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Spectrophotometric Study of Copper(II) Chloride Complexes in Propylene Carbonate and in Dimethyl Sulfoxide

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Copper(II) chloro complexes were characterized in dimethyl sulfoxide (Me_2SO) and in propylene carbonate (PC) media. The spectrophotometric investigation was performed in the UV–visible and near-infrared regions with 1 M $Li^+(ClO_4^-, Cl^-)$–Me_2SO and 0.1 M $Et_4N^+(ClO_4^-, Cl^-)$–PC constant ionic strength copper(II) chloride solutions. The stability constants and individual electronic spectra were calculated from a large set of absorbance values covering the whole UV–visible and near-IR wavelength ranges. The overall formation constants of three copper(II) chloro complexes $Cu(Me_2SO)_3Cl^+$, $Cu(Me_2SO)Cl_3^-$, and $CuCl_4^{2-}$ in dimethyl sulfoxide are log β_1 = 2.99, log β_3 = 6.91, and log β_4 = 7.53. In PC solution, four successive copper(II) chloro complexes, probably very weakly solvated, were found, and the corresponding calculated stability constants are log β_1 = 12.0, log β_2 = 22.7, log β_3 = 28.9, and log β_4 = 34.1. The different solvation properties are seen in the charge-transfer bands of the less coordinated cationic or neutral species much more than for the anionic tri- and tetrachlorocuprates. The calculated electronic spectra of the unsolvated $CuCl_4^{2-}$ are remarkably similar in both solvents. The regular shift of the individual complex absorption maxima above 800 nm, when the number of coordinated chloride ligands increases, indicates a progressive change from a square-planar copper(II) ion to a flattened tetrahedral configuration for $CuCl_4^{2-}$.

Introduction

We recently published a spectrophotometric study of copper(II) chloro complexes in dimethylformamide[1] and characterized quantitatively in this medium two solvated species, $Cu(DMF)_3Cl^+$ and $Cu(DMF)Cl_3^-$, as well as the unsolvated tetrachlorocuprate ion $CuCl_4^{2-}$. The absence of the dichloro complex was related to the fact that the Gutmann's donor numbers of the solvent and the ligand are similar, which induces a dissociation of the neutral molecule and auto complex formation leading to the mono- and trichloro species.[2] Structural conclusions were supported by near-infrared results.

The present work concerns the investigation of the copper(II) chloride system in two other solvents:propylene carbonate (PC), which has a very high dielectric constant (ϵ = 69), a low Gutmann donor number (DN = 15) and a fairly weak solvation power for cations, and dimethyl sulfoxide (Me_2SO), the characteristics of which are quite similar to those of DMF (Me_2SO, ϵ = 45, DN = 29.8; DMF, ϵ = 36, DN = 26.6).[2]

Very few quantitative results have been established for these two systems partly because of the experimental difficulties encountered with precise potentiometric determinations of the activities of the free copper(II) or chloride ions. For example, in propylene carbonate the copper(II) electrode is not stable enough because of solvent–solid copper phase interactions in the presence of relatively high chloride ion concentration.[3] In PC, a three-complex model involving $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ has been proposed by Scharff[4] from potentiometric and spectrophotometric data. The molar ratio method used may also lead to other models and is too approximate to obtain accurate quantitative conclusions.

The Me_2SO copper chloride system has been investigated by Courtot and co-workers[5] who identified three successive copper(II) chloro complexes, $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and two copper(I) chloro complexes, CuCl and $CuCl_2^-$, from voltamperometric, potentiometric and coulometric data.

One year later, Suarez, Iwamoto, and Kleinberg[6] reported their own study of the copper(I) and copper(II) chloro complexes using spectrophotometric and electrochemical techniques. These spectrophotometric results are doubtless approximate as these authors assumed the presence of one unique species, or at most two, to calculate the corresponding stability constants. The graphical Hildebrand–Benesi method[7] used is inadequate as is the molar ratio method when more than two complexes are present. This is particularly true in the case of absorbing species characterized by overlapping individual absorption spectra. These authors assigned the 440-nm band to $CuCl_4^{2-}$, recalling Furlani and Morpurgo, who, on the contrary, found the tetrachlorocuprate charge-transfer absorption maxima at 410 and 296 nm.[8] The band at 440 nm corresponds, as we demonstrate in this work, to the trichloro complex.

Recently, Libus and co-workers[9] reported ionization equilibria of copper(II) chloride in Me_2SO and could only define three successive chloro complexes by using near-infrared absorption data. These results were obtained from a set of $CuCl_2\cdot 2Me_2SO$ solutions where the chloride ion concentration ranged from 0.00043 to 0.1738 M. The determination of each complex was performed from absorption spectra with the assumption that only one species was present despite the fact that higher chloride ion concentration induces shifts of the observed absorption maxima. This approximation is valuable in a restricted range of concentration but also implies a degree of formation of the complex close to 100%. On the other hand, the reported experimental absorption maxima changes indicate clearly, even at low or restricted chloride ion concentration ranges, the presence of a minimum of two if not of three species.

In this work, our investigation is based, as previously described for the DMF–copper(II) chloride solution study, upon an analysis covering the largest possible range of absorbance data in the UV, visible, and near-infrared regions. All measurements contribute to quantitatively characterize the nature, the stability, and the structure of the copper(II) chloro com-

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plexes and also the individual electronic spectra corresponding to the charge-transfer and d–d transition bands.

For each system, the calculations are performed on the basis of several hypotheses about the number and nature of the species present in solution, all compatible with a preliminary matrix rank analysis of the data. The final choice between the different models studied is made on the basis of statistical criteria and by taking into account the solvent and solvation properties of Me_2SO and PC.

Experimental Section

Reagents. The propylene carbonate (PC) (Fluka) was used after several steps of purification according to the procedure indicated by Gosse and Denat.[10] After a 12-h contact with solid $KMnO_4$, the solvent is separated from the excess of solid and heated at 120 °C for 4 h. After cooling, MnO_2 and the impurities such as propylene glycol, allyl alcohol, and propylene oxide oxidized by $KMnO_4$ are separated by filtration. A first quick distillation is performed under reduced pressure (about 15 mmHg). The first 30% of the solution is eliminated, and the remaining solution comes through an Al_2O_3 column for elimination of the acidic impurities. A second distillation under reduced pressure (1 mmHg) leads to pure anhydrous (water content <100 ppm) propylene carbonate which does not display any UV absorption over 205–210 nm, whereas the commercial product shows a strong absorption between 210 and 250 nm.

Dried dimethyl sulfoxide (Merck) was purified by two successive distillations over CaH_2 at 45 °C (1 mmHg). The Karl Fischer test indicated less than 100 ppm of water in the purified Me_2SO, which was used immediately after distillation. The lower wavelength limit of 260 nm was used for the spectrophotometric investigation of the copper(II) chloride–Me_2SO solutions because of the strong absorption of the solvent.

Tetraethylammonium salts were used in the PC medium as recommended by Lagowski;[11] Et_4NCl (Merck) was recrystallized in water and the corresponding Et_4NClO_4 (Fluka) in acetone. The salts were dried under reduced pressure before utilization.

In the Me_2SO system, due to higher solubility ($\simeq 2$ M), lithium chloride and perchlorate (Alfa) could be used after recrystallization.

The ionic strength was maintained constant in all experiments at 1 M in the Me_2SO solutions and at 0.1 M in the PC solutions. The ionic strength values are different in both solvents because of different solubilities of the support electrolytes and also because of the need to cover the largest possible range of chloride concentration.

In propylene carbonate, the copper(II) ion remains unsolvated. In this case we used copper(II) perchlorate which was tetrahydrated after drying under reduced pressure but still very hygroscopic. We have checked that the presence of this small amount of residual water has no effect upon the spectra.

Solid $[Cu(Me_2SO)_x](ClO_4)_2$ was prepared from $Cu(ClO_4)_2 \cdot 6H_2O$ (Alfa) dissolved in Me_2SO under reduced pressure (15 mmHg) at about 80 °C. A blue greenish powder was separated, and the microanalysis of the dried solid indicated four molecules of Me_2SO coordinated to the copper(II) ion ($x = 4$).

In the UV–visible investigation, we used a 5×10^{-4} M copper(II) ion concentration. The stock solution of the copper(II) ion was standardized in aqueous medium by EDTA at pH 8 with murexide. The chloride ion concentration ranged from 5×10^{-4} to 4×10^{-3} M in the copper(II)–PC system and from 5×10^{-4} to 1 M in the copper(II)–Me_2SO system. The ionic strength was maintained constant with lithium or Et_4N perchlorate salts. The low value of the higher limit of the chloride ion concentration in the PC system is related to the invariance of the absorption at higher chloride ion concentration, indicating a 100% formation of the highest coordinated complex.

For the near-infrared measurements, the copper(II) ion concentration was brought up to 10^{-2} M and the higher chloride ion concentration limits were the same as in the solutions used for the UV–visible investigation. Under these experimental conditions, we obtained a satisfactory absorbance scale with a 1-cm cell in the UV–visible and near-infrared wavelengths range. No evidence for polynuclear species was obtained.

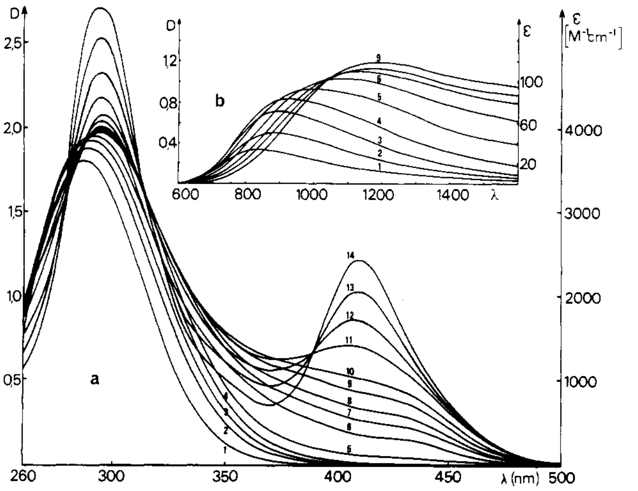

Figure 1. Absorption spectra of Me_2SO–copper(II) chloride solutions (spectrum, $[Cl^-]$). (a) UV–visible ($[Cu^{2+}]_{solvated} = 5 \times 10^{-4}$ M): 1, 0; 2, 5×10^{-4}; 3, 10^{-3}; 4, 2×10^{-3}; 5, 4×10^{-3}; 6, 10^{-2}; 7, 1.5×10^{-2}; 8, 2×10^{-2}; 9, 3×10^{-2}; 10, 4×10^{-2}; 11, 10^{-1}; 12, 2×10^{-1}; 13, 4×10^{-4}; 14, 1. (b) Near-IR ($[Cu^{2+}]_{solvated} = 10^{-2}$ M): 1, 0; 2, 5×10^{-3}; 3, 10^{-2}; 4, 2×10^{-2}; 5, 4×10^{-2}; 6, 10^{-1}; 7, 2×10^{-1}; 8, 4×10^{-1}; 9, 1.

We used the same spectrophotometric reference solution over the whole concentration range, with 0.5 M and 0.05 M equiv of chloride and perchlorate salts in the Me_2SO and PC solutions, respectively.

Due to the relative instability of these nonaqueous solvents, the free copper(II) ion was added as the last reagent just prior to the spectrophotometric measurement. The color of the copper(II) chloride mixtures shifts with increasing chloride ion concentration from greenish blue to dark yellow and orange.

The absorbance data were obtained with a Cary 17D (Varian) instrument, and the numerical treatment was performed in the same way as reported earlier[1] for all absorption data collected in the UV–visible and IR regions.

The absorption determinations ranged in the copper(II)–PC system from 220 to 550 nm and from 700 to 1500 nm; in the copper(II)–Me_2SO system the wavelength interval was limited between 270 and 500 nm in the UV–visible and between 600 and 1600 nm in the near-IR region. No absorption of the copper(II) chloride solutions between 500 and 600 nm is observed.

Results and Discussion

Electronic Spectra of the Copper(II) Chloride Solutions. The experimental spectra were obtained for the Me_2SO solutions at constant copper(II) ion concentration by increasing chloride ion concentration up to 1 M (Figure 1). The upper right part of Figure 1 shows the corresponding measurements in the near-infrared region. Spectrum 1 was obtained from a copper(II) solution containing no chloride and indicates an absorption maximum at 287 nm, which characterizes the copper(II) solvate $[Cu(Me_2SO)_4]^{2+}$; in the near-IR region, the corresponding maximum is centered at 820 nm (curve 1), which is good evidence for a square-planar structure for the copper(II) ion.[18] Small increasing chloride ion concentrations (spectra 2–5) induce a regular shift of the absorption maximum from 287 nm toward higher wavelengths. This is an indication of the presence of more than one species in the system. At higher C values (0.010–0.040 M; spectra 6–10), the absorption maximum stabilizes at 300 nm. In addition, the absorption tail between 350 and 500 nm increases in intensity and a low-intensity shoulder appears at 440 nm. For higher C values (0.1–1 M; spectra 11–14), this shoulder is completely hidden under the intense band at 410 nm. Two clearly defined absorption maxima are observed for these high chloride concentrations: the first one of higher intensity stabilizes at 294 nm and the second at 410 nm. These two peaks certainly characterize the most coordinated species, in fact the unsolvated $CuCl_4^{2-}$ complex ion, as will be shown later. Some

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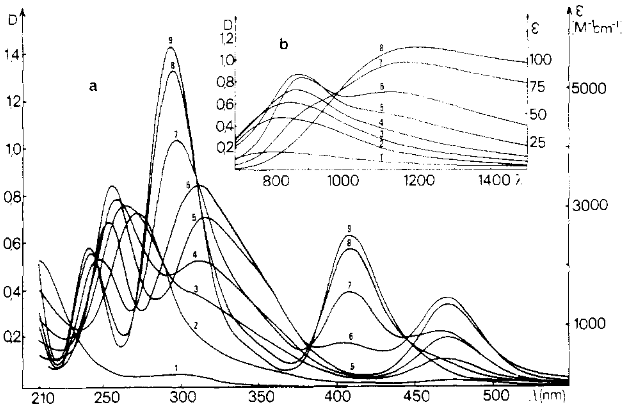

Figure 2. Absorption spectra of PC–copper(II) chloride solutions (spectrum, [Cl$^-$]). (a) UV–visible ([Cu^{2+}] = 5 × 10^{-4} M, l = 0.5 cm): 1, 0; 2, 2.5 × 10^{-4}; 3, 5 × 10^{-4}; 4, 7.5 × 10^{-4}; 5, 10^{-3}; 6, 1.5 × 10^{-3}; 7, 1.75 × 10^{-3}; 8, 2 × 10^{-2}; 9, 4 × 10^{-2}. (b) Near-IR ([Cu^{2+}] = 10^{-2} M, l = 1 cm): 1, 0; 2, 10^{-2}; 3, 1.5 × 10^{-2}; 4, 2 × 10^{-2}; 5, 2.5 × 10^{-2}; 6, 3 × 10^{-2}; 7, 3.5 × 10^{-2}; 8, 4 × 10^{-2}.

isosbestic points at 314 and 388 nm can be located for C values ranging from 0.1 to 1 M. In the near-IR region, regular shifts of the absorption maximum from 880 (curve 2) to near 1200 nm (curve 9) are observed with increasing chloride ion concentration from 0.005 to 1.0 M. These regular changes will doubtless correlate with structure variations from lower to higher coordinated complexes.

The propylene carbonate–copper(II) chloride solutions give rather complicated general features (Figure 2). Spectrum 1 corresponding to the unsolvated copper(II) ion shows a very small absorption around 300 nm and the expected maximum at 210 nm. In the near-IR region, a very broad maximum is seen at 790 nm and is consistent with a square-planar configuration.[18] With the 1:1 chloride:copper(II) molar ratio (R) solution (spectrum 2), an absorption maximum appears at 273 nm and this yellow-green solution corresponds to the predominant presence of the monochloro complex.

By increasing R from 2 to 3 (spectra 2–6), continuous shifts of the absorption maxima toward 255 nm are observed: several complexes are present in the mixture. A new peak rises around 312 nm and reaches its maximum intensity in spectrum 6 (R = 3); a lower absorption band is also observed at 410 nm belonging to yet another complex. This corresponds to one of the absorption maxima of $CuCl_4^{2-}$. At higher chloride ion concentrations (spectra 7–9), all previous maxima shift by more than 10 nm toward lower wavelengths. Finally, three absorption maxima are obtained for spectrum 9: the highest intensity is observed for the 295-nm peak and two other maxima of half this intensity are located at 242 and 410 nm. No further intensity and wavelengths variations of these 3 maxima appear even if R is increased up to 100: this observation indicates a close to 100% formation for the most coordinated species. Consequently, spectrum 9 is expected to be essentially the individual electronic spectrum of the highest copper(II) chloro complex, $CuCl_4^{2-}$. The changes of the experimental spectra depending upon the chloride concentration qualitatively indicate the presence of four chloro complexes in the PC–copper(II) chloride solutions. Five isosbestic points are observed for R greater than 3: 246, 271, 310, 384, and 444 nm.

The corresponding near-IR spectra are essentially characterized by two absorption ranges (Figure 2b). In the first, a regular shift of the absorption maximum from 790 to 880 nm is observed (curves 1–5; $0 < C < 2.5 \times 10^{-2}$ M). In the second, for higher chloride ion concentration an absorption band centered at 1180 nm appears (curves 6–8). Again, as in the UV–visible range, this absorption maximum at around 1200 nm does not change even for higher C values. The most coordinated complex, $CuCl_4^{2-}$, will be characterized by an individual d–d transition band spectrum close to that observed for the curve 8 and by a flattened tetrahedral configuration.[18]

Table I. Overall Stability Constants of the Cu(II) Chloro Complexes in Me$_2$SO

	[1,2,3]	[1,3,4]	[1,2,3,4]
log β_1	2.47	2.99	3.40
log β_2	4.05		5.18
log β_3	4.88	6.91	7.30
log β_4		7.53	7.85
σ_1(UV–visible)	0.069	0.044	0.027
σ_2(infrared)	0.040	0.031	0.015
$\langle\sigma\rangle$	0.059	0.038	0.023

Numerical Analysis and Number of Complexes. From the experimental spectra reported in Figures 1 and 2, qualitative predictions can be made about the possible number of species present in the two different solvents. A more precise conclusion is obtained by the calculation of the minimum of absorbing species which form in each system. We used, for this purpose, the matrix rank method initiated by Wallace[12] and more recently described by Hugus and El-Awady.[13] The method requires a large set of absorbance values measured for different solutions at different wavelengths with the unique restriction that the number of solutions be larger than the number of wavelengths. Plots of the absorbances at each wavelength as a function of the analytical ligand concentration were used to get N optical density values for L selected wavelengths.

The matrix rank treatment, in the case of the Me$_2$SO system, was performed for 1236 experimental points (UV–visible N = 39, L = 24; near-IR N = 15, L = 20). In the case of the PC system, 1342 points were used (UV–visible N = 28, L = 34; near-IR N = 13, L = 30). In both systems, this analysis is consistent with the assumption of a minimum of four absorbing species including the free copper(II) ion absorption. As seen before, the copper(II) ion is unsolvated in the PC solution and shows a small absorption contribution over the whole wavelength range. This would predict four chloro complexes in the PC system while three complexes would be sufficient to characterize the Me$_2$SO solutions.

Stability Constants of the Copper(II) Chloride Complexes. The overall formation constants β_j and the specific extinction coefficients ϵ_j of the copper(II) chloro complexes were calculated as previously described in our DMF–copper(II) chloride investigation[1] and are based on a set of more than 1200 data covering the whole absorption range in the UV–visible and near-IR regions. A new procedure was used in the Marquardt algorithm[14] when the minimum of the sum S of the squares of the residuals of experimental and calculated absorbance values was calculated. The β_j's and ϵ_j's are no longer considered as equivalent parameters in the analytical expression of the absorbance. The ϵ_j's are expressed as a function of the β_j's, which evidently leads to a linearization of the analytical expression. This minimizes the strong correlation between these two parameters. Time saving for the whole calculation is another important advantage of this new way of calculation which will be explained in detail in another paper.[15]

Among the possible theoretical models compatible with the matrix rank analysis results, only three were tested for both systems; four successive mononuclear complexes model [1,2,3,4] and two three-complex models [1,2,3] and [1,3,4] for CuCl$^+$, CuCl$_2$, and CuCl$_3^-$ and CuCl$^+$, CuCl$_3^-$, and

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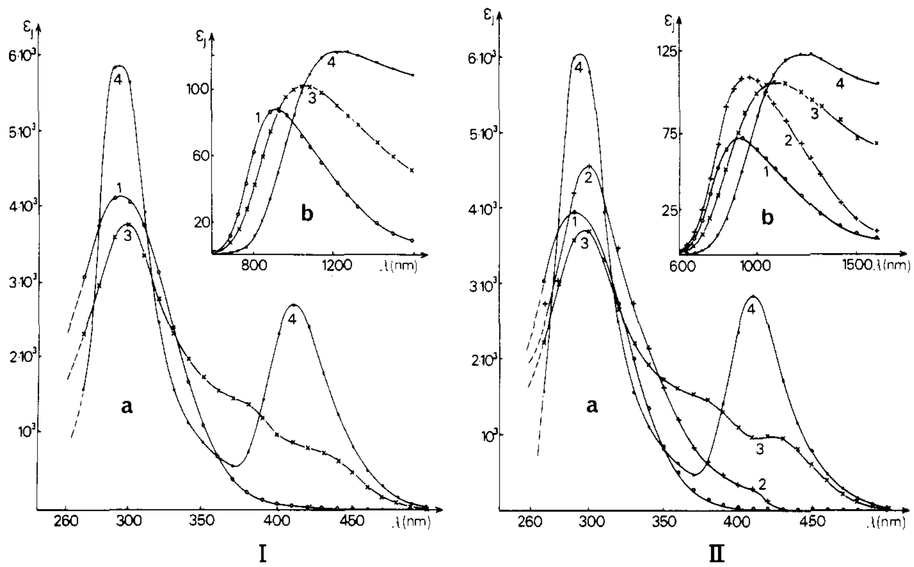

Figure 3. Electronic spectra of Me_2SO–copper(II) chloro complexes for the [1,3,4] (I) and [1,2,3,4] (II) models: (a) UV–visible region; (b) near-IR region.

$CuCl_4^{2-}$, respectively. In this last case, the absence of the neutral copper(II) dichloro complex can be related to some particular solvent and ligand properties already suggested for other systems.[1]

The stability constants for all investigated models are reported in Tables I and III for Me_2SO and PC, respectively. In the last line of these tables, the statistical criteria $\langle\sigma\rangle$, the mean value of the standard deviation for the whole set of data, indicates the goodness of fit between the experimental data and the theoretical model.

(i) Dimethyl Sulfoxide System. In the Me_2SO system, little variation of the $\langle\sigma\rangle$ values from one model to the other is observed. However, a clearly superior result was obtained for the more complicated [1,2,3,4] model than for [1,2,3] as expected. But other criteria must be found to choose between the [1,3,4] and the [1,2,3,4] models for which the $\langle\sigma\rangle$ are not significantly different. The difficulty found for choosing the best model from the numerical treatment can also be related to the superimposed absorption bands of the different chloro complexes. Two important absorption ranges are seen in Figure 1, around 290 and 410 nm. The absorption changes are very regular in terms of ligand concentration increase without any particular indication for one or another complex. This absorption overlapping of the different chloro complexes in the mixture appears also in the numerical analysis by an overlapping of several models.

The individual calculated electronic spectra are represented in Figure 3 for both models [1,3,4] and [1,2,3,4]. Despite very different stability constant values in both models, no significant change or shift of the spectra of $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$ can be noticed, either in the UV–visible or in the near-IR region. When there is a change from the [1,3,4] to the [1,2,3,4] model, the absorption band of $CuCl_2$ appears in [1,2,3,4] as a result of partial decomposition of the $CuCl^+$ and $CuCl_3^-$ spectra in [1,3,4]. Only very negligible absorption intensity variation are observed from one model to another. These two models seem to be equivalent in terms of $\langle\sigma\rangle$ values and of individual electronic spectra. The input of β_2 clearly produces a better fit, but the [1,2,3,4] model is not a significantly better representation of physical reality.

In Table II we report the comparison at the experimental and calculated isosbestic points. The fit is better for the [1,3,4] model, but the four-complex model is still acceptable. It is our hypothesis that the absence of $Cu(Me_2SO)Cl_2$ is due to autodissociation of this species as soon as it is formed, as already considered for the copper(II) chloride–DMF system.[1]

Table II. Comparative Isosbestic Point Wavelengths (nm) in Me_2SO

	calcd			calcd	
exptl[a]	[1,3,4][b]	[1,2,3,4][b]	exptl[a]	[1,3,4][b]	[1,2,3,4][b]
314	315	317	388	388	389

[a] Figure 1. [b] Figure 3.

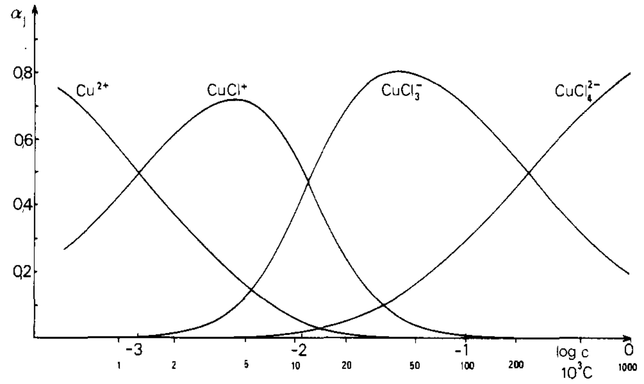

Figure 4. Formation curves of the individual copper(II) chloro complexes in 1 M $Li^+(ClO_4^-, Cl^-)$–Me_2SO solutions ([1,3,4] model). *C* and *c* are the analytical and free ligand chloride ion concentrations.

This provides the only criterion which enable the choice between these two models.

The formation curves, in Figure 4, of the copper(II) chloro complexes in the Me_2SO solutions indicate a large range of conditions for the existence of each species. We also observe the beginning of formation of the highest coordinated complex at rather low chloride ion concentrations.

(ii) Propylene Carbonate System. The β_j's obtained from the PC system investigation in the UV–visible region (Table II) lead to only slightly different σ_1 values in models [1,3,4] and [1,2,3,4]. The numerical result for [1,2,3] is much different from the other two. But the input of the near-IR data (σ_2) in the numerical treatment clearly gives a better mathematical result for [1,2,3,4], significantly different from the two other models ($\langle\sigma\rangle$) (Table III).

The formation curves of the copper(II) chloro complexes characterized in the PC solutions show a remarkable feature over the whole ligand concentration range. The plot is completely symmetric having symmetry axis located at ligand concentration value corresponding to a molar ratio of 2 and

Table III. Overall Stability Constants of the Cu(II) Chloro Complexes in PC

	[1,2,3]	[1,3,4]	[1,2,3,4]
log β_1	15.0	10.8	12.0
log β_2	19.9		22.7
log β_3	23.9	29.7	28.9
log β_4		35.0	34.1
σ_1 (UV-visible)	0.30	0.12	0.10
σ_2 (infrared)	0.20	0.11	0.05
$\langle\sigma\rangle$	0.25	0.11	0.07

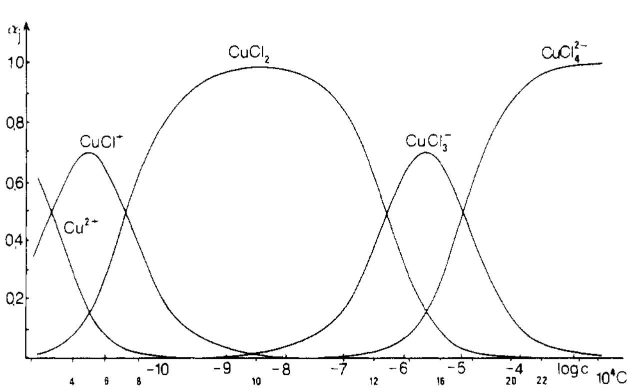

Figure 5. Formation curves of the individual copper(II) chloro complexes in 0.1 M $Et_4N^+(ClO_4^-, Cl^-)$–PC solutions. *C* and *c* are the analytical and free ligand chloride ion concentrations.

3, respectively. For the mono-, di-, and trichloro complexes or the di-, tri-, and tetrachloro complexes, the curves can be superposed by using these symmetry axes.

We observe also, in Figure 5 the successive formation of the four complexes with 100% of formation for the dichloro- and the tetrachloro complex. The most important property of these curves appears for the maximum of formation of each complex which is located exactly at ligand concentration for which R is equal to 1, 2, 3 and 4 respectively for $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$. Consequently, if the degree of formation of the complex is close to 100%, the experimental spectrum obtained at these ligand concentrations will be identical with the calculated individual electronic spectrum for the respective complexes. That is exactly the case for $CuCl_2$ and $CuCl_4^{2-}$: the curves 4 and 8 in Figure 2 for which the chloride:copper(II) ratio is 2 and 4, respectively, have exactly the same absorption maxima and absorption intensity variations as the calculated spectrum of $CuCl_2$ and $CuCl_4^{2-}$ represented in Figure 6.

All these stability constant values were calculated by using the Marquardt algorithm where the numerical criterion for a minimum is no change in the first two significant numbers after successive iterations. For the β_j's standard deviations a classical least-squares nonlinear regression[16] was used. The constants' uncertainties are only a result of the calculation: local linearity of the sum of the squares of the absorbance residuals depending upon the parameters β_j and ϵ_j is assumed in the vicinity of the minimum. This is approximated by a second-order function which is easily solved. But unfortunately its representation does not fit to the real surface in many cases and the discrepancy observed particularly in systems involving three or more complexes cannot be neglected. As a consequence of this linear assumption, the results obtained for standard deviations are much smaller than the real values corresponding to a 95% confidence interval.

Electronic Spectra of the Copper(II) Chloride Complexes. In the copper(II) chloride–Me_2SO system, we propose the [1,3,4] model as the best. This conclusion is related to the dichloro complex autodissociation assumption which is due to comparable donor numbers of the solvent and the ligand. The individual electronic spectra are shown in Figure 3(I). Part b of this figure corresponds to the near-IR region.

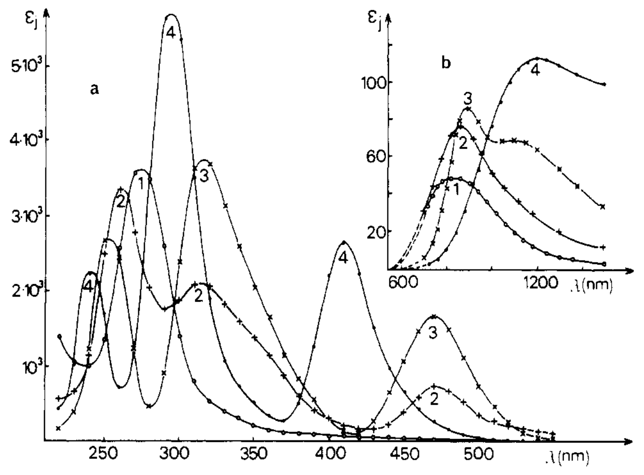

Figure 6. Electronic spectra of the PC–copper(II) chloro complexes $CuCl^+$ (1), $CuCl_2$ (2), $CuCl_3^-$ (3), $CuCl_4^{2-}$ (4): (a) UV–visible region; (b) near-IR region.

For the copper(II) chloride PC system, the [1,2,3,4] model is doubtless the best conclusion. As seen before in Figure 5, the maximum degree of formation of each complex is obtained at corresponding chloride:copper(II) ion molar ratio values. The individual copper(II) chloro complexes electronic spectra in the PC solution are reported in Figure 6.

$CuCl^+$. Only one maximum at 294 nm with an extinction coefficient of 4120 M^{-1} cm^{-1} characterizes the monochlorocuprate in the Me_2SO system. The part at lower wavelengths is hidden by the solvent absorption (260 nm). In the PC system, a lower intensity absorption maximum (ϵ 3620 M^{-1} cm^{-1}) is located at lower wavelength (274 nm) and a very low intensity shoulder can be observed at 390 nm.

$CuCl_2$. Evidence for the dichloro complex is found in the PC system only. Three absorption maxima were calculated at 261 nm (3360 M^{-1} cm^{-1}), 315 (2100), and 470 (730). The absorption band centered at 315 nm is asymmetric, having a shoulder at 355 nm. In the [1,2,3,4] Me_2SO model (Figure 3(II)), the electronic spectrum of $CuCl_2$ would show a feature analogous to those observed for the mono or trichlorocuprates; but its nonsymmetrical absorption band would be centered at 299 nm (4560 M^{-1} cm^{-1}) with a small absorption residual at 410 nm. The latter results only from the calculation. The absence of $CuCl_2$ in Me_2SO solutions can also be related to solvation properties. Because Cu(II) is unsolvated by PC, the normal $CuCl_2$ species would be expected to form in that solvent. However, since Cu(II) shows fourfold solvation by Me_2SO, the normal species is most likely a solvent-separated ion pair which would not be detected in the visible and also near-IR spectral range for complexes in Me_2SO solutions. For such ion pair, there is obviously no Cu–Cl bonding in the primary coordination sphere of Cu(II).

$CuCl_3^-$. The Me_2SO trichlorocuprate has an electronic spectrum similar to that of $CuCl^+$, with an absorption maximum at 298 nm (3720 M^{-1} cm^{-1}) and two low-intensity shoulders in the visible at 380 and 440 nm (Figure 3(Ia)). In the PC medium, this complex has three absorption maxima, like $CuCl_2$, at 253 nm (2700 M^{-1} cm^{-1}), 315 (3750), and 470 (1670) (Figure 6). The difference from the $CuCl_2$ spectrum consists essentially of a shift of the lowest wavelength maximum (i.e., from 261 to 253 nm) and higher intensity absorption bands for the two other maxima at the same wavelengths.

$CuCl_4^{2-}$. The unsolvated tetrachlorocuprate is characterized by identical absorption bands in both solvents (Figure 3(Ia), Figure 6a). This complex has a spectrum with a very high

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Table IV. Near-IR Absorption Maxima Wavelengths and Extinction Coefficients of the Copper(II) Ion and Copper(II) Chloro Complexes in Me_2SO and PC [λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})].

	Me_2SO[a]	PC[b]		Me_2SO[a]	PC[b]
Cu^{2+}	820 (33)	790 (18)	$CuCl_3^-$	1050 (103)	860 (86), 1080 (68)
$CuCl^+$	908 (89)	840 (49)			
$CuCl_2$		868 (76)	$CuCl_4^{2-}$	1210 (127)	1200 (115)

[a] Figure 3(Ib). [b] Figure 6b.

intensity maximum at 294 nm with very close ϵ values (5720 M^{-1} cm^{-1} in Me_2SO and 5840 M^{-1} cm^{-1} in PC) and a half-intensity absorption maximum at 410 nm (2720 M^{-1} cm^{-1} in Me_2SO and 2650 M^{-1} cm^{-1} in PC). These very similar characteristics demonstrate clearly the invariance of the electronic spectrum of $CuCl_4^{2-}$ with the solvation power of the two solvents. The peaks at 294 and 410 nm were already found in our previous study in DMF medium.[1] A third absorption maximum, observed only in the PC solutions, is calculated at 241 nm (2240 M^{-1} cm^{-1}). This has also been assigned to $CuCl_4^{2-}$ in the solid state.[17]

d–d Transition Bands of the Copper(II) Chloro Complexes. The individual electronic spectra of the copper(II) chloro complexes were calculated for the corresponding models in both solvents and are plotted in Figures 5(Ib) and 6b, and, as far as we know, are given for the first time for the near-IR region. This quantitative analysis allows a precise assignment of the different absorption maxima for each chloro complex. The d–d transition band characteristics of the individual complexes are reported in Table IV.

The solvated copper(II) ion $Cu(Me_2SO)_4^{2+}$ has a broad maximum at 820 nm, which indicates a square-planar configuration. In both solvents, the absorption bands of the individual complexes are regularly shifted toward higher wavelengths, illustrating the structural changes as a function of the copper(II) chloride ion coordination. A particular feature is found for the trichloro complex in PC medium, for which two distinct absorption maxima separated by 220 nm have been calculated. These two d–d transition bands indicate a possible equilibrium of the trichloro complex present in two different configurations: one square planar; the other, a flattened tetrahedron.

The calculated extinction coefficient of approximately 120 M^{-1} cm^{-1} for $CuCl_4^{2-}$ in both solvents is consistent with the noncentrosymmetric copper(II) system as predicted by ligand field theory calculation.[18] Consequently, the unsolvated tetrachlorocuprate is characterized by a flattened tetrahedron configuration (D_{2d} symmetry).

Dimethyl Sulfoxide, Propylene Carbonate, and Copper(II) Solvation Properties. Our Me_2SO and PC investigations show significant differences in both nature and stability of the copper(II) chloro complexes. The calculated electronic spectra in the UV–visible and particularly in the near-IR region enable some comparisons with previous results obtained in DMF[1] and some recent investigations performed in water.[19]

Concerning the overall formation constants, the values found in Me_2SO are comparable to those found in DMF,[1] equal values for $CuCl^+$ and slightly lower values for $CuCl_3^-$ and $CuCl_4^{2-}$. But a very large increase of all formation constants is observed in the PC medium: a factor of 10^9 for $CuCl^+$ and about a factor 10^{20} for those of $CuCl_3^-$ and $CuCl_4^{2-}$. One of the observed consequences in the formation curves (Figures 4 and 5) is a wider range of existence for the higher coordinated species. In the Me_2SO system, over 10% of $CuCl_3^-$ is already formed at the $CuCl^+$ maximum level and about 40% when the chloride:copper(II) ion concentration ratio is only 2. For the PC chloro complexes formation curves, the second complex reaches nearly 100% of formation and the third complex begins to form when the molar ratio is equal to 2.

Table V. Absorption Maxima Characteristics of the Electronic Spectra of Copper(II) Chloro Complexes [λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})]

	Me_2SO	PC
Cu^{2+}	287 (3600)	208 (2120)
	820 (33)	790 (18)
$CuCl^+$	294 (4120)	274 (3620)
	908 (89)	840 (49)
$CuCl_3^-$		252 (2690)
	298 (3760)	315 (3750)
	440 (650)	470 (1670)
		890 (86)
	1050 (103)	1080 (69)
$CuCl_4^{2-}$		241 (2240)
	295 (5840)	295 (5710)
	410 (2710)	410 (2650)
	1210 (124)	1200 (113)

However, the stepwise formation constant K_4 of $CuCl_4^{2-}$ in Me_2SO is very low (4 mol L^{-1}). This result is illustrated in Figure 4 as incomplete degree of formation. In the PC system, on the contrary, K_4 is 10^5 mol L^{-1}, consistent with a 100% formation of this complex (Figure 5). This is also predicted by the absorption maxima stabilization at 296 and 410 nm with increasing the chloride ion concentration, even up to the solubility limit.

The stabilization of the chloro complexes was also observed by Ahrland in his study of the chloride solutions of Zn^{2+}, Cd^{2+}, and Ag^+ in water and in Me_2SO.[20] Compared to the aqueous copper(II) chloro complexes for which the β_j's range between 1 and 10, the high stabilization observed in Me_2SO can be related to entropic factors. Solvent molecule must be removed from the solvated copper ion, and this process is easier in solvents like Me_2SO than in highly structured waterlike solvents. This must entail a large entropic change.

But in the PC medium, the complex stabilization is much stronger than in Me_2SO with an increase of the β_j's by a factor of 10^8 for $CuCl^+$, and around 10^{20} for $CuCl_3^-$ and $CuCl_4^{2-}$. Such a large increase must probably be related to an enthalpic factor. PC has a poor solvating power compared to Me_2SO or to DMF; consequently, the complex formation needs less energy for the prior rupture of the cation–solvent bonds, enabling easier ligand substitution than in better solvating solvents. More details about these thermodynamic aspects will be published in a future article.[21]

The d–d transition bands illustrate the structural changes of the copper(II) chloro complex. For each complex the bands position depends upon the coordinated ligand electrostatic field which is evaluated by the crystal field parameter *Dq*. Hypsochromic or bathochromic shifts reflects a *Dq* decrease or increase, respectively. This parameter does also influence the CT bands positions, as pointed out by Jørgensen.[22] This affects the electron-transfer process from the coordinated ligand to the cation. The shifts of the d–d transition bands should parallel those of the charge-transfer bands. Comparison of these bands in Me_2SO and PC for the square-planar copper(II) and monochlorocuprate cations (Table V) indicates a crystal field parameter decreasing from Me_2SO to PC. This

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enables us to classify these solvating solvents in a spectrochemical sequence $Dq(\mathrm{Me_2SO}) < Dq(\mathrm{PC})$. This sequence has also been observed for ocahedral Ni(II) and Cr(III).[23]

The anions are less solvated, and this property is reflected in the very small absorption maxima differences. But the bathochromic shift of about 200 nm is good evidence for a structural change from square-planar to D_{2d} symmetry, even for the trichlorocuprate. The characteristics of the unsolvated $CuCl_4^{2-}$ are identical regardless of the solvents and for this complex the D_{2d} structure is well established. As opposed to aqueous solution, the absorption maxima for the highest complexes are located under 1000 nm, indicating clearly nonconfigurational changes from the square-planar structure.[19]

Summary

The spectrophotometric analysis of the copper(II) chloride solutions in two different solvents, $\mathrm{Me_2SO}$ and PC, shows contributions of the solvents and the solvation to the stability, the electronic spectra, and the structure of the copper(II) chloro complexes. In $\mathrm{Me_2SO}$, the system can be characterized by three species. The absence of the dichloro complex is due to similar donor numbers of the solvent and the ligand.

As in the DMF solutions,[1] the overall stability constants are much higher in both solvents than in water and a drastic increase of the β_j's is found in the propylene carbonate medium. The complexes formed and their stability constants are very similar in DMF and $\mathrm{Me_2SO}$, which are solvents of analogous properties.

The charge-transfer bands of the individual calculated spectra show maxima at 294 and 274 nm for $CuCl^+$, for $CuCl_3^-$ at 298 and 440 nm, and at 252, 312, and 470 nm for $\mathrm{Me_2SO}$ and for PC, respectively; for the unsolvated $CuCl_4^{2-}$, the maxima are identical and located at 295 and 410 nm. Their d–d transition bands are located at 908 and 840 nm for $CuCl^+$, at 1050 and 1080 nm for $CuCl_3^-$, and at 1200 nm for $CuCl_4^{2-}$, in both solvents. These quantitative IR results are given for the first time in these solvents and enable some structural conclusions: $CuCl^+$ is the square-planar $CuCl(\mathrm{Me_2SO})_3^+$ ion in $\mathrm{Me_2SO}$ and $CuCl_3^-$ and $CuCl_4^{2-}$ are flattened tetrahydra with one molecule of $\mathrm{Me_2SO}$ coordinated to copper in $CuCl_3(\mathrm{Me_2SO})^-$ of D_{2d} symmetry.

Registry No. $Cu(\mathrm{Me_2SO})_3Cl^+$, 80340-11-0; $Cu(\mathrm{Me_2SO})Cl_3^-$, 80340-12-1; $CuCl_4^{2-}$, 44000-59-1; $CuCl^+$, 15697-17-3; $CuCl_2$, 7447-39-4; $CuCl_3^-$, 15697-18-4; PC, 108-32-7.

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Use of Ligand Probes in Light Scattering. 3. Preresonance-Enhanced Depolarized Rayleigh Scattering of Dibenzoylmethane and Selected Diorganotin(IV) Complexes

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The depolarized Rayleigh light scattering of cyclohexane solutions of 1,3-diphenyl-1,3-propanedione (dibenzoylmethane) and its neutral, six-coordinate dibutyltin(IV) and dicyclohexyltin(IV) complexes has been studied interferometrically at the wavelengths 514.5, 488.0, and 457.9 nm. The data clearly indicate that significant preresonance enhancement of the central Rayleigh line occurs for the solutions studied. Rayleigh intensities and line shapes for the ligand and complexes support the conclusion that the complexes are monomeric and predominantly of "trans" or distorted "trans" structure. The complexes cannot be "cis".

Introduction

In principle, depolarized Rayleigh scattering can be used to determine the structure of molecules in solution. If a vertically polarized incident light beam is incident on a solution containing molecules with molecular optical anisotropy, γ, the depolarized scattered-light intensity I_{VH} is given by[1]

$$I_{VH} = G_n L_n \gamma^2 \rho g_2$$

where G_n is a geometric factor, L_n a local field correction, ρ the number density of scattering molecules, g_2 is a static orientation correlation parameter, and n is the refractive index of the solution. Estimates of L_n and g_2 may present problems,[2–4] but if these quantities can be calculated or estimated, the relation between the measurable I_{VH} and the structurally sensitive, calculable γ^2 is direct for many relatively simple molecules.

Potentially one should be able to calculate molecular optical anisotropies from bond polarizabilities,[5] and to identify a solute molecule's structure by comparing[6] measured and calculated depolarized scattered-light intensities. In practice there are severe problems with such an approach even if the local field corrections and static orientation correlation parameters are reliably known. One of the most severe problems concerns the difficulty in calculating reliable bond polarizability components and then combining these to provide reasonable molecular optical anisotropies for candidate structures. Values of the molecular optical anisotropy calculated from bond polarizability components have been shown to be uncertain by 1 order of magnitude or more.[7]

More recently, we have noted the possibility of using ligands as optical probes[8] in complexes. If a ligand is highly anisotropic and polarizable, nearly all of the depolarized scattering of an associated complex will be due to the ligands alone. Furthermore, the depolarized scattering will be very sensitive to the relative positions of the ligands if two or more ligands

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