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## Electron paramagnetic resonance study of the physical gelation of a copper complex in cyclohexane

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**Résumé.** — La dynamique moléculaire et la cinétique de gélation d'un complexe de cuivre substitué par huit chaînes paraffiniques dans le cyclohexane sont étudiées par spectroscopie de Résonance Paramagnétique Electronique en bande X et Q. Dans la phase fluide le complexe présente une structure hyperfine dont l'anisotropie permet d'estimer le temps de corrélation de la réorientation moléculaire à environ  $4 \times 10^{-10}$  s. Dans la phase gel, la structure hyperfine est moyennée par l'échange électronique. La variation de l'anisotropie du tenseur  $\mathbf{g}$  en fonction de la fréquence est expliquée par une réduction du temps de corrélation du mouvement ( $\tau \approx 8 \times 10^{-9}$  s). La variation en fonction du temps du signal de RPE permet d'étudier les cinétiques de ségrégation et de gélation.

**Abstract.** — The dynamical behaviour and gelation kinetics of a copper complex substituted by eight paraffinic chains in cyclohexane has been investigated by X-band and Q-band Electron Paramagnetic Resonance spectroscopy. In the fluid-phase the complex exhibits a hyperfine structure, the anisotropy of which allows an estimate of the tumbling correlation time of the order of  $4 \times 10^{-10}$  s. In the gel-phase, the electron exchange between stacked complexes averages out the hyperfine structure, and the frequency dependence of the  $\mathbf{g}$  tensor anisotropy is analysed in terms of a reduction of the tumbling rate to  $\tau \approx 8 \times 10^{-9}$  s. The time dependence of the EPR signal provides a simple method to study the kinetics of segregation and gelation.

### 1. Introduction.

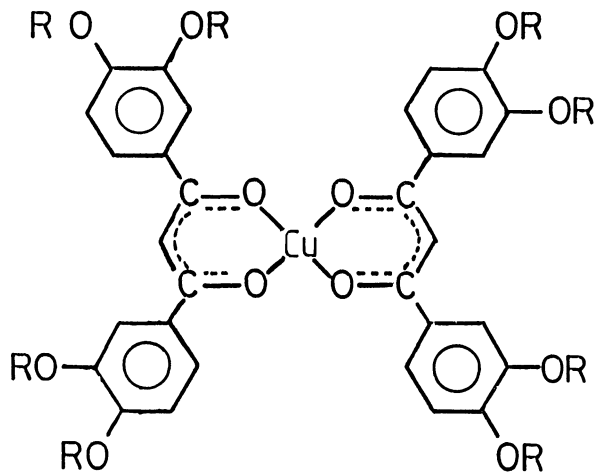
Gelation is related to the growth in the bulk solution of a colloidal infinite network [1]. Mechanical cohesion of the gel-phase is of variable strength, depending on the class of gel system considered.

Physical gelation [2] is a thermoreversible phase transition involving weak interactions which can be balanced by thermal agitation usually near room temperature. Ionic interactions, hydrogen bonding and (or) Van der Waals forces are very often involved in the reversible gelation process while strong covalent bonds are responsible for the irreversibility of chemical gelation. As an example, thermoreversible physical gels can be contrasted in this way to polyacrylamide chemical gels [3]. Beside macromolecular compounds, physical gelation may also be obtained from low-molecular weight molecules [4]. For these systems, a fundamental

difference in mechanism is that the first step is obviously an aggregation step in order to build the large objects which will constitute the three-dimensional network for the gel-phase. For each solute molecule a specific mechanism is involved for this aggregation taking both the steric volume and the functionality of the molecule into account. For instance, when amphiphilic molecules are used, as alkyl alcohols, surfactant ions..., the rule during the molecular association process is the minimization of contact surfaces of opposed polarity between solute molecules and solvent.

In this paper, we are concerned with a new paramagnetic copper complex (CC) substituted by eight paraffinic chains synthesized by Giroud-Godquin [5]. This molecule displays a particular tendency to aggregation as can be noticed by the existence, in the pure liquid-phase, of a discotic mesophase [6, 7] constituted by a hexagonal array of columnar as-

sociated disk-like CC molecules. This trend is also demonstrated in solutions by the gelation of some apolar solvents when a given range of temperature and concentration of CC molecules is satisfied. A sol-gel transition is exhibited by these solutions near room temperature and its study constitutes the object of this work.



R = C<sub>9</sub>H<sub>19</sub>

Cupric ion is well-known to form complexes with a large variety of organic ligands [8, 9]. The originality of the present system is twofold. First, the gelifying complex is paramagnetic and needs no spin labelling procedure for electron paramagnetic resonance (EPR) study of the aggregation reaction. Second, the discotic mesophase of the pure solute is a good incitation to explore thoroughly the phase diagram and specially the structural analogies between the thermotropic phase and the xerogel.

EPR is a well-adapted method to study the local molecular modifications in aggregation reactions. Thus, micelles which are finite aggregates of molecules are a valuable field of application of the technique (see for instance Ref. [10]). The infinite three dimensional aggregate of a gel-phase is obtained *via* a critical transition [11, 12] and has also been studied by EPR. As examples, we can mention works on sickle hemoglobine [13], silica [14], polyvinyl alcohol [15], agarose [16], vanadium pentoxide [17], and steroid gels [18]. The purpose of these studies is usually the determination of: (i) the rate of tumbling within the gel-phase, (ii) the motional dependence on the gel network pore size (iii) some structural parameters [19], and (iv) the phase diagram of the gelifying system [18].

We present here an EPR study of the thermoreversible gelation of cyclohexane by the CC complex. First we will be interested in the interpretation of typical spectra of the related fluid- and gel-phases. Then we will describe the various spectral modifications with concentration, and temperature

in kinetics experiments. The first physical interpretations within the aggregation and gelation framework will be given.

## 2. Methods.

**2.1 MATERIAL.** — The CC complex has been synthesized following [5]. Gels are prepared by dissolving CC in hot reagent grade cyclohexane. On cooling, gelation gives green gel samples. The range of concentration studied is 0.3-11.2 % wt. For concentrations above ca. 1 % wt gels are quite homogeneous while, for lower concentrations, demixtion occurs giving an inhomogeneous flocculated suspension covered by a clear solution.

**2.2 EXPERIMENTAL.** — Q-band E.109 and X-band E.104 Varian spectrometers are used. For the *g*-factor determinations, magnetic fields and frequencies are measured with a gaussmeter (DRUSCH RMN2) and a frequencymeter (EIP 545A) respectively. At 9 GHz a Varian variable temperature system with a nitrogen gas flow temperature regulator is used. Temperatures are measured with a copper-constantan thermocouple.

## 3. Results.

Aggregation of CC complex in cyclohexane from solution to the gel-phase is first inferred from a spectroscopic analysis of typical EPR spectra of the CC isolated species. For this purpose, the choice of non-gelling solvents is governed by experimental constraints: boiling and melting points and ability to give a homogeneous glassy state. For these reasons, we have chosen carbon tetrachloride (CCl<sub>4</sub>) and chlorobenzene. This analysis is done assuming a square coplanar structure (D<sub>4h</sub> symmetry) for the CC complex [5].

### 3.1 ISOLATED CC COMPLEX IN NON-GELLING CONDITIONS.

**3.1.1 Static description: frozen solution.** — The non-averaged spectroscopic parameters are obtained from frozen solution spectra. However, CC complex in CCl<sub>4</sub> (and other solvents) has a tendency to aggregation and we have not succeeded in preparing frozen solutions with totally non-interacting complexes. The presence of inter-complex interactions adds features which complicate the spectrum. For this reason EPR spectra of frozen solutions are not presented.

EPR spectra of isolated square planar complexes are described by a spin Hamiltonian with two dominant terms.

$$H = \beta HgS + SAI \quad (1)$$

with  $S = 1/2$  the electronic spin corresponding to the d<sup>9</sup> Cu<sup>2+</sup> ion and  $I = 3/2$  the copper nuclear spin.

Both  $\mathbf{g}$  and  $\mathbf{A}$  tensors have axial symmetry with a common axis ( $z$ ) which is the normal to the molecular plane [8]. The resonance condition is given :

$$H_r = \frac{1}{g\beta} (h\nu_0 - m_1 A) \quad (2)$$

with :

$$g = [(g_z^2 - g_{x,y}^2) \cos^2 \theta + g_{x,y}^2]^{1/2} \quad (3)$$

and :

$$A = \frac{1}{g} [(A_z^2 g_z^2 - A_{x,y}^2 g_{x,y}^2) \cos^2 \theta + g_{x,y}^2 A_{x,y}^2]^{1/2}, \quad (4)$$

where  $m_1$  is the nuclear quantum number,  $\nu_0$  the spectrometer frequency and  $\theta$  the angle between the magnetic field and the symmetry axis of the  $\mathbf{A}$  and  $\mathbf{g}$  tensors.

From the frozen solution EPR spectra two parameters are extracted :  $A_z$  and  $g_z$ . We calculate the other two parameters characterizing the complex,  $A_x = A_y$  and  $g_x = g_y$ , from the measurement of  $g_0$  and  $A_0$  at high temperatures in fluid solution. These parameters are given in table I.

The above simplified expressions do not take into account the second order shift of resonance lines due to the off diagonal elements of the spin Hamiltonian matrix. We have verified by computer simulations of the spectra in the rigid limit and in fast motional conditions that these shifts, which were between 0.01 and 1 mT according to the value of  $m_1$ , are not perceptible on the experimental spectra because of the line broadening. The same is true for the effects due to the existence of two copper isotopes,  $^{63}\text{Cu}$  (69 %) and  $^{65}\text{Cu}$  (31 %), of relative magnetogyric ratio  $\frac{\gamma_{63}}{\gamma_{65}} = 0.933$ . The difference between

the spectra simulated in the aforementioned conditions for  $^{63}\text{Cu}$  only and for the natural isotope composition is negligibly small under our experimental conditions.

### 3.1.2 Dynamic description.

**3.1.2.1 Low temperature : slow tumbling regime.** — The EPR spectrum of the CC complex at  $-85^\circ\text{C}$  in  $\text{CCl}_4$  at X-band is shown in figure 1a. In the low-field region, three of the four lines of a quartet are clearly seen and resemble closely the low-field region of typical frozen solution spectra of copper complexes with oxygenated organic ligands in a  $D_{4h}$  symmetry [8, 9]. However, we notice that even at  $-85^\circ\text{C}$  the  $g$ -value and the hyperfine coupling along the principal axis are slightly reduced with respect to the values observed in frozen solution.

In this case, equations (2)-(4) are still valid and hereafter, for the sake of clarity, we shall denote the reduced values of the principal components of the  $\mathbf{A}$  and  $\mathbf{g}$  tensors by the subscripts  $\parallel$  and  $\perp$ . We have tried to simulate the spectrum of figure 1a by means of equations (2)-(4). Although the positions of the lines are closely reproduced, we failed to simulate exactly their shape in the  $g_{\perp}$  region (Fig. 1a). Additional peaks also contribute to the  $g_{\perp}$  region of the spectrum. These peaks have been extensively described in the literature [21, 22] and originate from special sets of  $\mathbf{g}$  and  $\mathbf{A}$  principal values. The reduction of these values with temperature results from the motion of the CC molecules.

As the temperature is raised, the motion influences the spectra more and more. Up to  $40^\circ\text{C}$  the  $g_{\parallel}$  region may be distinguished from the  $g_{\perp}$  region (Fig. 1b). This temperature range correspond to the

Table I. — Principal  $g$ - and hyperfine coupling values of the CC complex

Solvent	$g_z(g_{\parallel})$	$g_{x,y}(g_{\perp})$	$A_z(A_{\parallel})$ (a) mT	$A_{x,y}(A_{\perp})$ (a) mT	$g_0$	$A_0$ mT
$\text{CCl}_4$ frozen solution	$2.252 \pm 0.002$	$2.063$ (b)	$18.1 \pm 0.1$	$1.9$ (b)	—	—
Chlorobenzene -T > 385 K)	—	—	—	—	2.126	7.3
$\text{CCl}_4$ (T $\approx$ 300 K)	$2.233 \pm 0.002$	$2.066 \pm 0.002$	14.5	—	—	—
$\text{C}_6\text{H}_{12}$ fluid-phase	{ X-band $2.235 \pm 0.003$ { Q-band $2.241 \pm 0.003$	$2.066 \pm 0.002$ $2.068 \pm 0.002$	13	—	—	—
$\text{C}_6\text{H}_{12}$ gel-phase	{ X-band $2.247 \pm 0.002$ { Q-band $2.260 \pm 0.002$	$2.070 \pm 0.002$ $2.054 \pm 0.002$	—	—	—	—

(a) Absolute value

(b) Calculated value (see text).

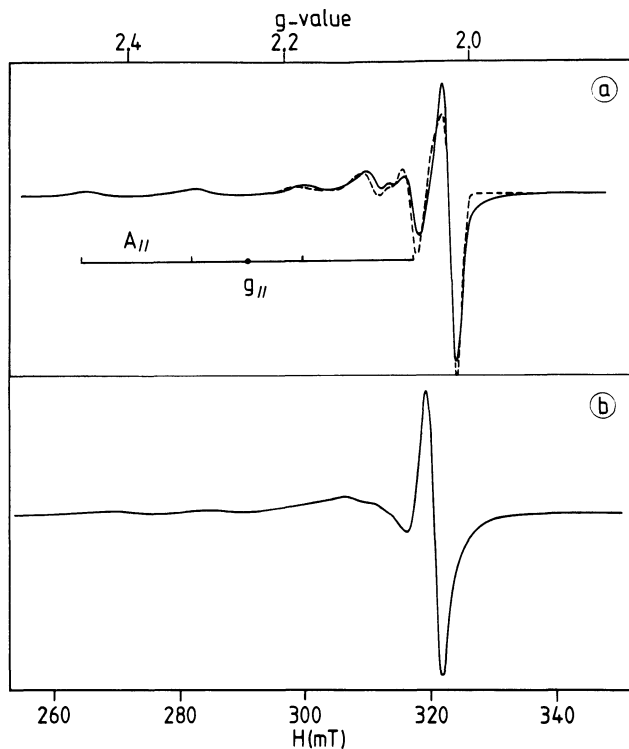


Fig. 1. — X-band EPR spectra of the CC complex in  $\text{CCl}_4$ . Modulation frequency : 100 kHz ; modulation amplitude : 0.5 mT ; microwave power : 15 mW. a)  $T \sim 200$  K. Full line : experimental spectrum ; dashed line : simulated spectrum using a Gaussian lineshape the width of which was taken anisotropic and with a term depending on  $m_1$  ; b) room temperature.

slow tumbling regime, since the  $\mathbf{g}$  and  $\mathbf{A}$  tensors are only partly averaged. At Q-band (Fig. 2) the two regions are well separated and the line width is increased (see Table I). This increase could be attributed to a motional effect as described by McConnell [23]. But a contribution of the «  $g$ -strain

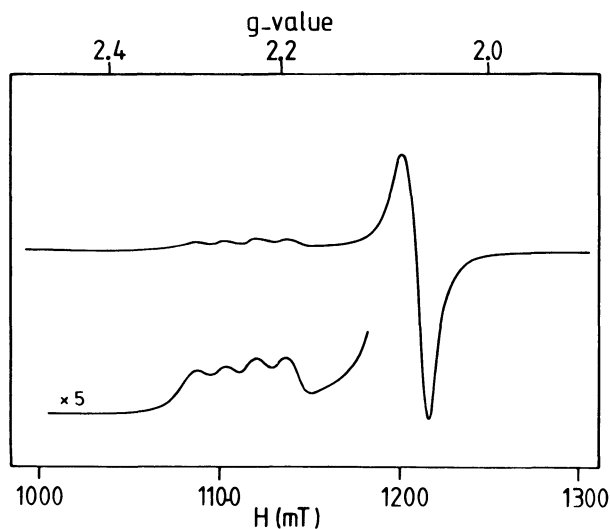


Fig. 2. — Q-band spectrum of the CC complex in  $\text{CCl}_4$  at room temperature. Same conditions as in figure 1.

effect » due to a distribution of  $g$ -values as already described in the case of Cu-complexes in frozen solutions cannot be excluded [24]. In the slow motional regime, empirical formulae have been proposed in the case of nitroxide [25] and vanadyl ion [26] which connect the correlation time ( $\tau$ ) of the motion and the variation of  $A_{||}$  with temperature :

$$\tau = \alpha (1 - S)^\beta, \quad (5)$$

where  $\alpha$ ,  $\beta$  are constants depending on the reorientational mode and  $S = \frac{A_{||}}{A_z}$ .

Due to the disk-like geometry of the complex, it may be assumed that the diffusion tensor is axially symmetric about the  $z$  axis (the principal axis of  $\mathbf{g}$  and  $\mathbf{A}$  tensors) with  $D_{||} > D_{\perp}$ . The  $\mathbf{g}$  and  $\mathbf{A}$  tensors being nearly axial, the line positions and widths are dependent on the diffusion coefficient  $D_{\perp}$  only, the relevant correlation time being :

$$\tau = (6 D_{\perp})^{-1}. \quad (6)$$

**3.1.2.2 High temperature : fast tumbling regime.** — The determination of motional parameters requires experiments in a wide temperature range covering the slow and fast tumbling regimes.

In  $\text{CCl}_4$ , the temperature range corresponding to the fast tumbling regime cannot be reached, due to the low boiling temperature ( $E = 76.7^\circ\text{C}$ ). For this reason, we have studied this temperature range using chlorobenzene ( $E = 131.7^\circ\text{C}$ ) as solvent. The EPR spectra in this regime are characterized by a quartet of lines whose width (Fig. 3) depends drastically on  $m_1$ . In this regime, the motional correlation time is readily obtained from the linewidth ( $\Delta H$ ) dependence using an expression of the form [27] :

$$\Delta H(m_1) \sim \frac{1}{T_2} \sim a + bm_1 + cm_1^2 + \Delta H' \quad (7)$$

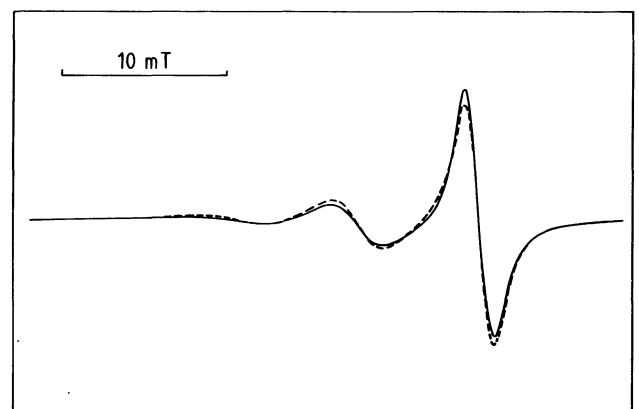


Fig. 3. — X-band EPR spectra of the CC complex in chlorobenzene at  $134^\circ\text{C}$ . Full line : experimental spectrum (the two lines at lowfield are unresolved due to their broad width) ; dashed line : spectrum simulated with  $\tau = 1.35 \times 10^{-10}$  s and a residual linewidth  $\Delta H' = 1$  mT.

$a$ ,  $b$ ,  $c$  are coefficients which depend upon  $\mathbf{g}$  and  $\mathbf{A}$  tensor anisotropies and are nearly proportional to  $\tau$  only or depend on  $\tau$  and  $D_{\parallel}$  if the magnetic and diffusion tensors are not aligned.  $\Delta H'$  is an additional width independent of  $m_1$  which contains the contributions of the electron spin-spin and spin-rotation interactions [28] as well as the modulation broadening. The spectra have been simulated by a least square adjustment of the linewidth, assuming a Lorentzian lineshape and taking  $\tau$  and  $\Delta H'$  as adjustable parameters. The parameter of interest  $\tau$  is proportional to the solution viscosity  $\eta = \eta_0 \exp\left(\frac{E}{kT}\right)$  and of the form :

$$\tau \propto \frac{\eta}{kT}. \quad (8)$$

An activation energy of  $2.5 \text{ kcal.mole}^{-1}$  is deduced from the plot of  $\ln(\tau T)$  vs.  $1/T$ .

The anisotropies of the hyperfine and Zeeman interactions are averaged out by motions of correlation time  $\tau$  much smaller than  $\Delta A = (A_{\parallel} - A_{\perp})/h$  and  $\Delta G = (g_{\parallel} - g_{\perp})\beta H_0/h$ . In the present case, the fast motional conditions are fulfilled for  $\tau \ll 10^{-9} \text{ s}$  since  $\Delta G = 9 \times 10^8$  and  $3.5 \times 10^9 \text{ s}^{-1}$  at X- and Q-band respectively and  $\Delta A = 5 \times 10^8 \text{ s}^{-1}$ . The achievement of these conditions may be appreciated from the spacing of the resolved lines which tend towards the isotropic limit  $A_0 = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$ . The evolution of the spectra of CC in chlorobenzene and copper acetylacetonate in  $\text{CHCl}_3$ -toluene solutions with temperature shows that the boundary between the fast and slow motional regimes corresponds approximately to  $\tau \approx 4 \times 10^{-10} \text{ s}$  where the residual  $\mathbf{A}$  and  $\mathbf{g}$  anisotropies are still perceptible. The use of equation (7) for determining  $\tau$  is however precluded in the  $2 \times 10^{-10} \leq \tau \leq 4 \times 10^{-10} \text{ s}$  range because of the excessive broadening of the two low field lines  $\left(m_1 = \frac{1}{2}, \frac{3}{2}\right)$ .

The values obtained for  $\tau$  in the slow tumbling regime enable the determination of the  $\alpha$  and  $\beta$  parameters of expression (5), using a procedure describes by Chachaty [29]. The  $\tau$  values obtained in  $\text{CCl}_4$  have been rescaled to the chlorobenzene values to take into account the viscosity differences of the two solvents.  $\alpha$  and  $\beta$  parameters for the plot  $\ln(\tau T)$  vs.  $1/T$  (Fig. 4) are  $4.8 \times 10^{-11} \text{ s}$  and  $-1.6$  respectively. These values are comparable to those obtained for instance for vanadyl acetyl-acetonate under similar conditions [29].

### 3.2 GELATION OF THE CC COMPLEX/CYCLOHEXANE SYSTEM.

**3.2.1 Fluid-phase.** — The EPR spectra of the CC complex in the fluid-phase in cyclohexane are presented in figure 5a and 5b at X- and Q-band

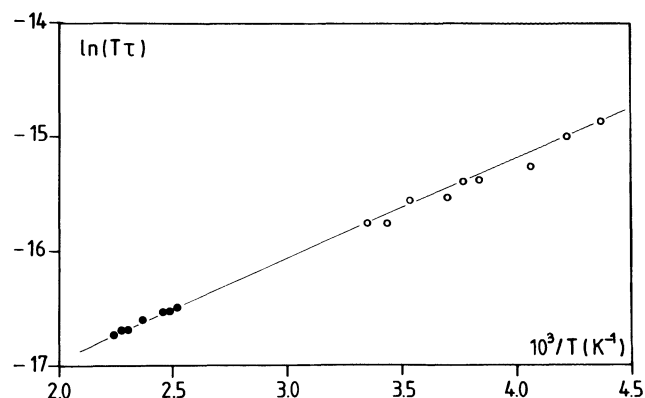


Fig. 4. — Plot of  $\ln(T\tau)$  versus  $10^3/T$ . Black dots : fast tumbling regime ; white dots : slow tumbling regime.

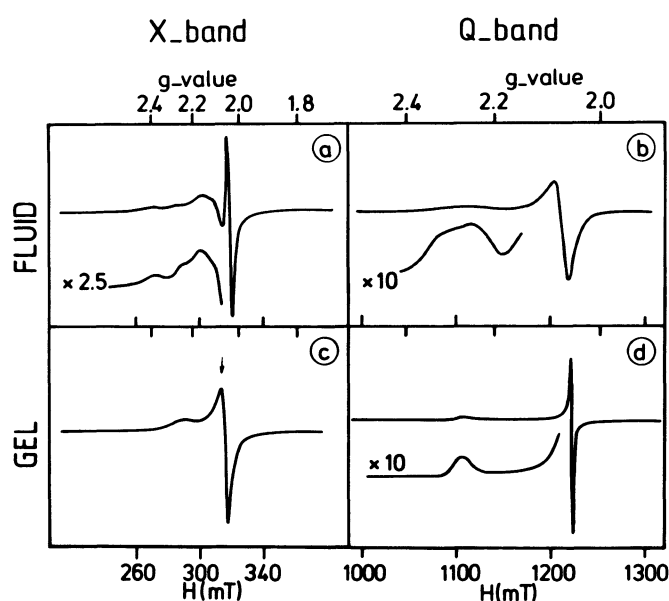


Fig. 5. — Comparative EPR spectra of the CC complex in cyclohexane ; same conditions as figure 1. a) Fluid-phase, X-band, b) Fluid-phase, Q-band, c) Gel-phase, X-band, d) Gel-phase, Q-band.

respectively at about  $40^\circ \text{C}$ . The spectrum of figure 5a closely resembles the spectrum of figure 1b. The same is true for the corresponding spectra at Q-band. The spectroscopic parameters characterizing the CC complex in cyclohexane are essentially the same as in  $\text{CCl}_4$  (Table I). We note also an increase in the line-width when going from X- to Q-band (Table II). The linewidth is larger in cyclohexane (Fig. 5b) than in  $\text{CCl}_4$  (Fig. 2 and Table II) resulting in a reduction of the resolution (Fig. 5b). The concentration of CC complex in cyclohexane is higher and the existence of non-averaged dipolar interactions between neighbouring complexes could explain such a broadening.

The similarities between spectra of the fluid-phase in cyclohexane and  $\text{CCl}_4$  solutions suggest a quite

Table II. — EPR line-width of the CC complex.

Solvent	X-band		Q-band	
	$g_{\parallel}^{(a)}$	$g_{\perp}^{(b)}$	$g_{\parallel}^{(a)}$	$g_{\perp}^{(b)}$
CCl <sub>4</sub>	4	—	8.5 ± 1.5	14
C <sub>6</sub> H <sub>12</sub>	fluid	6.5	—	14
	gel	10.5	4.2	2.8

(<sup>a</sup>) Half-width at half-height (in mT).

(<sup>b</sup>) Peak to peak (in mT).

similar dynamical behaviour. We have tried to follow the temperature dependence of  $\tau$  as described for CCl<sub>4</sub> using expression (5). At the lowest temperature where the fluid-phase is observed ( $T \approx 308$  K), the anisotropy parameter  $A_{\parallel}/A_z$  reduces to  $S \sim 0.7$  and relation (5) yields  $\tau \approx 4 \times 10^{-10}$  s. This estimate is confirmed by the comparative study of the copper acetylacetonate in 1 : 1 toluene/chloroform solution which has nearly the same principal values of  $\mathbf{g}$  and  $\mathbf{A}$  tensors. In this system, the fast motional regime, where the lines are separated by  $A_0$  and where (7) is valid, holds down to ca.  $-55$  °C. The transition to the slow motional regime, where the parallel edges become apparent at low field, occurs with  $15^\circ$  below this temperature. A simple extrapolation of the  $\tau$  determined in the fast motional regime suggests that the correlation time corresponding to figure 5a is ca.  $5 \times 10^{-10}$  s, in reasonable agreement with the value obtained using (5) with, the rigid limit value  $A_z = 18.5$  mT [28].

**3.2.2 Gel-phase.** — Spectra of the CC complex in the gel-phase are presented in figure 5c and 5d. The parameters associated with these spectra are given in table I. We may notice that the  $\mathbf{g}$  tensor components of the complex in CCl<sub>4</sub> frozen solution lie between the two sets of values for the gel-phase measured at X- and Q-band. This is an indication that only minor structural changes are experienced by the complex in the gel-phase as compared to the frozen solution.

An important change in the spectra of figures 5c and 5d is the reduction of the hyperfine coupling. This fact is clearly seen in the  $g_{\parallel}$  region where the quartet coalesces into a single line. In the  $g_{\perp}$  region this is also noticeable, since the line-width is considerably reduced in the gel-phase Q-band spectrum (see Table II). This reduction is a consequence of an exchange interaction between neighbouring complexes. The width of the single line is 10.5 mT (Table II) corresponding to a maximal hyperfine coupling of 3.5 mT, which is to be compared to 15 mT of the fluid phase : the reduction is at least a factor of 5. This is compatible with the existence of large chains of CC molecules in the gel-phase.

The set of  $g$ -values at X-band being less aniso-

tropic than at Q-band, this may result from a partial motional averaging as observed for the complex in CCl<sub>4</sub> on going from the frozen solution to the room temperature solution. We have attempted to attribute this reduction of the  $\mathbf{g}$  tensor anisotropy (denoted as  $\Delta g/\Delta g_0$  with  $\Delta g_0 = g_z - g_x$ ) to a Brownian motion of the complex, using Kneubühl's theory [30]. According to this theory, the motionally averaged principal values of the  $\mathbf{g}$  tensor are given by :

$$g_k^2 = s + \frac{2}{\pi} (g_k^2 - s) \tan^{-1} \frac{\tau}{T_2'} \quad (9)$$

with

$$s = \frac{1}{3} (g_z^2 + g_y^2 + g_x^2). \quad (10)$$

$T_2'$  being an effective spin-spin relaxation time related to the Lorentzian half-width at half-height  $\Delta H_{1/2}$  ( $T_2' = (\gamma \Delta H_{1/2})^{-1}$ ). It may be pointed out that the invariance of  $g_0 = \frac{1}{3} (g_z + 2g_x)$  with the motion requires a single value of  $T_2'$ , inconsistent with the orientation dependence of the linewidth (see Table II). Moreover, equation (9) does not explicitly account for the reduction of  $\Delta g$  from Q-band to X-band. Assuming nevertheless that the Q-band value of the tensor anisotropy corresponds to  $\Delta g_0$ ,  $\tau$  may be estimated to be ca.  $3 \times 10^{-9}$  s taking  $\Delta g/\Delta g_0 = 0.86$  and a mean linewidth  $\Delta H_{1/2} \approx 7.5$  mT.

Electron microscopy shows that the aggregation of CC complexes gives rise to bundles of thread-like macromolecules. They are not therefore expected to undergo Brownian reorientational motions in a time scale short enough to reduce the anisotropy of the Zeeman interaction. We have therefore considered an alternative model where this anisotropy is partially averaged by random flexions and torsions of macromolecular segments in the nanosecond time scale. In these segments, the symmetry axis of the complex, associated with the  $g_{\parallel}$  principal value, makes a  $\theta$ , angle with  $H_0$  and then changes suddenly its orientation to  $\theta_s$ . Assuming that the lifetime  $\tau$  is the same for all orientations and that the probability of change from  $r$  to  $s$  sites is independent of  $\theta_r$  and  $\theta_s$ , the magnetization at site  $r$  is given by Bloch equations modified for multisite exchange. Under steady state conditions, one has :

$$M_r (T_{2r}^{-1} + \tau^{-1} + i(\omega_r - \omega)) - p_r \tau^{-1} \sum_s M_s = i\gamma H_1 M_0 p_r. \quad (11)$$

The total magnetization at Larmor frequency  $\omega$  being  $\sum_s M_s$  or  $\sum_r M_r = G(\omega)$ , the absorption signal is proportional to the imaginary part of the expression :

$$G(H) = i\gamma H_1 M_0 \times \frac{\sum_r \rho_r (\gamma \Delta H_r + \tau^{-1} + i\gamma(H_r - H))^{-1}}{1 - \tau^{-1} \sum_r \rho_r (\gamma \Delta H_r + \tau^{-1} + i\gamma(H_r - H))^{-1}} \quad (12)$$

$H_1$  is the radiofrequency field,  $M_0$  the equilibrium magnetization,  $\gamma$  the electron magnetogyric ratio;  $\tau$  denotes the lifetime of an orientation  $\theta_r$  of probability  $\rho_r \propto \sin \theta_r$ , with respect to the magnetic field.  $H_r$  is given by (2) and  $\Delta H_r$  is given by :

$$\Delta H_r = ((\Delta H_{\parallel}^2 - \Delta H_{\perp}^2) \cos^2 \theta_r + \Delta H_{\perp}^2)^{1/2} \quad (13)$$

$\Delta H_{\parallel}$  and  $\Delta H_{\perp}$  being the half-linewidth at half-height for  $\theta_r = 0$  and  $90^\circ$ , respectively; they have been measured under slow exchange conditions on the 35 GHz spectrum (Table I). This finite angle jump model has been recently applied to the  $^{31}\text{P}$  NMR lineshape in a liquid crystalline phase [31].

Taking  $\Delta g_0 = 2.26 - 2.054 = 0.206$ , we have plotted  $\Delta g/\Delta g_0$  against  $\tau$  for the two spectrometer frequencies (Fig. 6). The observed ratio  $(\Delta g)_X/(\Delta g)_Q$  yields  $\tau \approx 8 \times 10^{-9}$  s. The simulated spectra displayed in figure 7 show that this model accounts for the observed line broadening also.

**3.2.3 Sol-gel transition.** — Kinetic curves are obtained by recording the EPR signal at a fixed value of magnetic field in the initial fluid-phase at a given temperature. The signal variation is thus plotted against time during the aggregation process.

The variation of the EPR signal amplitude from the fluid-phase, unstable at the experimental temperature, to the stabilized gel-phase is illustrated by figure 8. Important spectrum modifications (men-

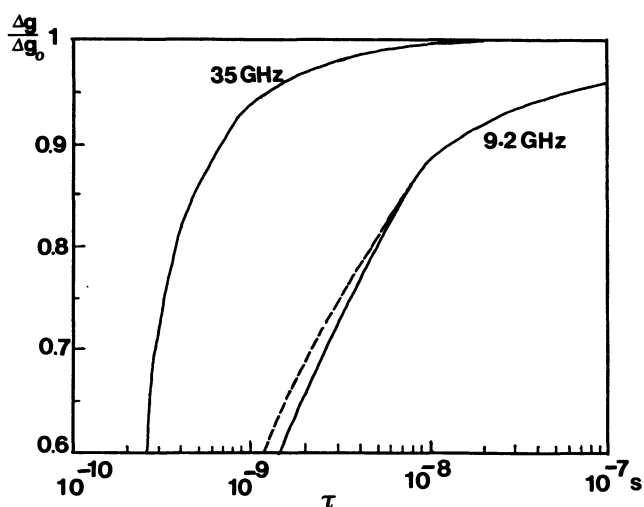


Fig. 6. — Reduction of the  $g$  tensor anisotropy for the finite angle jump model. (—),  $\Delta g/\Delta g_0$ ; (---)  $(\Delta g)_X/(\Delta g)_Q$  computed from (11) with  $\Delta g_0 = 0.206$  (X: X-band; Q: Q-band).

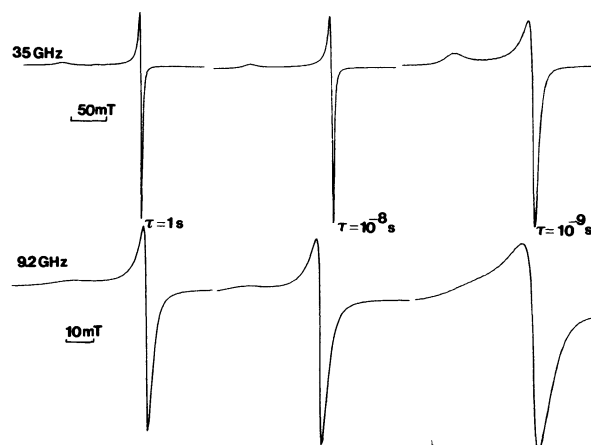


Fig. 7. — Finite angle jump model. Simulation of X- and Q-band spectra taking  $g_z = 2.26$ ,  $g_x = g_y = 2.054$ ,  $\Delta H_{\parallel} = 10.5$  mT,  $\Delta H_{\perp} = 2.8$  mT. The scales have been taken inversely proportional to the microwave frequencies.

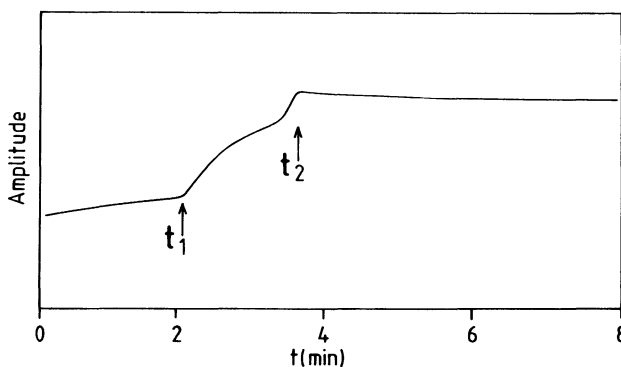


Fig. 8. — Kinetic amplitude variation of the EPR signal from the solution to the gel-phase. This amplitude variation was recorded at fixed magnetic field in the region indicated by the arrow in figure 5c and corresponds to the growth of the signal of the gel-phase.

tioned above in § 3.2.1 and § 3.2.2) from solution to the gel-phase account for such variations. The most important variations are obtained in the  $g_{\perp}$  region where the decrease of amplitude of the narrow quasi-symmetric line of the fluid-phase is recorded. The field was set in the region indicated by the arrow of figure 9. From these kinetics records some general facts can be derived.

Induction time, defined as the time delay during which no variation is detected from the initial solution, is easily seen in figure 8 ( $t_1$ ). Characteristic kinetic times defined as  $(t_2 - t_1)$  are evaluated. Aside from effects of the time delay for temperature stabilization ( $0 \rightarrow t_1$ ) of the sample, one notices a rather short two-step reaction time (102 s, Fig. 8). These characteristic times show a moderate concentration dependence ( $t_1 \sim 90$  s,  $\text{Co} \sim 11.2$  % wt;  $t_1 \sim 270$  s;  $\text{Co} \sim 1.5$  % wt).

At equilibrium, the gel phase spectrum is concentration dependent. As shown in figure 9, two kinds



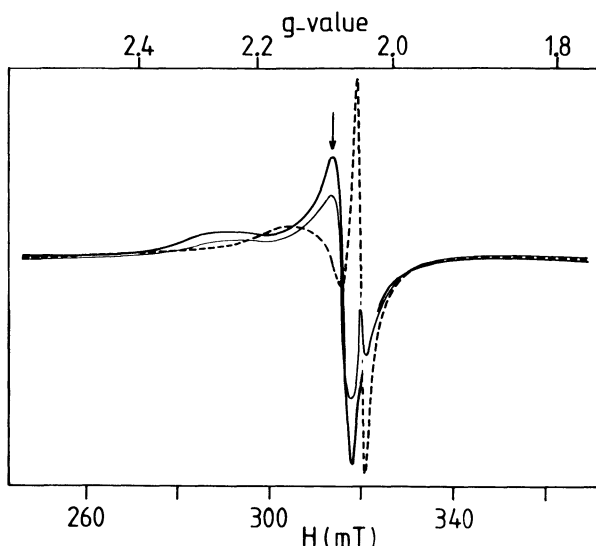


Fig. 9. — X-band EPR spectra of gel-phase at various concentrations of the CC complex in cyclohexane. 10.0 % wt (heavy line) ; 1.0 % wt (fine line). The spectrum of the fluid-phase is also presented (dotted line) as a reference.

of spectra are obtained on going from diluted gels (1 % wt) to concentrated ( $\geq 4$  %). A more or less resolved shoulder in the high field region is typical of diluted gels and is equivalent to a fluid-phase spectrum component. This component becomes undetectable as the concentration is increased.

Concentration, temperature and time are equivalent variables in the sense that the same sequence of spectra may be obtained when two of them are kept constant while the third is varied. For instance, figure 9 is also representative of the different spectra of the system during the gelation kinetics: the dashed spectrum is obtained first, then the shoulder disappears with time.

#### 4. Discussion.

**4.1 AGGREGATION AND GELATION MECHANISM.** — One of the purposes of this study deals with the mechanism of cohesion between the constitutive copper complex molecules in the gel network. Very often, in amphiphilic gelifying molecules, hydrogen bonding is implied in the aggregation process [32-34]. With the CC complex, the non-polar part is easily identified as being the eight paraffinic chains; the polar part being the copper diketonate residue.

With EPR, one investigates the participation of copper in the aggregation process during which gelation occurs. The first piece of information is the existence of an exchange interaction between the copper atoms in the gel-phase. The EPR study gives the minimum value of the exchange interaction to be of the order of  $A_{\parallel} = 0.02 \text{ cm}^{-1}$ , which is sufficient to average the hyperfine interaction. Considering the electronic structure of the complex, the unpaired

electron in the  $d_{x^2-y^2}$  type orbital, and the absence of covalent bridges between neighbouring complexes, the exchange is expected to be weak. For comparison, when similar square-planar copper complexes are packed in linear chains, a super-exchange between two neighbouring copper atoms takes place *via* the oxygen ligand of the molecular plane ( $J_{\text{ex}} \sim 0.7 \text{ cm}^{-1}$  [35]). Preliminary electron microscopy experiments on the dried gel of CC complex show that the network is built with such very long fibers. Compared to energies involved in classical physical gels where hydrogen bonding and/or ionic interactions are often implied, the exchange energy is by no means sufficient to ensure cohesion in the constitutive chains. This cohesion is probably obtained by some Coulombic interactions between the out-of-plane  $e_g$  orbitals [36] of neighbouring stacked complexes.

An interesting extension to this EPR work should be to decrease the exchange interaction by intercalating homologous diamagnetic compounds in the solid-like gel network. In such a situation, the strength of the exchange interaction should be determinable and characterization of the tumbling motion should be facilitated by the recovery of hyperfine splittings in the spectra.

Finally, the physical cross-linking which connects the various linear aggregates in an infinite elastic network probably does not involve copper, if copper participates in a linear stacking model as described above.

**4.2 THERMODYNAMICS AND KINETICS OF AGGREGATION.** — For concentrated gel samples, a single EPR spectrum is observed. Only one type of copper complex molecule is detected i.e. the aggregated species. For some diluted gels, the EPR signal of free molecules appears as a shoulder on the high field side of the gel spectrum (Fig. 9). This shoulder is assigned, in the gel, to some fluid part containing isolated copper complex molecules. Even for concentrated gels, some amount of free molecule is probably still present, but in a weak proportion. Aggregation of these residual free molecules to the ends of the network has low probability and their evolution is more directly governed by the chemical potentials of the system. Thus, while concentrated gels ( $> 4$  % wt) are stable, diluted system ( $< 1$  % wt) are demixing and intermediate gels are more or less deswelling. The upper demixed fluid part is pure solvent cyclohexane while the aggregated part retains a solid-like EPR spectrum.

Another kinetic feature of this gelling system is the two-step shape of the EPR kinetic records of figure 8, which is probably relevant to an actual molecular mechanism since it is qualitatively weakly sensitive to the fixed magnetic field value in the  $g_{\perp}$  region.

Finally, the effective time delay of aggregation is rather short for this kind of compounds. For instance, for the low molecular weight solute steroid in cyclohexane [34], equilibrium values can only be obtained after about 30-40 min. In the steroid case the aggregation reaction is mechanistically complicated by the formation of a helical double strand filament in a reverse micelle configuration compared to the supposed growth of linear chains by stacking of the copper complex molecules. This easier mechanism may account for a faster kinetic behaviour.

The body of these results suggests that the building principle of this gel is not only based on solubility considerations as for the steroid/cyclohexane system but also on analogies with thermodynamics of some polymers in solution [37]. This competition between segregation or demixtion and gelation may be

analysed in terms of long chains in poor solvents [38].

This work deserves a more detailed study on structural aspects, the phase diagram and kinetics. The whole range of concentrations and temperatures must be considered, from the diluted demixing systems to the xerogel. Electron microscopy and small angle X-ray scattering experiments are underway for determination of the network structure. Ultraviolet absorption spectroscopy and complementary EPR studies will improve knowledge of the mechanism.

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