

The ^{15}N chemical shift changes, which are very important, suggest variation in the local paramagnetic contribution to the ^{15}N chemical shifts. An observed correlation between ^{15}N shifts and the wavelength of the electronic transition substantiates this interpretation.

The Fermi contact contribution to the one-bond coupling constants in $J(^{15}\text{N}-^{13}\text{C})$ is likely to be small and explains the low values of 1J compared to the 2J values of the α -anti carbon atom, which are always dominated by the Fermi contact term.³¹ The 2J values of the α -syn carbon atom remain zero.

The ^{15}N isotope effect on the ^{13}C chemical shifts appears rather insensitive to protonation and coordination of H_2vi^- .

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UV-Visible and Infrared Investigation of Tetrahydrofuran-Copper(II) Chloride Solutions

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The formation of copper(II) chloride complexes in the nondissociating tetrahydrofuran solvent was investigated at 25 °C in the UV-visible range from 220 to 550 nm and in the near-IR range from 600 to 1600 nm with copper(II) perchlorate, lithium chloride, and lithium perchlorate mixtures. A large set of absorbance values, covering the whole UV-visible and near-IR wavelength range, was used in the numerical treatment involving matrix rank and combined least-squares and Marquardt methods for the determination of stability constants and individual electronic spectra of the chloro complexes. The THF-copper(II) chloride solutions are characterized by four molecular complexes $\text{Cu}(\text{ClO}_4)\text{Cl}$, CuCl_2 , LiCuCl_3 , and Li_2CuCl_4 for which the overall formation constants are respectively $\log \beta_1 = 11.8$, $\log \beta_2 = 20.3$, $\log \beta_3 = 23.9$, and $\log \beta_4 = 25.7$. The nondissociating solvent properties are reflected in both number and position of the UV and visible absorption maxima of all four molecular species. More specific spectroscopic properties are observed in absorption bands of the tri- and tetrachloro complexes for which significant hypsochromic shifts are obtained compared to analogous complexes characterized in dissociating solvents. In addition, the regular bathochromic shift of the d-d transition bands beyond 800 nm is consistent with a structural change from square-planar to flattened-tetrahedral copper(II) configuration in these complexes.

Introduction

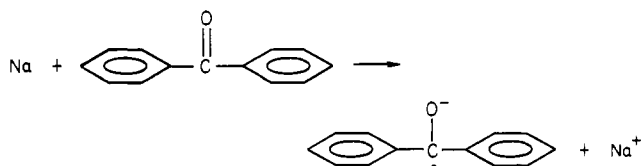
The copper(II) chloride system was recently investigated in several nonaqueous solutions such as DMF,¹ Me_2SO ,² propylene carbonate,² and acetic acid.³ The emphasis was made upon quantitative conclusions established from accurate analysis of spectrophotometric data. Stability constants and individual electronic spectra of the copper(II) chloro complexes were calculated for several theoretical models that are taken into account according to the optical densities matrix rank treatment.⁴ Statistical, spectroscopic, and chemical criteria were used to improve the best representation of the physical reality.

In this work, our investigation concerns the copper(II) chloride mixtures in tetrahydrofuran (THF). The nature of this solvent must induce significant changes in the stability and the electronic spectra of the individual copper(II) chloro complexes compared to the results obtained in dissociating solvents. The dielectric constant of THF is very low (7.6) as it is for acetic acid (6.1) compared to DMF (36) or propylene carbonate (69); one of the consequences of this low value is that ionic association will occur in the medium. On the other hand, the scale of Gutmann's donor numbers indicates for THF a value of 20, intermediate between the values for propylene carbonate (DN = 15) and DMF (DN = 28). The molecular complexes present in this nondissociating solvent should be characterized by thermodynamic and spectroscopic properties different from those established in DMF or propylene carbonate.

As described in our previous papers,^{1,2} the method has its original basis in the numerical treatment of the whole set of spectrophotometric data obtained in the UV-visible and also near-infrared regions. This last wavelength range provides also some structural evidence for the copper(II) configurations. The copper(II) chloride system has to our knowledge never been investigated in THF, and this lack of even qualitative conclusions is certainly due to the difficulty of handling this solvent.

Experimental Section

Reagents. The tetrahydrofuran (Merck, Uvasol) was used after several steps of purification according to the procedure generally used by organic synthesis chemists.⁵ THF decomposes easily with traces of water or oxygen into several products such as 4-hydroxybutyric and 4-hydroxyperbutyric acids, butyraldehyde, and essentially peroxides. The solvent was heated with reflux for 48 h in the presence of an excess of solid potassium hydroxide; salt formation from the acids and polymerization of the peroxides, aldehydes, and other secondary decomposition products are produced and recognized from the orange brown coloring of solid KOH. After distillation at 67 °C under reduced pressure (15 mmHg), the procedure continues by a treatment with sodium and benzophenone. The deep blue color of the solution corresponding to the reaction



indicates a stabilization of the benzophenone anion radical and consequently the absence of peroxides in the solvent. This blue solution is distilled with a weak excess pressure of argon and gives an excellent pure solvent containing less than 100 ppm of water (Karl Fisher test)

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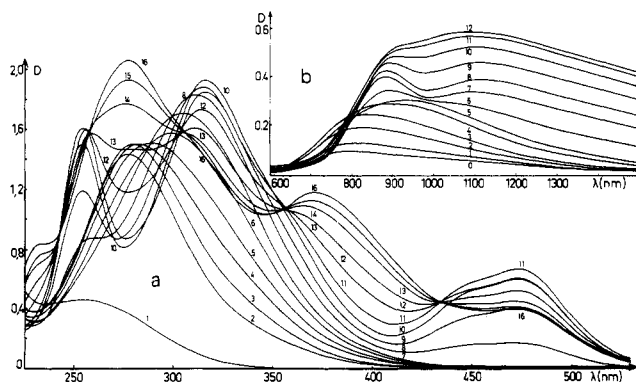


Figure 1. Absorption spectra of copper(II) chloride in THF solutions (spectrum, $10^3[\text{LiCl}]$). (a) UV-visible ($[\text{Cu}(\text{ClO}_4)_2] = 5 \times 10^{-4} \text{ M}$, $l = 1 \text{ cm}$): 1, 0; 2, 0.5; 3, 0.6; 4, 0.7; 5, 0.8; 6, 0.9; 7, 1; 8, 1.2; 9, 1.5; 10, 2; 11, 4; 12, 10; 13, 20; 14, 40; 15, 60; 16, 100. (b) Near-IR ($[\text{Cu}(\text{ClO}_4)_2] = 5 \times 10^{-3} \text{ M}$, $l = 1 \text{ cm}$): 0, 0; 1, 1; 2, 3; 3, 5; 4, 8; 5, 10; 6, 13; 7, 16; 8, 20; 9, 30; 10, 50; 11, 80; 12, 100.

that must be stored in an inert atmosphere.

Lithium chloride and lithium perchlorate (Merck) are recrystallized in acetone and in water, respectively. Their solubility in THF (1.2 M for LiCl, 3.9 M for LiClO₄) is much higher compared to that of alkylammonium salts. Use of lithium salts enables the preparation of high chloride concentration solutions and consequently a large chloride-copper(II) molecular ratio that favors the formation of highly coordinated complexes.

Copper(II) hexahydrate perchlorate (Alfa) was dried at 120 °C for 48 h and used without further purification. A copper(II) solvate preparation was prohibited because of possible explosive mixtures. In the UV-visible investigation we used a constant copper(II) perchlorate concentration at $5 \times 10^{-4} \text{ M}$. This value was brought up to $5 \times 10^{-3} \text{ M}$ for the near-IR measurements. Lithium chloride concentrations increased from 5×10^{-4} (UV-visible) or 5×10^{-3} (IR) to 0.1 M. Standardization and preparation of the samples were made as described earlier.^{1,2}

According to the associative property of this solvent, there is no question of maintaining a constant ionic strength. Nevertheless, lithium perchlorate was added to the mixtures so that the analytical concentrations of LiCl + LiClO₄ remained equal to 0.1 M.

Spectrophotometric Measurements. The absorbance data were obtained with a Cary 17D (Varian) instrument, and temperature was controlled at 25 °C. The numerical treatment was performed in the same way as reported before for all data collected in the UV-visible and near-IR regions. The lower wavelength limit was fixed at 220 nm because of the THF absorption. No significant absorbance changes were observed between 550 and 600 nm and beyond 1600 nm. Consequently, the investigation area was extended in the UV-visible from 220 to 550 nm and in the near-IR from 600 to 1600 nm.

Results and Discussion

Electronic Spectra of the Copper(II) Chloride-THF Solutions. An absolutely pure solvent, essentially free of peroxides and stored in an argon atmosphere, is necessary to obtain the experimental spectra shown in Figure 1. Preliminary absorbance measurements of the copper(II) chloride solutions indicate a satisfactory stability of the mixtures during several hours. The experimental spectra reported in Figure 1 were obtained from THF solutions at constant copper(II) concentration and by increasing regularly the lithium chloride concentration, C , to 0.1 M.

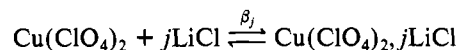
Spectrum 1 corresponds to the copper(II) perchlorate solution without chloride and indicates a broad absorption maximum at 255 nm, characterizing the copper(II) solvate; in the near-IR spectrum, the corresponding maximum is centered at 790 nm already found in water⁶ and in propylene carbonate² with good evidence of a square-planar configuration for copper(II).⁷

Regular bathochromic shifts of the absorption maxima with a small increase of chloride ion concentration (UV-visible spectra 2–6) are consistent with the presence of more than one species in the low ligand concentration mixtures. At higher C values (0.0012–0.004 M, spectra 8–11), the UV absorption maximum continues to shift by 15 nm toward 315 nm. In addition, two other maxima with smaller intensities are observed and stabilize at 252 and 475 nm, respectively; a third complex will be characterized by three absorption maxima.

For higher C values (0.02–0.10 M, spectra 13–16), again the general behavior of the spectra changes; a high-intensity absorption maximum is observed around 280 nm, another one of half intensity at 375 nm, and two others of small intensity around 230 and 475 nm. These absorption bands characterize a different species, the tetracoordinated complex as will be shown later. At this concentration range, five isobestic points appear at 240, 257, 305, 357, and 434 nm.

In the near-IR spectrum, regular bathochromic shifts over 300 nm are observed with increasing ligand concentration but without clearly separated absorption maxima; this behavior is consistent with a continuous overlap of the individual spectral characteristics of the complexes. However, two broad maxima are observed at 880 nm and around 1150 nm (spectra 6–12), corresponding to the higher ligand concentration ranges. As there is no evidence of isobestic points, one of the highest coordinated complexes must be characterized by two absorption band maxima. On the other hand, the absorption intensity is still increasing at the highest ligand concentration level ($C = 0.1 \text{ M}$); this is consistent with an incomplete degree of formation of the most coordinated copper(II) complex.

Number and Stability Constants of the Copper(II) Chloro Complexes. The numerical treatment is performed for $N \times L$ experimental data measured over the whole wavelength range; N and L are the number of solutions and the wavelengths, respectively. In the UV-visible region, $N = 36$ and $L = 34$, and in the IR region, $N = 20$ and $L = 26$. The matrix rank treatment⁴ indicates a minimum of five absorbing species in the mixture, i.e. the solvated copper(II) perchlorate and four chloro complexes. This numerical approach makes possible the choice of theoretical models for which the stability constants β_j and extinction coefficients ϵ_j of the individual complexes are calculated. The determination of the β_j 's is performed by our original computer program, which combines least-squares and Marquardt methods⁸ and concerns the numerical resolution of the equilibria



This general expression takes into account the fact that no ionic complex is present in the associative THF solvent. Lithium perchlorate is not directly involved in the complex formation, but its addition to the mixtures ensures an identical environment of the formed complexes.

As predicted from the matrix rank treatment, the theoretical model [1,2,3] corresponding to three successive mononuclear complexes leads to a very poor fit between experimental and calculated absorbance values with a standard deviation for all 1744 data to 0.20. On the contrary, the [1,2,3,4] model including the tetrachloro complex is the best representation of the physical reality; the β_j 's and the standard deviation (σ) calculated for this model are reported in Table I. It is our assumption that the perchlorate ion is progressively replaced by the ligand with release of lithium perchlorate molecules. In the molecular complexes, LiClO₄ will not participate directly in the primary coordination sphere of copper(II).

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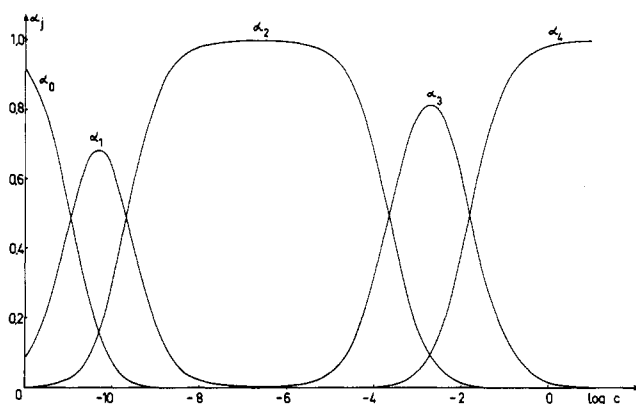
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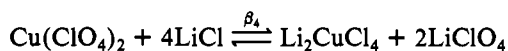
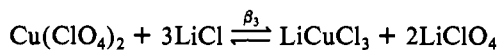
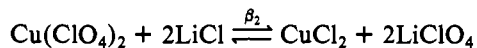
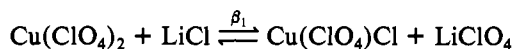
Table I. Stability Constants and Absorption Maxima of the Copper(II) Chloro Complexes in Tetrahydrofuran for the [1,2,3,4] Model

	log β_j	λ_{\max} , nm (ϵ_{\max} , M ⁻¹ cm ⁻¹)		sym
		UV-vis	near-IR	
Cu(ClO ₄) ₂		255 (930)	795 (19)	<i>D</i> _{4h}
Cu(ClO ₄)Cl	11.8	275 (3480)	840 (53)	<i>D</i> _{4h}
CuCl ₂	20.3	305 (3530)	960 (59)	<i>D</i> _{4h}
LiCuCl ₃	23.9	253 (3230)	880 (78)	intermed confign
		318 (3960)	1150 (71)	
		475 (1520)		
Li ₂ CuCl ₄	25.7	230 (1700)		<i>D</i> _{2d}
		277 (4520)	1120 (113)	
		378 (2430)		
		485 (620)		

(σ) 0.044

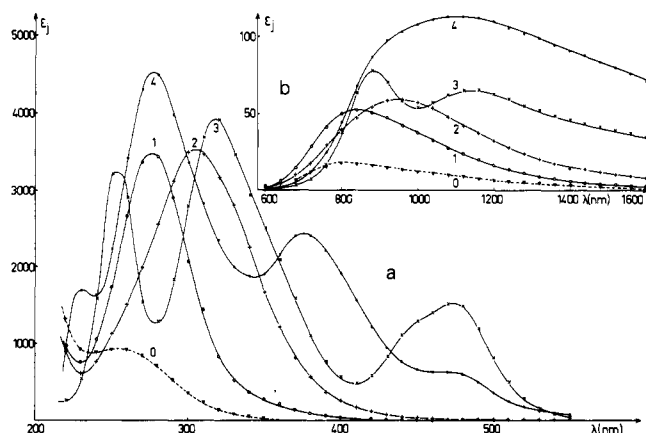
**Figure 2.** Formation curves of the individual copper(II) chloro complexes in 0.1 M (LiCl, LiClO₄)-THF solutions. *c* is the free-ligand concentration.

The d-d transition bands calculated for the individual complexes in the [1,2,3,4] model are consistent with the configuration changes reported in the last column of Table I. Consequently, the equilibria involving the molecular complexes obtained in the THF-copper(II) chloride mixtures are proposed as follows:

**Formation Curves of the Copper(II) Chloro Complexes.**

From the experimental spectra (Figure 1), it is suggested that the existence of the complexes will be related to two distinct ligand concentration ranges: the two first complexes Cu(ClO₄)Cl and CuCl₂ form essentially for 0 ≤ *C* ≤ 0.001 M and, the higher molecular complexes LiCuCl₃ and Li₂CuCl₄, for 0.01 ≤ *C* ≤ 0.10 M. Evidence for this latter concentration range is shown by spectra 11-16 in Figure 1, and the unique existence of the two higher coordinated species is supported by the presence of several isobestic points.

The formation curves represented in Figure 2 confirm the range of existence of Cu(ClO₄)Cl and CuCl₂, well separated from that of LiCuCl₃ and Li₂CuCl₄. The very wide range of existence of CuCl₂ is also correlated with the stepwise formation constant *K*₂ (5 × 10⁸), which is much higher than *K*₃ (4 × 10³) and *K*₄ (63). The degree of formation for CuCl₂ is close to 100%, and the maximum of α₂ is observed at the coordinate corresponding exactly to the chloride/copper(II)

**Figure 3.** Electronic spectra in THF of the copper(II) perchlorate (0) and chloro complexes Cu(ClO₄)Cl (1), CuCl₂ (2), LiCuCl₃ (3), and Li₂CuCl₄ (4): (a) UV-visible region; (b) near-IR region.

concentration ratio equal to 2. The complete formation of CuCl₂ holds as seen in the excellent fit between the experimental spectrum (spectrum, 7 in the UV-visible region and spectrum 5 in the IR region of figure 1; λ_{max} = 305 and 960 nm; ε_{max} = 3480 and 56 M⁻¹ cm⁻¹, respectively) for which the molar ratio is exactly 2 and the calculated spectrum of CuCl₂ (Figure 3; λ_{max} = 305 and 960 nm; ε_{max} = 3520 and 59 M⁻¹ cm⁻¹, respectively). For Li₂CuCl₄, complete formation would only be obtained if the ligand concentration would be increased above 1 M, but this value cannot be determined experimentally because of solubility limits.

Our quantitative conclusions obtained for the [1,2,3,4] model are also supported by the comparison of observed and calculated isobestic points related to the existence of Li₂CuCl₄ and LiCuCl₃ in the higher concentration range. The experimental and calculated wavelengths (240/240, 257/258, 305/304, 357/358, and 434/433 nm) show very little differences and confirm the excellent agreement between theoretical model and physical reality.

Electronic Spectra of the Copper(II) Chloro Complexes. The individual electronic spectra of the complexes were calculated for the [1,2,3,4] model and are represented in Figure 3 for both UV-visible and near-IR ranges.

Cu(ClO₄)₂. Curve 0 in Figure 3 corresponds to the uncomplexed copper(II) perchlorate. The molecular interactions with the solvent result in a specific absorption band with a broad maximum at 255 nm (930 M⁻¹ cm⁻¹). In the near-IR spectrum, the well-known d-d transition band centered at 795 nm (19 M⁻¹ cm⁻¹) corresponds to the square-planar configuration of copper(II), also recognized in other solvents such as propylene carbonate,² acetic acid,³ or water.⁶

Cu(ClO₄)Cl. The monochloro complex is characterized by a single symmetrical absorption band with an intense maximum at 275 nm (3400 M⁻¹ cm⁻¹) (Figure 3, curve 1). The corresponding d-d transition band shows a well-defined maximum at 840 nm (53 M⁻¹ cm⁻¹), still consistent with a square-planar configuration of copper(II).

CuCl₂. The electronic spectrum of the dichloro complex (Figure 3, curve 2) presents a wide and intense absorption maximum located at 305 nm with an extinction coefficient of 3500 M⁻¹ cm⁻¹. As for the monochloro complex no further peak is obtained. In the near-IR region, the calculation leads to a unique broad maximum located at 960 nm (59 M⁻¹ cm⁻¹), consistent with a configuration similar to that of Cu(ClO₄)Cl (*D*_{4h}).

LiCuCl₃. This complex is characterized by two important absorption bands in the UV region with maxima at 253 (3200) and 318 nm (3950 M⁻¹ cm⁻¹) and a less intense maximum calculated in the visible peaks at 475 nm (1520 M⁻¹ cm⁻¹)

(Figure 3, curve 3). The left part of this absorption band maximum is characterized by a slight shoulder at 445 nm, never observed for the same charge-transfer band calculated for the trichloro complex in other solvents. A particular behavior analogous to that found in propylene carbonate² is observed in the near-IR region: the existence of two absorption maxima at 880 (78) and 1150 nm ($71 \text{ M}^{-1} \text{ cm}^{-1}$) can be related to a configurational equilibrium between two trichloro complexes of different structure.

Li₂CuCl₄. The electronic spectrum of the tetracoordinated complex (Figure 3, curve 4) shows an intense UV absorption maximum at 277 nm ($4520 \text{ M}^{-1} \text{ cm}^{-1}$) and another one of feeble intensity at the lower wavelength limit (230 nm, $1700 \text{ M}^{-1} \text{ cm}^{-1}$) in the visible range. The corresponding absorption maximum is located at 378 nm ($2480 \text{ M}^{-1} \text{ cm}^{-1}$), and a significant shoulder is also assigned to this complex at 485 nm ($620 \text{ M}^{-1} \text{ cm}^{-1}$). The near-IR spectral results indicate a wide absorption band with a maximum centered at 1120 nm and an extinction coefficient of $113 \text{ M}^{-1} \text{ cm}^{-1}$: these values are consistent with the d-d band in a noncentrosymmetric copper(II) system as predicted by ligand field spectra calculations.⁷ The tetrachloro complex has a flattened-tetrahedral configuration of D_{2d} symmetry.

Solvent Effects and Copper(II) Solvation Properties. For the first time some specific properties of both stability and electronic spectra of Copper(II) chloro complexes in THF are established. As the complexes are molecular, comparisons are made with the quantitative conclusions obtained in acetic acid³ for which the dielectric constant values and the solvation properties result in some similarities.

Concerning the overall formation constants, the values found in THF are much higher than those found in acetic acid³ ($\log \beta_1 = 3.38$, $\log \beta_2 = 5.57$, $\log \beta_3 = 7.36$, $\log \beta_4 = 7.83$). One of the consequences of this large increase of all formation constants is a wider range of existence for the higher coordinated species illustrated in the formation curves (figure 2). The donor properties of acetic acid are very weak⁹ whereas the Gutmann's donor number is 20 for THF, higher than that of propylene carbonate² ($\text{DN} = 15$). The stability differences found in THF and acetic acid demonstrate that, in associative solvents, the overall formation constants of the molecular copper(II) chloro complexes are a function of the solvent donor numbers. Our results show on the contrary that, in dissociating aprotic solvents, the β_j 's are an inverse function of the Gutmann's donor numbers.^{1,2}

Concerning the electronic spectra of the copper(II) chloro complexes, the influence of this nondissociating solvent is remarkable for both the number and the positions of the ab-

sorption band maxima. Only one maximum is observed for the mono- and dichloro complexes whereas several peaks were calculated for CuCl_2 in propylene carbonate.² The charge-transfer bands for the tri- and tetrachloro complexes are characterized by three absorption maxima with a behavior comparable to that observed in propylene carbonate; the positions of these maxima are very similar for the trichloro complex but undergo for the tetrachloro complex hypsochromic shifts of 10–15 nm for the UV peaks and 25 nm for the visible peak. These spectroscopic properties summarize the main effect of the solvent upon the copper(II) chloro complexes in THF.

The d-d transition bands reflect the configurational changes of the copper(II) complexes. The bathochromic shift observed for the individual spectrum is consistent with a structural evolution from a square-planar to a flattened-tetrahedral configuration of copper(II). The particularity of a splitted maximum observed for the trichloro complex (Figure 3) was already emphasized in the case of the electronic spectrum of the trichloro complex calculated in the propylene carbonate system;² it is our assumption that an equilibrium between two different LiCuCl_3 configurations exists in the mixture.

Summary

Copper(II) chloride solutions investigated in the nondissociating tetrahydrofuran solvent are characterized by four successive mononuclear complexes. Quantitative conclusions in terms of stability, electronic spectra, and structure of the copper(II) chloro complexes were established from the analysis of UV-visible and near-IR spectrophotometric data.

The overall formation constants are found to be much higher than in the molecular acetic acid solutions ($\log \beta_1 = 11.8$, $\log \beta_2 = 20.3$, $\log \beta_3 = 23.9$, $\log \beta_4 = 25.7$).

The charge-transfer bands of the individual calculated spectra have only one maximum for $\text{Cu}(\text{ClO}_4)\text{Cl}$ at 275 nm and for CuCl_2 at 305 nm; three important maxima are assigned to LiCuCl_3 at 253, 318, and 475 nm and four well-separated maxima to Li_2CuCl_4 at 230, 277, 378, and 485 nm.

The d-d transition bands centered at 840 nm for $\text{Cu}(\text{ClO}_4)\text{Cl}$, at 960 nm for CuCl_2 , at 880 and 1150 nm for LiCuCl_3 , and at 1120 nm for Li_2CuCl_4 are quantitatively assigned for the first time for chloro cuprates in THF solutions. These characteristics result in the structural conclusions that, in THF, copper(II) probably has a square-planar configuration in the mono-, and dichloro complexes and a flattened-tetrahedral configuration of D_{2d} symmetry in the tetrachloro complex. The separated absorption maxima corresponding to the trichloro complex are consistent with an equilibrium involving LiCuCl_3 in two different configurations.

Registry No. $\text{Cu}(\text{ClO}_4)_2$, 13770-18-8; $\text{Cu}(\text{ClO}_4)\text{Cl}$, 15230-45-2; CuCl_2 , 7447-39-4; LiCuCl_3 , 38581-59-8; Li_2CuCl_4 , 15489-27-7.

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