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Incorporation of 2-(5-Amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide in Crosslinked Polyvinylformal: Formation and Properties of the Copper(II) Complex in the Matrix

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Abstract. The metal(II) coordinating anion 2-(5-amino-3,4-dicyano-2*H*-pyrrol-2-ylidene)-1,1,2-tricyanoethanide ($C_{11}N_7H_2^-$, L′, λ_{max} = 570 nm) has been incorporated by impregnation as the sodium salt in a membrane (0.1 mm thick) of crosslinked polyvinylformal (PVF) at a concentration 1.5×10^{-3} M. The L′-doped PVF membrane, soaked in a concentrated aqueous solution of Cu^{2+} (0.1 M), changes colour from violet to blue on formation of the corresponding pure bis-pyrrolizinato complex CuL_2 (λ_{max} = 660 nm). The CuL_2-doped PVF membrane reacts in the gas phase on exposure to species (X) that are copper-coordinating ligands stronger than L, generating the reverse colour change to violet. The remarkable stability towards water of CuL_2/PVF is a promising indication for prospective use of ML_2 complexes, incorporated in polymeric membranes, for the detection of (X) species in the atmosphere even in the presence of moisture, or directly in aqueous solutions.

Key words: Tetracyanoethylene, pyrrolizinato complexes, optical sensors, polyvinylformal.

Abbreviations: $\overline{MW}$, average molecular weight; wt, weight; min, minutes; max, maximum; M, molar; c, concentration.

1. Introduction

The bis-chelated metal(II) complexes ML_2, which we made for the first time from the title anion (L′) [1], are phthalocyanine-like dyes: λ_{max} = 623 (Fe) [2a], 645 (Co) [2a], 656 (Ni) [2b], 664 (Cu) [2c], 662 nm (Zn) [2d]. In solution, after interaction with a metal-coordinating ligand (X) stronger than L (e.g. X = CN^-, NH_3, pyridine) they undergo a fast ligand exchange, as outlined in the scheme below, with the formation of [MX] and L, generating a colour change from blue to violet, since L, which is not stable as a metal-free anion, isomerizes promptly to L′ (λ_{max} = 546 nm, acetone) [3]. Following these observations, ML_2, with a proper choice of the matrix material, may be considered for the fabrication of

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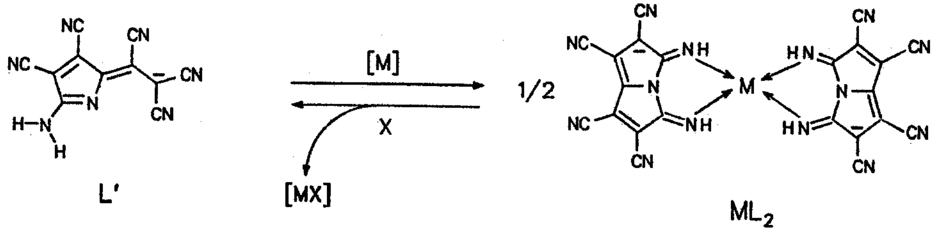

Scheme 1.

optical chemical sensors, on which our current interest is mainly concentrated. Our recent contribution to the subject in this journal concerns CuL_2 incorporated in polystyrene (PS) [4].

Thick films were obtained simply by evaporating a tetrahydrofuran solution of CuL_2/PS. Subsequently, attempts were made to make PS porous by adding a compatible plasticizer in order to allow CuL_2 to fully display its possible sensing properties. Unfortunately the plasticizer used, tris(2-ethylhexyl)phosphate, caused the undesirable ligand dissociation $CuL_2 \rightarrow Cu^{2+} + 2L'$. A different host matrix, such as crosslinked polyvinylformal (PVF) which is inherently macroporous, was then tried. Concomitantly, the change made it necessary to envisage a new strategy for incorporating CuL_2 in such a matrix, since PVF is completely insoluble in the common organic solvents. Instead, PVF has a great affinity for water, and is swollen by it [5]. So successive impregnation and evaporation techniques of PVF in appropriate aqueous solutions were found suitable for our purposes, as reported in this paper.

2. Experimental

2.1. MATERIAL

Poly(vinylalcohol) (PVA, $\overline{MW}$ 9000, d 1.25, from 80% hydrolyzed polyvinylacetate) and formaldehyde (37 wt% solution in water) were used as received from Fluka. Anhydrous $CuCl_2$ was prepared by heating $CuCl_2 \cdot 2H_2O$ at 120 °C. Tetrahydrofuran (THF) was refluxed over sodium-benzophenone ketyl and freshly distilled under N_2 before use. NaL′ (MW 255) [6] and $CuL_2 \cdot 2THF$ [1] were prepared following our procedures.

2.1.1. *Preparation of* NaL′/PVF *Membrane*

The PVF membrane was prepared after formalization of a PVA film (a disk, diameter 5 cm) according to a literature recipe [5], slightly modified in order to obtain an optically clear membrane. The formalization was stopped as soon as the membrane became cloudy (after 25 min at 60 °C for a 0.1 mm thick PVA film). The membrane was thorougly washed with water until it no longer smelled of formalin (5 × 50 mL of water in an ultrasonic bath), then stuck on to a flat glass support and dried in air. Subsequently, the PVF membrane was soaked in an aqueous solution of NaL′ (6.0×10^{-3} M) for 5 min and washed with water. The resulting violet NaL′-doped PVF membrane was dried in air as before. The concentration of NaL′ in PVF was measured spectrophotometrically (570 nm, ϵ_{570} 35 000 M^{-1} cm^{-1}) and found to be 1.5×10^{-3} M.

2.1.2. *Preparation of* CuL_2 *in PVF Membrane*

The NaL′-doped PVF membrane was soaked in an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.1 M) for 30 min. The colour of the membrane changed from violet to blue. It was then purified by repeated soaking in distilled water (3 × 50 mL), and dried in air. A CuL_2-doped PVF membrane was obtained. It was analyzed for the Cu and L contents independently as follows. [Cu] was determined by atomic absorption spectroscopy after destroying the membrane in concentrated HNO_3. [L] was determined as [L′] spectrophotometrically after washing CuL_2 out of the membrane with DMF and then adding $[(C_2H_5)_4N]^+ \cdot CN^-$ in order to cause the complete dissociation: $CuL_2 \rightarrow Cu^{2+} + 2L'$. A molar ratio Cu/L = 0.513 was found. In order to test the validity of the analysis, the same method was applied for determining the Cu/L molar ratio in a powder sample of $CuL_2 \cdot 2THF$. A satisfactory Cu/L value was found (0.496). The final concentration of CuL_2 in PVF was 9.26×10^{-4} M.

2.1.3. *Reaction of* CuL_2*-Doped PVF Membrane with Pyridine or Ammonia*

A CuL_2-doped PVF membrane was left for some time at 20 °C in a closed chamber, pre-saturated with pyridine or ammonia, so as to have a comparable partial pressure (12–15 mmHg) of the base in the gas phase; this was achieved by placing neat pyridine [7] or a 2 wt% aqueous solution of ammonia in the chamber [8].

2.2. INSTRUMENTATION

The optical spectra were recorded on a Cary 5 instrument; the NaL′- or CuL_2-doped PVF membrane was held between two glass microscope slides and inserted vertically across the light beam; an undoped PVF membrane was placed in the reference compartment. EPR spectra were obained with an X-band Varian spectrometer; the magnetic field was measured with a Bruker Model B-NM.20 NMR gaussmeter; spectra at low temperature were recorded in a standard liquid nitrogen Dewar flask inserted in the EPR cavity; the minimum temperature attainable in the sample compartment was slightly above 77 K. Atomic absorption analyses were performed with a Varian model Spectr AA 10 instrument.

3. Results and Discussion

3.1. INCORPORATION OF L′ IN PVF

L′ was incorporated in PVF as the sodium salt (NaL′) by absorption through impregnation on exposing the porous support (a membrane, 0.1 mm thick) to a concentrated aqueous solution of NaL′. The membrane, after washing and evaporation in air, shrank to its original volume, remaining homogeneously embedded with L′, probably immobilized onto the cavities of the support by hydrogen bonding. In this connection we observe that both L′ and PVF carry several hydrogen bonding sites: —NH_2 and —C≡N of L′ and >C(H)—O—CH_2— and >C(H)—OH of PVF. The optical spectrum of the membrane (Figure 1) shows a profile identical to that of an authentic sample of NaL′ in aqueous solution ($c = 1.5 \times 10^{-5}$ M; optical pathlength = 1 cm). This comparison suggests that L′ is in the same form in the two media, that is a non-interacting monomer, given that L′ exists in aqueous solution at a concentration as high as 10^{-2} M (from molecular weight measurements) [3] and it obeys Beer's law down to 10^{-5} M. Also the L′ concentration in PVF can be calculated ($c = 1.5 \times 10^{-3}$ M), making the reasonable assumption that the molar extinction coefficients of its absorption maximum in PVF and in water (at 570 and 549 nm, respectively) have the same value: 35 000 M^{-1} cm^{-1}. Not surprisingly, the absorption maximum of L′ in PVF is red-shifted (21 nm) in comparision to that in aqueous solution, indicating that PVF has a lower polarity than water. Furthermore, we tried to quantitatively extract NaL′ from the membrane with DMF, a solvent usually very efficient in washing such species out of a matrix, in order to measure the absolute concentration of NaL′ in PVF. Repeated washing left the membrane pale violet in colour, revealing that a significant amount of NaL′ is strongly bound to the network matrix and cannot be easily washed out. Despite these limitations, L′, in PVF swollen by water, is totally accessible to outer species diffusing into the matrix from an aqueous solution and, unexpectedly, it shows a reactivity towards M(II) parallel to that of L′ in a homogeneous water-free organic solution, in particular towards Cu(II) as is discussed in detail below.

3.2. FORMATION OF CuL_2 IN PVF

Let us first examine the formation reaction of CuL_2 in homogeneous organic solution. On adding increasing amounts of $CuCl_2$ to a water-free THF solution of L′, the spectral changes occurring are characterized by the appearance of two new bands (α, β) at low energy (Figure 2). Clearly, more than one species is formed, due to: (i) the lack of any isosbestic point; and (ii) the irregular variation of the intensity of the β band with increasing Cu^{2+}/L′ ratio in solution. Previously [2c], the spectrum (A) characterized by the highest maximum absorbance ratio of the two new prominent peaks, A_α/A_β (hereafter identified by the symbol Φ), corresponding to the highest Cu^{2+}/L′ ratio in solution (Cu^{2+}/L′ = 10), was taken as the real spectrum of CuL_2 (Φ = 3.3). This assumption was based on the experimental

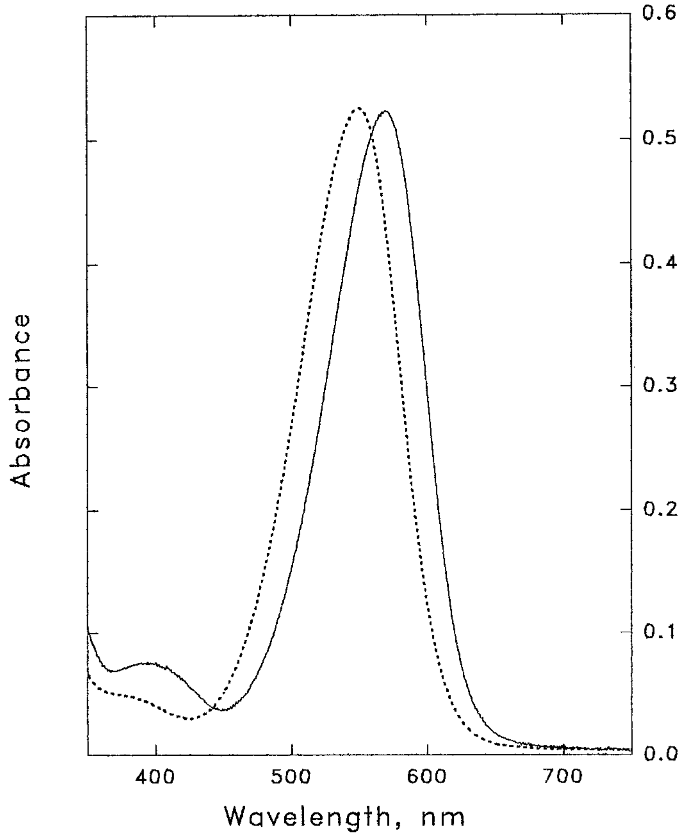

Figure 1. Optical spectra of NaL′-doped PVF 0.1 mm thick membrane (——) and of NaL′ in aqueous solution (- - - -, $c = 1.5 \times 10^{-5}$ M, optical pathlength = 1 cm).

evidence regarding the preparation and the isolation of CuL_2 in the solid state from solution: CuL_2 could be isolated only on adding a large excess of Cu^{2+} to a THF solution of L′. This implies that the significant reactions occurring in solution are:

$$Cu^{2+} + L' \rightarrow [>CuL]^+$$

$$[>CuL]^+ + L' \rightarrow CuL_2$$

and a large excess of Cu^{2+} is needed to shift the equilibria to the right. Furthermore, it is to be noted that even a THF solution of an authentic sample of CuL_2 contains more than one complex species in equilibrium. As a consequence Beer's law is not obeyed, as reported previously [2c]; in this case, the little adventitious water in solution, unavoidably present in hygroscopic ethereal solvents such as THF, enhances the ligand dissociation, shifting the equilibria to the left. A similar trend was observed and similarly interpreted for the reactions in solution between L′ and other metal(II) cations: Fe, Co, Ni, Zn. Subsequently, recent results on the

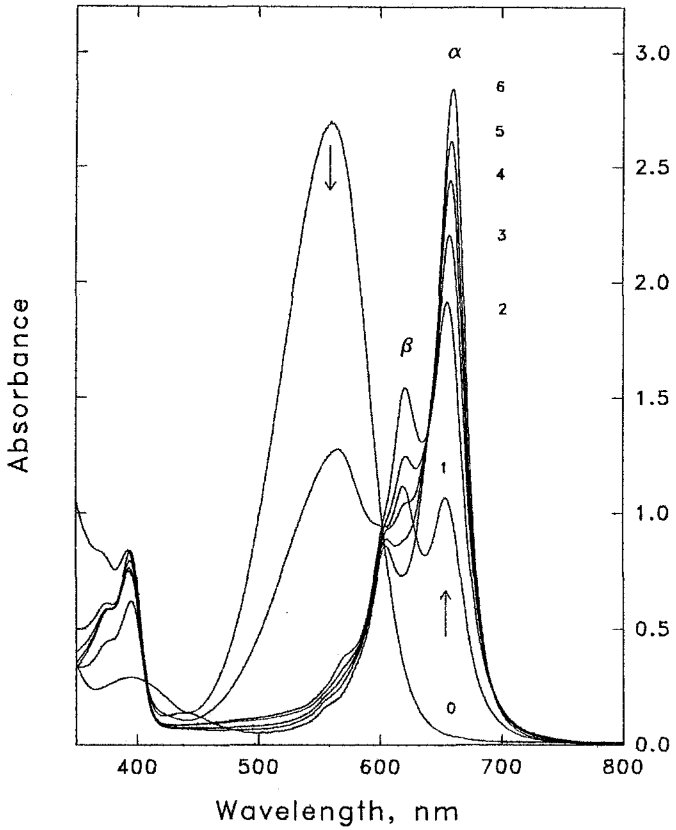

Figure 2. Spectral changes of NaL′ in anhydrous THF ($c = 8.276 \times 10^{-4}$ M, optical pathlength = 0.1 cm) on adding increasing amounts of $CuCl_2$ in THF ($c = 4.138 \times 10^{-3}$ M). The curves, normalized to the volume of the solution, refer to increasing Cu/L′ molar ratios: 0, 0; 1, 0.25; 2, 0.5; 3, 1; 4, 2; 5, 4; 6, 10. Arrows indicate the direction of the spectral changes.

analogous reaction with Pd(II) [9] and the current results, as will be seen, have challenged this interpretation. An L′-doped PVF membrane, after being soaked in a concentrated aqueous solution of Cu^{2+}, exhibited the optical spectrum A, characterized by $\Phi = 3.05$ (Figure 3). This spectrum changed significantly after repeatedly washing the membrane with water (see Experimental Section). The membrane faded a great deal because of the extensive leaching of the dopants out of the matrix, but did not show the presence of any amount of free L′, since the absorbance at the diagnostically most sensitive wavelength (570 nm) did not increase significantly.

Instead, the absorbance ratio of the two major peaks decreased, gradually approaching a constant value ($\Phi = 1.22$), thus indicating the presence in the membrane of only one species, which turned out to be CuL_2, as will be shown shortly. For comparison, we investigated the effect of water on a homogeneous solution of

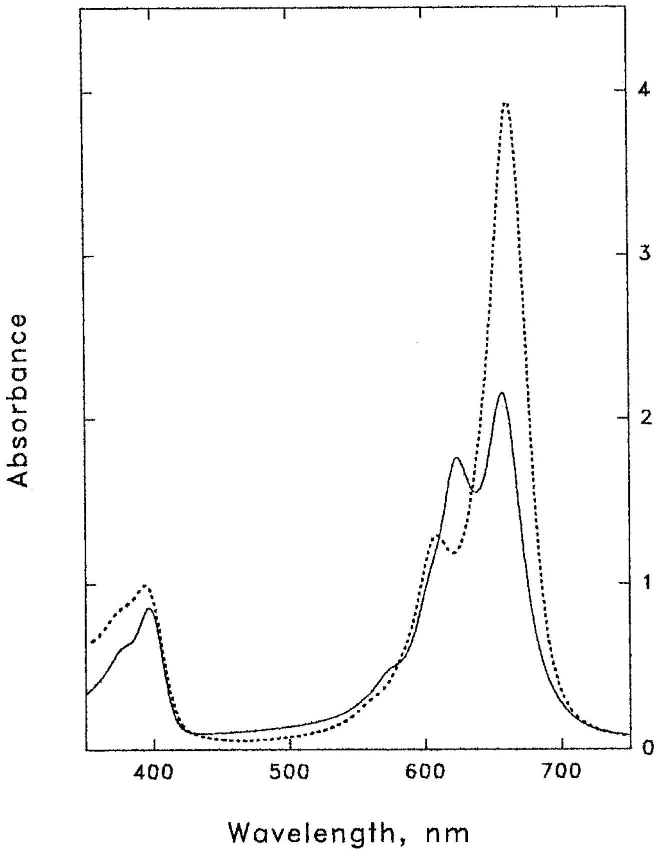

Figure 3. Optical spectra of CuL_2-doped PVF membrane: before washing (- - - - - -) and after exhaustive washing (——).

CuL_2, spectrophotometrically following the associated absorbance changes with time. The amount of added water in this experiment (50%) is comparable to the water content (40–60%) of a PVF membrane swollen by water [5]. The results (Figure 4) clearly indicate the occurrence in solution of an extensive ligand dissociation caused by water ($CuL_2 + nH_2O \rightarrow [Cu(H_2O)_n]^{2+} + 2L'$), monitored by the absorbance increasing at $\lambda = 563$ nm. We conclude, then, as follows. L' and Cu^{2+} react in the same way both in PVF swollen by water and in a water-free organic solvent, furnishing a mixture of metal complexes. Water purifies this mixture in the membrane leaving pure undissociated CuL_2 incorporated into the matrix, while it causes CuL_2 to release free L' in homogeneous organic solution.

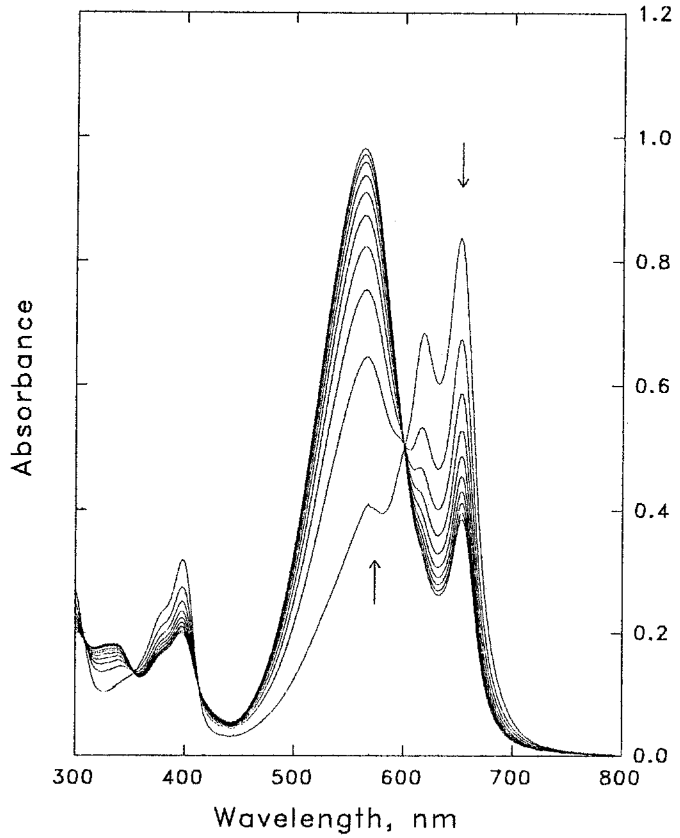

Figure 4. Spectral changes with time (every 3 min), undergone by a solution of CuL_2 (c = 1.81×10^{-5} M; optical pathlength = 1 cm) in THF/water (1/1). Arrows indicate the direction of the spectral changes.

3.3. CHARACTERIZATION OF CuL_2 IN PVF

The copper complex, anchored on PVF, was analyzed after exhaustive washing as the bis-chelated CuL_2 species from independent absolute determinations of Cu^{2+} and L'. The weight percentage CuL_2/PVF was also determined (0.04% wt/wt). Therefore, for the same membrane, knowing the thickness (s, 0.1 mm) and the specific gravity (1.238), the concentration of CuL_2 was calculated (c, 9.26×10^{-4} moles per liter of membrane). Then, from the optical spectrum, normalized to c and s, the variation of the molar extinction coefficient (ϵ) of CuL_2 in PVF against wavelength was found. This, reported in Figure 5, closely resembles the corresponding value associated with spectrum No. 2 of Figure 2. Therefore the species formed in solution from the reaction of Cu^{2+} and L' in the ratio Cu^{2+}/L' = 0.5 and giving rise to spectrum 2 of Figure 2 is just pure CuL_2, i.e. the same species anchored on PVF after exhaustive washing. Further support for the hypothesis that in the washed membrane only one copper complex species is present comes from the ESR data at low temperature (96 K). This technique has been successfully used

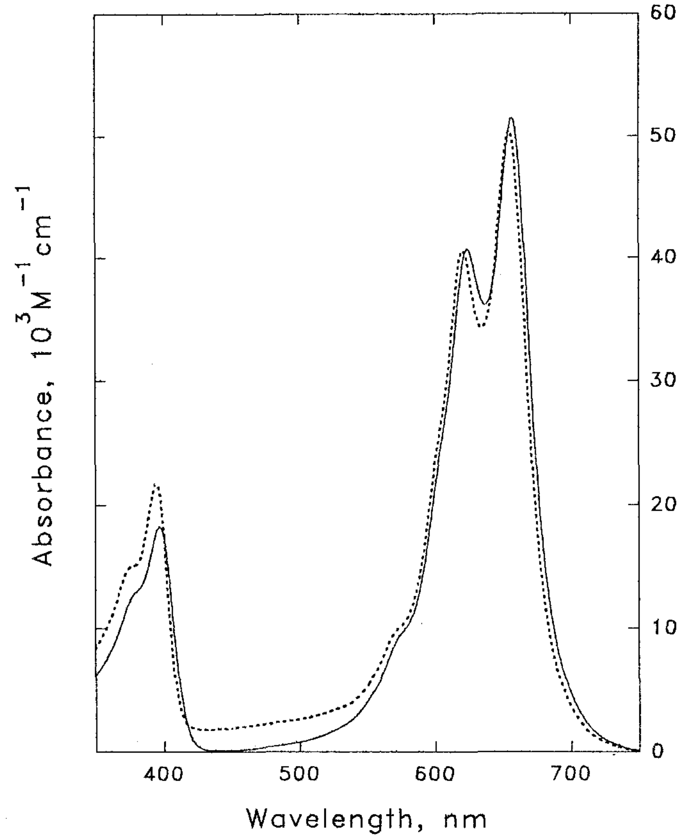

Figure 5. Optical spectra, normalized to the concentration and the pathlength of a CuL_2-doped PVF membrane (——), and a THF solution containing a molar ratio Cu/L′ = 0.5 (– – –).

to probe copper-containing complexes incorporated into polymeric matrices [10]. Thus, a significant change in the ESR spectrum of the membrane before (a) and after (b) washing was expected and observed (Figure 6) as an indication of the purification that occurred.

Spectrum **a** can be analyzed in terms of two copper-containing species (**1**, **2**) differing in $A_{||}$ and $g_{||}$ values. Species **1** has a larger value of $g_{||}$ (2.355) and a smaller value of $A_{||}$ (130 G) with respect to species **2** (2.250 and 160 G, respectively). Incidentally, we notice that the metal coordinating geometry in species **1** should be tetrahedrally or axially distorted with respect to CuL_2, since the associated $g_{||}/A_{||}$ quotient (164 cm) is far beyond the range suggested for copper in a square planar coordination geometry (105–135 cm) [11]. Instead, spectrum **b** is typical of pure CuL_2, showing parameter values ($g_{||}$ 2.21, $g_{\perp}$ 2.066, $A_{||}$ 185 G, $A_{\perp}$ 20 G, $g_{||}/A_{||}$ 116 cm) very similar to those extracted from the powder ESR spectrum at low temperature ($g_{||}$ 2.22, $g_{\perp}$ 2.03, $A_{||}$ 187.5 G, $A_{\perp}$ 23 G, $g_{||}/A_{||}$ 114 cm) of $CuL_2{\cdot}2THF$, structurally characterized [1].

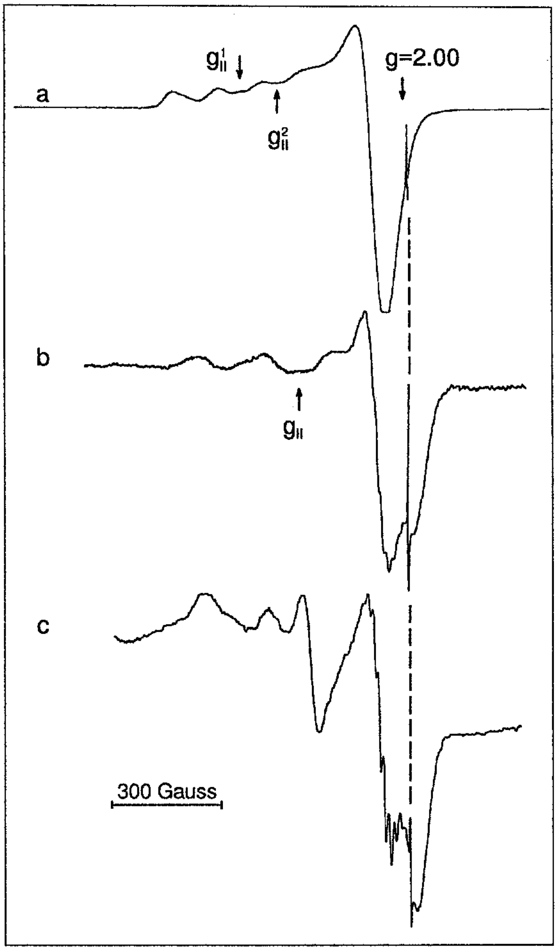

Figure 6. X-band EPR spectra of CuL_2-doped PVF membrane: before washing (a at 96 K) and after exhaustive washing (b at 96 K, c at 286 K).

For completeness, the variation of ESR spectrum **b** with increasing temperature was also examined. Spectrum **b** changes considerably, exhibiting at room temperature (286 K) a shape (**c**) like that of a liquid-type spectrum. This probably indicates that CuL_2 molecules are quite free to move in PVF at room temperature, as expected if they are in a relatively nonviscous medium. Further support for this hypothesis comes from the superhyperfine structure (shfs) present in the high field part of spectrum **c**, consisting of several peaks at a constant field separation ($\Delta H \cong 16$ G). Such shfs is due to the imino nitrogen nuclei of L; the corresponding coupling constant $\langle a \rangle^N$ can be evaluated

$$\langle a \rangle^N = \Delta H \cdot g \cdot \beta = 15 \times 10^{-4}\ \mathrm{cm}^{-1} \quad (\beta = 4.6685 \times 10^{-5}\ \mathrm{G}^{-1}\ \mathrm{cm}^{-1})$$

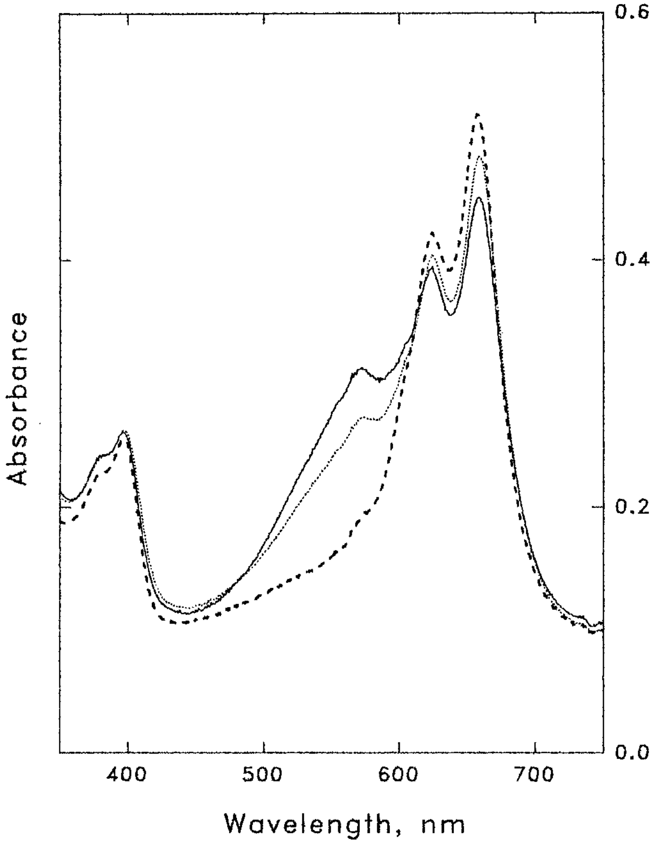

Figure 7. Optical spectra of a CuL_2-doped PVF membrane: after 30 min exposure to an aqueous solution of NH_3 2 wt% (——), after 60 min exposure to neat pyridine (·····), and prior to exposure (– – –).

A similar, but better resolved structure is observed in the solution ESR spectrum at room temperature of $CuL_2{\cdot}2THF$, from which $\langle a\rangle^N = 14.8 \times 10^{-4}$ cm^{-1}. These $\langle a\rangle^N$ values compare well with the analogous coupling constants of most copper(II) nitrogen-containing macrocycles, such as copper(II)-tetraaza-substituted porphyrins: $\langle a\rangle^N = 17.8 - 19.1 \times 10^{-4}$ cm^{-1} in the $g_\perp$ region [12].

3.4. SENSING PROPERTIES OF CuL_2 IN PVF

The CuL_2-doped PVF membrane reacts in the gas phase on exposure to species (X), which are copper-coordinating ligands stronger than L. The spectral changes occurring are characterized by the appearance of free L′ and the concomitant disappearance of CuL_2 (Figure 7). In a preliminary fashion this has been verified for X = NH_3 and pyridine. Under the adopted experimental conditions, the response time for NH_3 is much shorter than for pyridine, as monitored by the absorbance increasing at 570 nm or decreasing at 660 nm. A somewhat unexpected result is that in both instances the starting spectrum can be regenerated quantitatively simply by washing the membrane with water. Clearly, water dissociates the [CuX] complex and washes X away from the matrix. Then, CuL_2 is reformed from free Cu^{2+} and L' lying in close proximity. This behaviour is consistent with a particular relative stability order of the complexes involved in the matrix, notably different from that in homogeneous solution: water decomposes both ammonia-copper and pyridine-copper complexes in the matrix, but not CuL_2, while the reverse is observed in homogeneous solution.

4. Conclusions

We have shown that CuL_2 incorporated in PVF is remarkably stable towards water, so that a CuL_2-doped PVF membrane can be used for the detection of X species (Scheme 1) in the atmosphere even in the presence of moisture, or directly in water if the leaching of the dopant out of the matrix were reduced well below the current high level. It is likely that the stability towards water is not specific for CuL_2 in PVF. Recently, the same property has been found for HgL_2 in polymethylmethacrylate/SiO_2 [13]. These findings suggest many prospective uses of ML_2 as indicator phases in optical sensing devices.

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