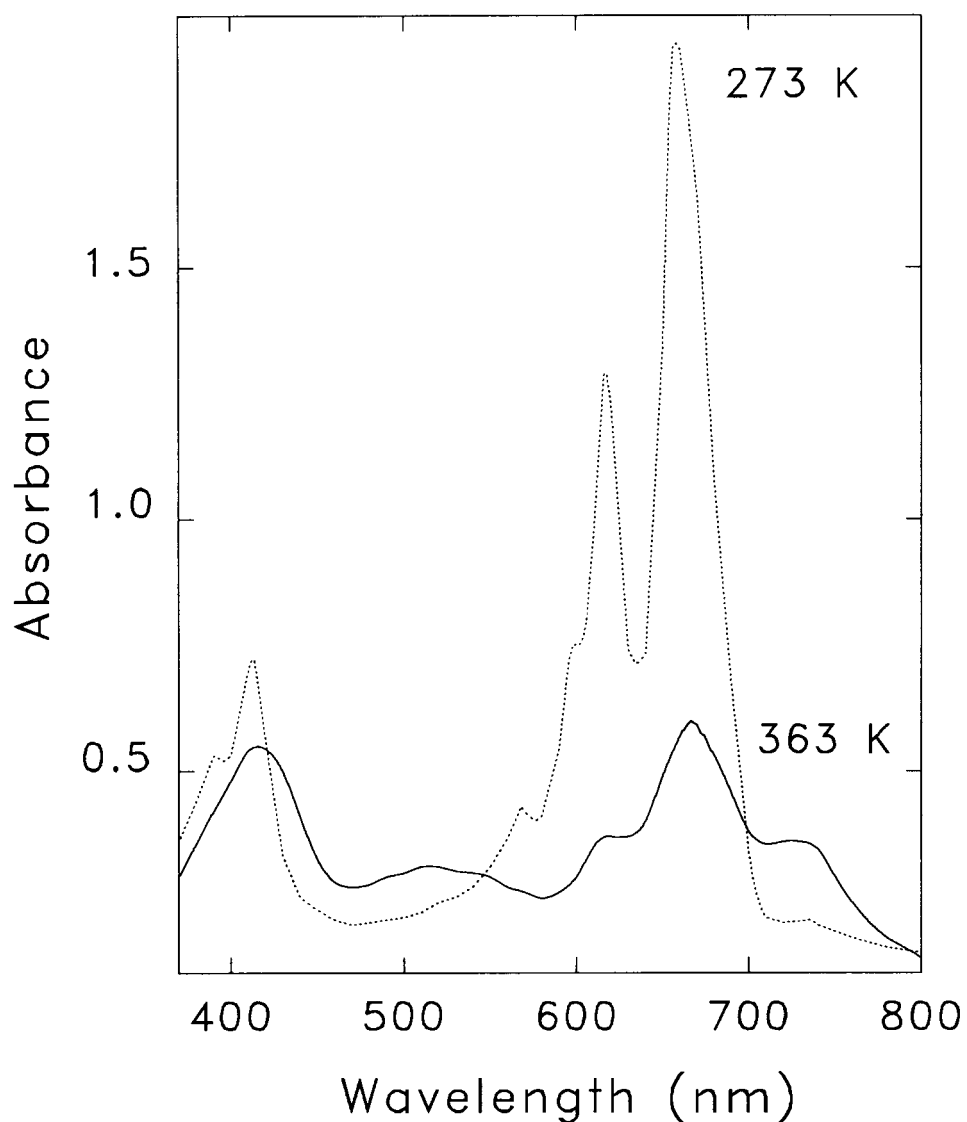


Figure 1. Solution optical spectra of NiL_2 in ethylacetate at two different temperatures (K).

glass (from transmission experiment) and for the film on silicon (from reflectivity measurements), respectively.

The same precursor solution (1.3 mL) was used to prepare free standing thicker films (thickness, $\sim 50 \mu\text{m}$) after evaporation to dryness in a leveled Petri dish (diameter 5 cm).

Both spin-coated and evaporated films were optically clear, tough and of uniform color and thickness.

2.3. FILM THICKNESS MEASUREMENTS

The thickness of the films were obtained from the interference modulation of the IR baseline using a suitable value for the index of refraction of the polymer material (around 1.5). As a check, the measured thickness values were compared for thicker films with thickness obtained by weighing. The uniformity degree of thickness was tested by measuring both the IR interference patterns and the visible reflectivity spectrum in different zones of the film itself. The variation of the thickness was estimated to be within 5%.

2.4. OPTICAL MEASUREMENTS

A Cary 5 spectrophotometer was used for recording optical spectra. The glass slide supporting the film, 0.8 cm wide, was inserted vertically across the light beam into a 1 cm square quartz cuvette (4.5 cm high).

All the experiments regarding the interaction of NiL₂/PVB with solvent vapors were carried out in a closed system containing air saturated with the solvent vapor at 25 °C. In particular, a glass slide (1.3 cm wide) was placed vertically and parallel to the diagonal of the cuvette in order to block it in a fixed position; an open capillary (3 cm high), filled with the solvent to be tested, was placed inside the cuvette, stuck with silicon grease along the edge of the cuvette. The cuvette was finally stoppered and immediately placed into the spectrophotometer for the measurement, after the time interval indicated in the corresponding figures (Figs. 5, 6, see later). For the evaluation of the response of the system to different organic solvents (Table I), nine thermally activated NiL₂/PVB films were prepared under identical conditions from the same batch. In order to compensate for small differences in the various films, the absorbance recovery (ΔA) at the most sensitive wavelength (661 nm) has been calculated as the ratio: $\Delta A = [(A^a - A^b)/(A^c - A^b)] \times 100$, where A^a , A^b and A^c are the absorbances relative to the baseline absorbance at 800 nm after exposure to the solvent, before exposure and before the thermal treatment, respectively. The recyclability test (Figure 6) was performed alternating 8 min exposure of the thermally activated NiL₂/PVB film to air saturated with methanol vapor in the spectrometer with 7 min of heating the same film at 90 °C in the oven. In all the experiments an uncoated glass slide was placed in the reference compartment.

2.5. IR MEASUREMENTS

Mid and far infrared (IR) measurements were performed with a Biorad 40-A FTIR spectrometer in transmission and reflection geometry for films on Si substrates and in transmission geometry for thicker free standing polymer films and reference NiL₂ powder samples (mixed with nujol between two CsI windows). Typical spectral resolution was 4 cm⁻¹ and the number of scans ranged from 256 to 1024.

Table I. Absorbance recovery at 661 nm of thermally activated NiL₂/PVB films, after 12 min exposure to various solvents

Solvent	Concentration ^a	ΔA^b	$\Delta A \%^{-1}$
CH ₃ OH	16	100	6.25
THF	21	62	2.95
EtOH	8	56	7.0
DME	22	54	2.45
CH ₂ Cl ₂	56	35	0.63
Acetone	29	34	1.17
CH ₃ CN	15	21	1.4
Dioxane	5	17	3.4
Toluene	4	13	3.25

^a Calculated as volume percentage in air at 25 °C from the empirical vapor pressure (p) expression of the corresponding solvent: $\text{Log } p = A - B/(25 + C)$, where A, B and C were taken from a handbook [8].

^b Measured as described in the Experimental.

After collection, the single beam spectra were subjected to data treatment (spectra comparison, smoothing, baseline removal, etc.) by the software GRAMS by Galactic.

3. Results and Discussion

A number of organic polymers were tested as hosting matrices for NiL₂. For instance: polymethylmethacrylate (PMMA), ethyl cellulose (ETC), PS and PVB. Most of them were discarded because NiL₂ is neither stable in the polymer towards ligand dissociation (ETC) nor does the resulting composite exhibit any sensing property (PMMA, PS). Only the NiL₂/PVB composite shows an interesting vapochromism after thermal activation, as anticipated above and detailed in the following sections.

3.1. CHARACTERIZATION OF THE NiL₂/PVB COMPOSITE

The NiL₂/PVB films, obtained as described in the *Experimental* section, were of good quality and very concentrated in NiL₂. Specifically, the concentration of NiL₂ in the film (0.021 moles per liter of PVB) is 15-fold higher than in the precursor solution. Correspondingly, the volume should reduce by 93.3% on film formation, in agreement with the estimated volume percentage of solvents removed: 93.1%, if the removal of the solvent is complete as in the current case and as proved by

the IR spectrum of the freshly prepared film, where even the strongest absorption bands of THF (e.g. 1070, 2860 and 2976 cm^{-1}) were not detected. Incidentally, we note that the solubility of NiL_2 in PVB is much higher than in any organic solvent (maximum solubility in MeOH, 0.001 M), according to the general trend of the solubility change of ML_2 complexes switching between organic solvents and polymeric matrices [1].

In order to gain insight into the dispersion degree of NiL_2 in the matrix, it is of interest to compare its spectra, in PVB and in homogeneous organic solution, normalized to the concentration and the pathlength (Figure 2). The former spectrum compared to the latter appears slightly broader with an associated lower ϵ_{max} (6% lower), extra shoulders at 750, 500 and 450 nm, a 11 nm red-shifted absorption maximum and a superimposed background absorption continuously rising towards high energy. These differences can be interpreted as due to an incipient modification of discrete NiL_2 molecules in PVB rather than to molecular aggregation, since they parallel those occurring in the solution spectrum of this complex upon heating (Figure 1). Thus, we conclude that the total amount of NiL_2 in PVB is truly dispersed as non interacting monomer.

The NiL_2/PVB composite has been characterized also by means of infrared spectroscopy. In Figure 3 we present the IR transmission spectrum in the range 400–2700 cm^{-1} of a PVB film deposited on a Si substrate, curve (a), and of a similar sample with NiL_2 inclusion in the polymer film, curve (b). In both spectra the baseline is modulated by optical interference of the same period (around 1800 cm^{-1}), thus confirming that the two films have almost the same thickness (around 1.8 μm in this case). Both spectra are dominated by the absorption bands of the PVB matrix but some weak extra features are present in spectrum (b) (see, e.g., the ones indicated by the asterisk) attributable to the guest molecules. After suitable data reduction and spectral subtraction between curve (b) and (a) the spectrum shown in Figure 4, curve (a), is obtained. For comparison, the transmission spectrum of the $\text{NiL}_2 \cdot x\text{H}_2\text{O}$ powder (dispersed in nujol between two CsI windows), curve (b), is also shown in the figure. The strong similarity of the two spectra suggests that the structural changes, if any, of NiL_2 molecules consequent to its incorporation in the matrix are not revealed by IR spectroscopy in this frequency range. Another valuable information provided by this technique is that the spin-coated film does not contain any of the solvents used for preparing the precursor solution (MeOH, THF, etc.).

The far infrared region of the spectrum was difficult to explore, since some instrumental limitations (e.g. insufficient signal to noise level of the DTGS detector) and the inherent weakness of the signal did not allow the detection of the low intensity bands observed at 221 and 267 cm^{-1} for bulk NiL_2 and attributable to vibrations involving the metal atoms.

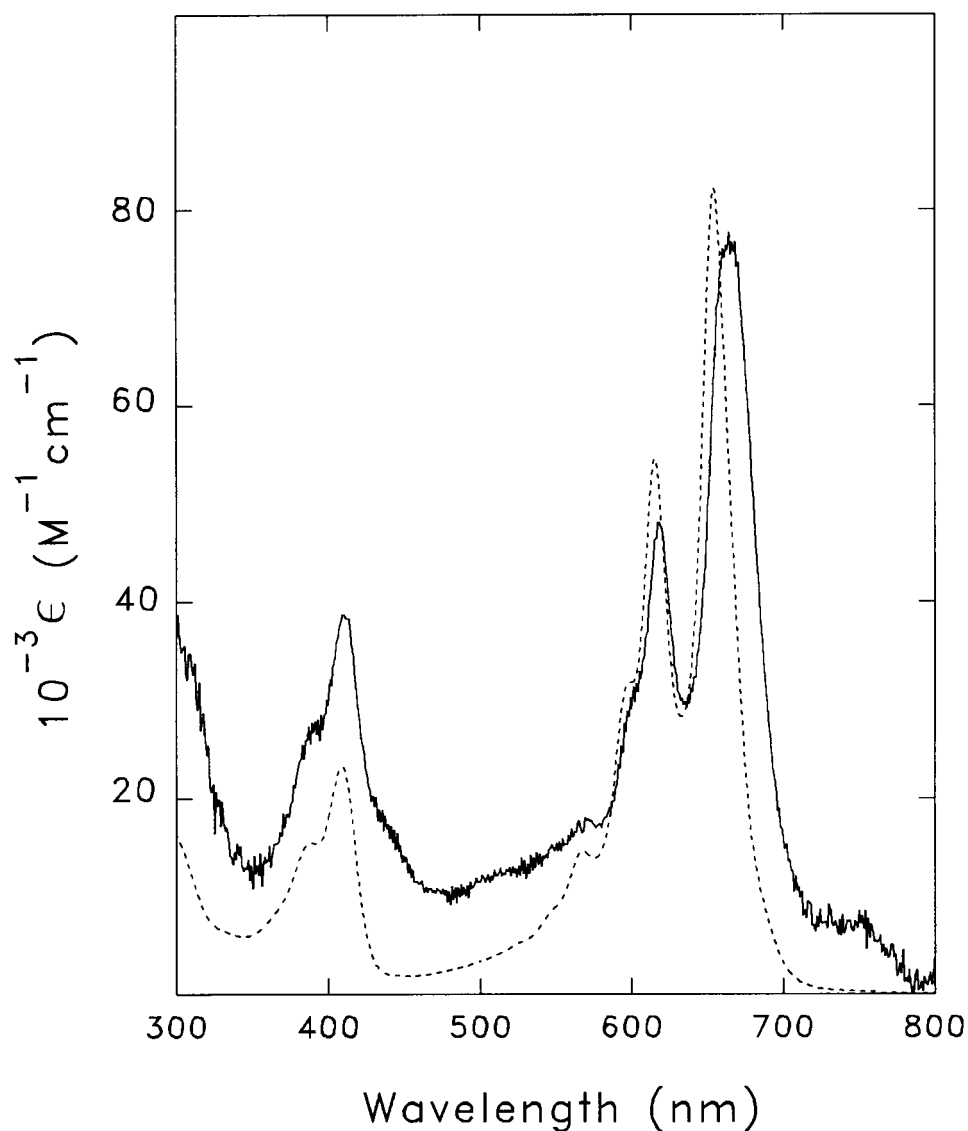


Figure 2. Normalized optical spectra of NiL_2 in PVB film (—) and in methanol (---).

3.2. BEHAVIOR OF THE NiL_2/PVB COMPOSITE ON HEATING

In general, on heating a dye/polymer composite material two common spectral changes occur, consisting in an intensity reduction and in a broadening of the spectrum, quantitatively dependent on the specific dye molecule. The overall change is due to molecular aggregation on heating and thus it cannot be reversed at all.

The composite NiL_2/PVB behaves differently on heating. The associated spectral changes parallel those occurring on heating NiL_2 in solution (see comments

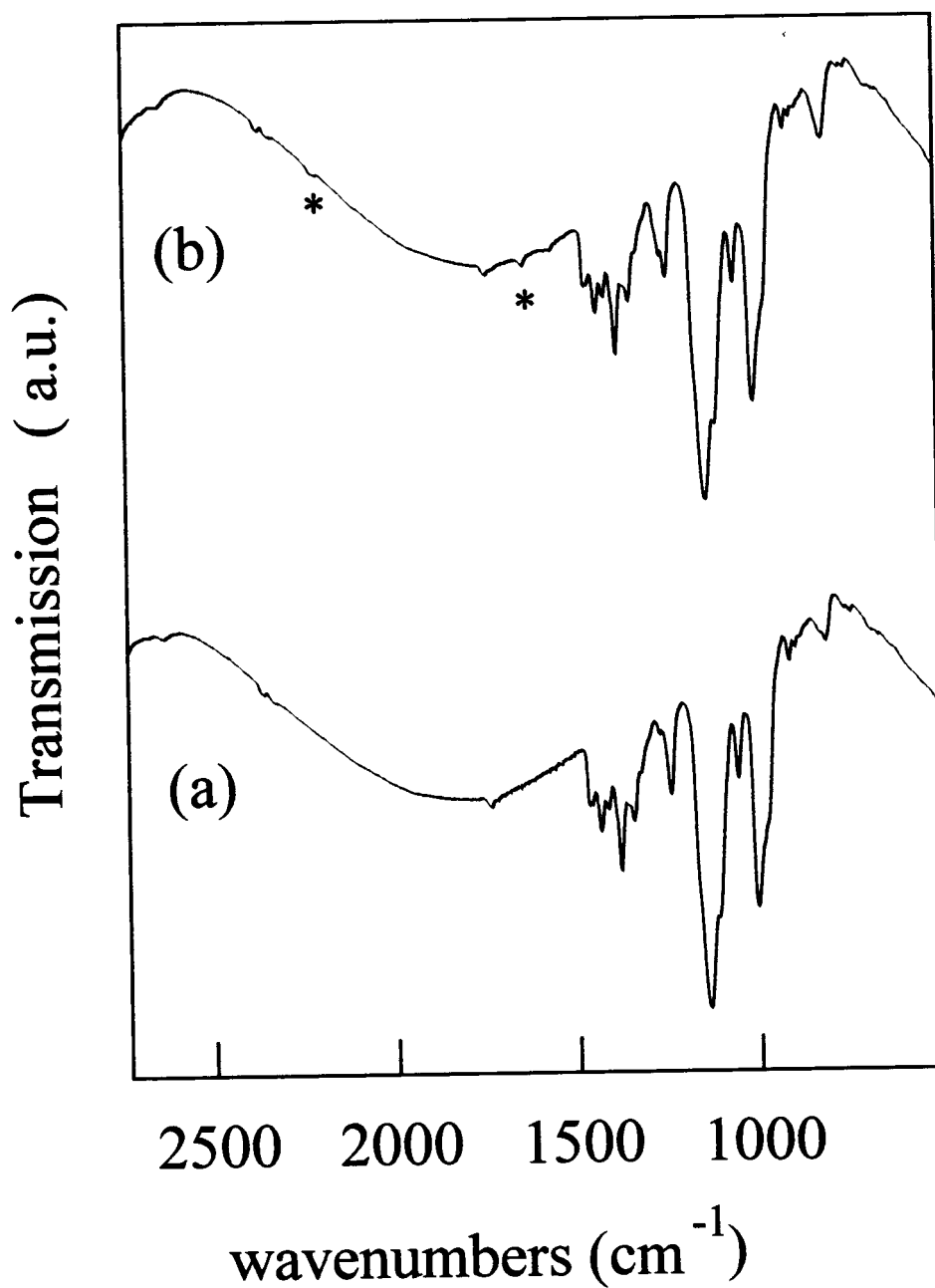


Figure 3. Infrared transmission spectra of a PVB film on a Si substrate, curve (a), and of a similar sample with NiL₂ inclusion, curve (b). The asterisks indicate some of the features attributed to the dye molecule.

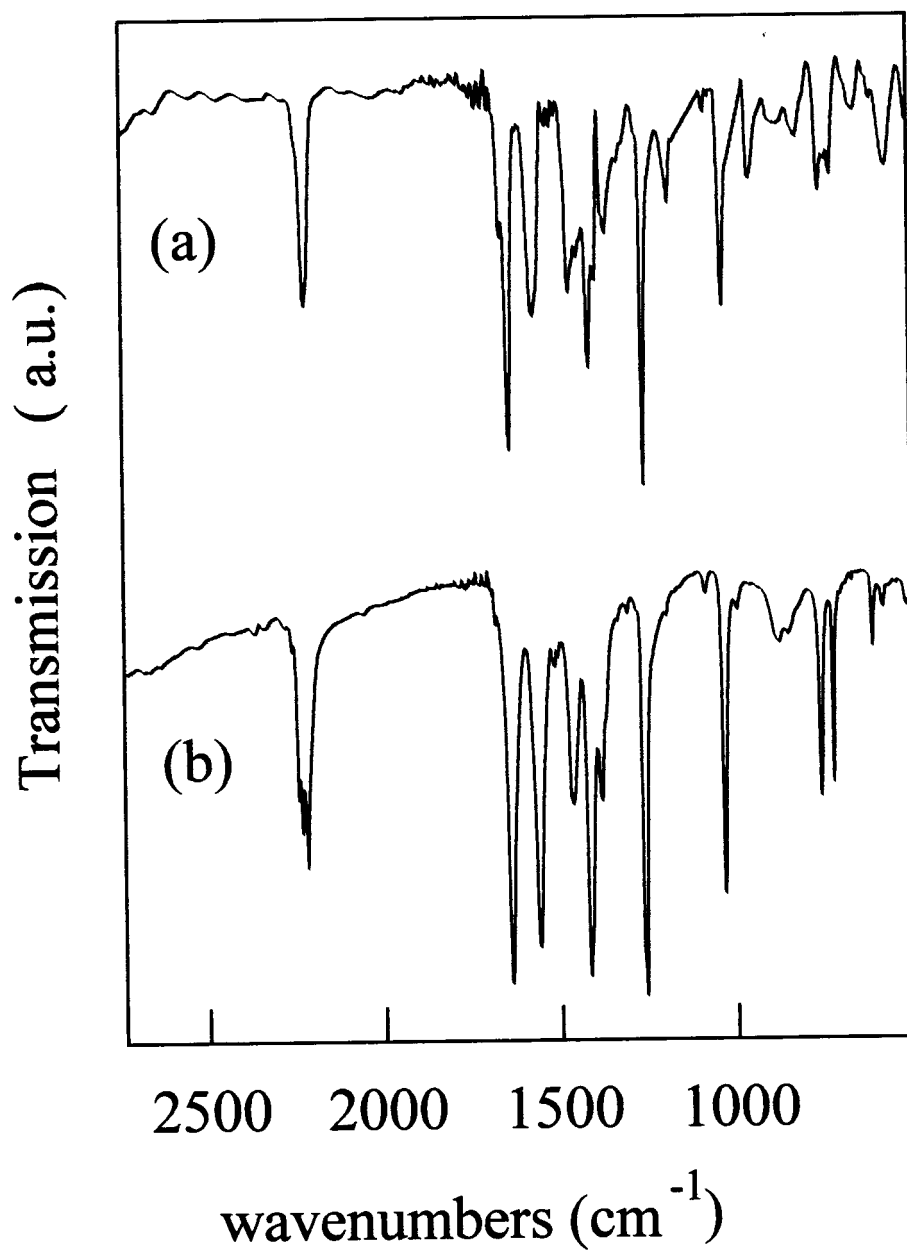


Figure 4. Infrared transmission spectrum of the sample with NiL₂ inclusion, curve (a), obtained, after a suitable treatment (see text), from spectra of Figure 3, compared to the one of a NiL₂ powder dispersed in nujol between two CsI windows, curve (b).

to Figure 2). Thus, we conclude that the spectral changes of NiL_2 on heating have similar origins in the two media. Noticeably, on cooling from 90 °C to room temperature these changes are not reversed in neat PVB. This aspect of the subject is considered further in the following. From recent structural and spectroscopic studies on a similar molecule [7], the monopyrrolizinato-nickel(II) complex NiLDPM (DPM = dipivaloylmethanide), we can now understand the origin of the changes in operation. NiLDPM shows a thermochromism and a vapochromism similar to those exhibited by NiL_2 . Furthermore, in contrast to NiL_2 , NiLDPM is soluble also in non-coordinating solvents (e.g. CH_2Cl_2) and, more importantly, it furnished single crystals, suitable for the X-ray structure analysis, of two distinct species depending on the crystallization solvent: square planar NiLDPM (**1**) and octahedral $\text{NiLDPM} \cdot 2\text{pyridine}$ (**2**). The two species show distinctly different first optical absorption bands ($\lambda_{\text{max}} = 758$ and 671 nm with associated $\epsilon_{\text{max}} = 11,550$ and $44,900 \text{ m}^{-1} \text{ cm}^{-1}$, for **1** and **2** respectively), responsible for the colour. Incidentally, we note that such a difference is due to a small variation of the in-plane Ni—N distance, which is 0.2 Å longer in **2** than in **1**. Thus, NiL_2 , either in solution of a coordinating solvent (e.g. ethylacetate) or in the PVB matrix, is intensely coloured at room temperature, like species **2**, since the chromophore, $\text{Ni(II)N}_4\text{O}_2$, is octahedral in both media. On heating, it fades because the chromophore changes to NiN_4 , the same chromophore as in species **1**, simply because the Ni—O distances elongate. Furthermore, the thermochromism is completely reversible in solution as expected, while it is not in PVB, because this polymer at room temperature, owing to its glassy state, does not relax appreciably after heating.

We also investigated whether these coordination geometry changes of NiL_2 in PVB can be detected by IR spectroscopy. In order to test this possibility, the spectra of samples in the mid infrared region were measured again after the thermal treatment at 100 °C and compared with the ones of the as prepared samples: no significant changes in the spectra were observed. As explained above, instrumental limitation as well as signal intrinsic weakness did not allow the study of the far infrared region, where the bands of the NiL_2 complex involving the Ni atoms vibrations, which are expected to be diagnostic for the changes in action, should appear.

3.3. INTERACTION OF NiL_2 /PVB COMPOSITE, THERMALLY ACTIVATED, WITH ORGANIC SOLVENT VAPORS

The optical spectrum of the thermally activated NiL_2 /PVB system, in contact with organic solvent vapors at room temperature, changes quite rapidly with time, evolving towards the spectrum before the thermal treatment, i.e. the spectrum of the as prepared film. The reversion to the initial spectrum is complete only with methanol as solvent. The associated spectral evolution is reported in Figure 5 (from a to b). In addition, a number of other solvents were tested with the results reported in Table I. The resulting responses deserve some comments. When the response

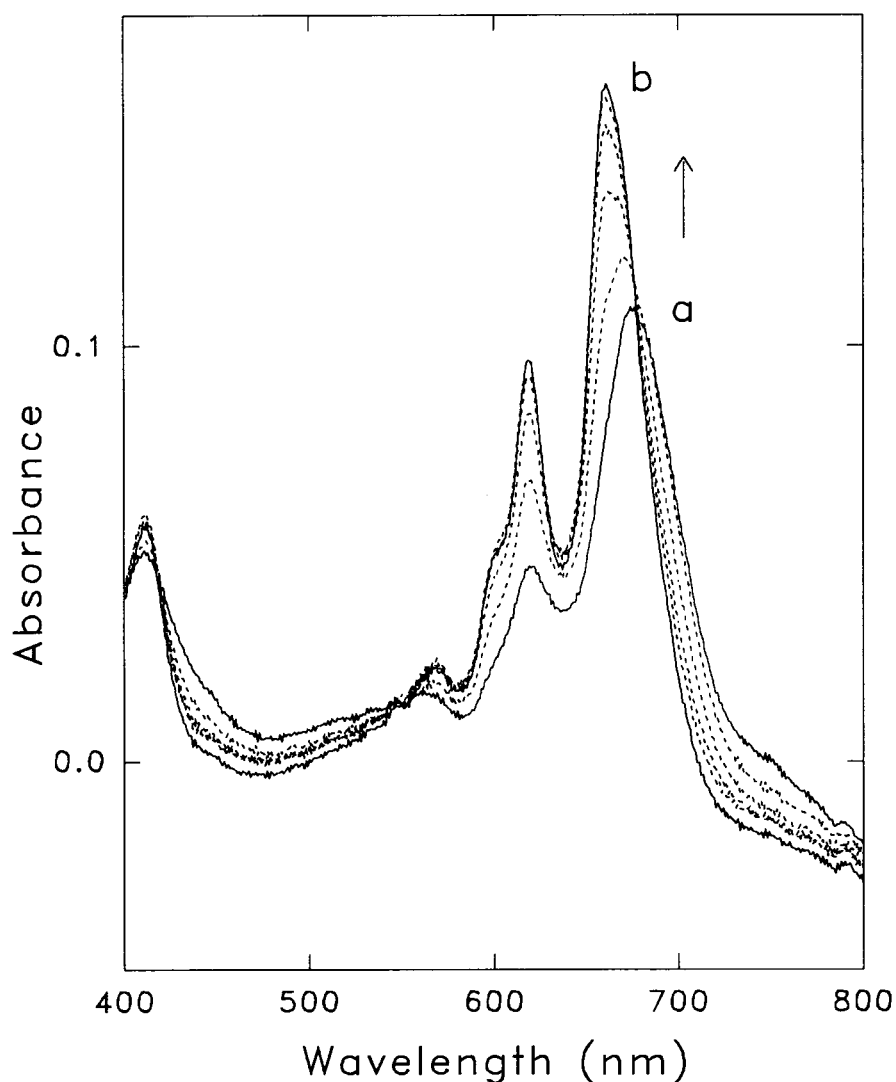


Figure 5. Spectral changes with time (every 2 min) undergone by a spin-coated NiL_2/PVB film heated at 90°C for 7 min, cooled to room temperature and exposed to air saturated with methanol. The arrow indicates the direction of the spectral changes. (a) Spectrum of the film after the thermal treatment and prior to solvent vapor exposure. (b) Spectrum of the as prepared film.

is expressed as signal change per % solvent in air (third column), a remarkable selectivity emerges. The system is more sensitive to alcohols, presumably because in the matrix they coordinate to NiL_2 more easily than the other tested solvents. The low effect of acetonitrile can be explained recalling that this solvent shows a poor coordinating ability towards any ML_2 complex even in homogeneous solution. The relatively large effect of toluene is presumably due to its large affinity for PVB.

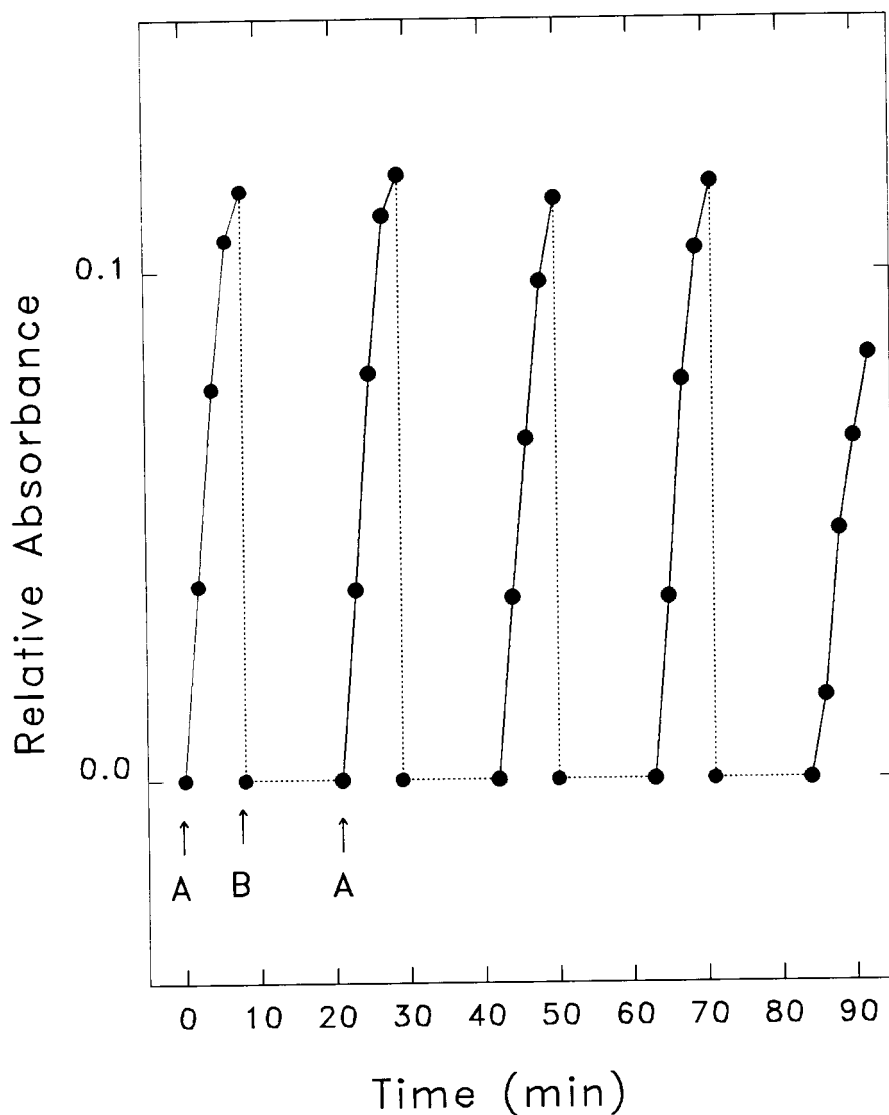


Figure 6. Response time and reproducibility of a spin-coated NiL_2/PVB film on exposure to methanol at the most sensitive wavelength (661 nm). At the time indicated by the arrow marked **A** the thermally activated film is exposed to air saturated with methanol vapor; in **B** the film was heated at 90 °C for 7 min. The **B–A** time interval is arbitrary. The absorbance has been calculated as the difference: $(A^{661} - A^{800})_t - (A^{661} - A^{800})_{t=0}$.

A possible accountable mechanism may be that this solvent makes the thermally activated NiL₂/PVB system relax to some extent allowing the oxygen of PVB, >CH-O-CH<, to coordinate to NiL₂. The fact that toluene is strongly absorbed by PVB is supported also by IR spectroscopy. As a result, the NiL₂/PVB film showed clearly the solvent diagnostic IR peaks only after exposure to toluene (e.g. strong and persistent peaks at 696, 730, 1496 cm⁻¹ etc. [9]). Transient responses resulting from replicate cycling are reported in Figure 6. The NiL₂/PVB film, after exposure to MeOH, can be regenerated by heating and eventually reused. The reversibility is good with no hysteresis during the first four cycles, afterwards some degradation occurs due to irreversible reactions between MeOH and thermally activated NiL₂, as proved by control experiments in homogeneous solution demonstrating that NiL₂, while stable in methanolic solution at room temperature, decomposes quite rapidly in this solvent on heating, even under dinitrogen.

4. Conclusions

The NiL₂ complex can be used as a dopant of conventional organic polymers in order to impart them some selectivity, that otherwise is poor, as active substrates in sensoristic applications [10]. For instance, the NiL₂/PVB composite can be exploited for sensing alcohols in air. We have just remarked that the observed specificity towards alcohols among other oxygen containing solvents depends on the enhanced coordination ability of alcohols towards NiL₂ in PVB. In other cases, the hosting polymer may impart a different selectivity to the system. For example, preliminary experiments on NiL₂ in crosslinked polyvinylformal (PVF) showed that the NiL₂/PVF composite is particularly sensitive to water vapor in air, whereas it is not so to organic solvent vapors, because of the enhanced hydrophilicity of PVF.

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