

For (2) the space group was uniquely defined by systematic absences as $P2_1/n$. Data for 2 were corrected for absorption, Lorentz, and polarization effects as for 1: minimum, 69.58%; maximum, 99.85%; average 93.58%. Data were collected in the $+h, +k, \pm l$ quadrant. An agreement factor for equivalent reflections was 0.024 (intensity) and 0.020 (F_0). The Ni and As positions were located by direct methods (MULTAN¹⁶). Subsequent difference Fourier maps followed by least-squares refinement were used to locate the remaining atoms. A non-Poisson-contribution weighting scheme was employed for least-squares refinement with an experimental instability factor of $p = 0.02$ (p is defined above).

All atoms are refined normally, but because of the limited number of observed data ($I > 3\sigma(I)$) only the nickel, arsenic, and methyl carbon atoms were refined anisotropically, and the hydrogen atoms were not located. The methyl carbon atoms in particular were chosen for anisotropic refinement because they exhibited greater thermal motion relative to the other carbon atoms, as evidenced by their larger isotropic thermal parameters. The largest peak in the final difference Fourier was 0.53 \AA^{-3} .

(16) Germain, G.; Main, P.; Wolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.

All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS (B. A. Frenz and Associates, College Station, TX 77840). Scattering factors were taken from ref 17. Thermal parameters and tables of observed and calculated structure factors are available.¹⁸

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. F-816) and the National Science Foundation (Grant No. CHE82-11883) for support. The X-ray diffractometer was purchased with funds from the NSF (Grant No. CHE82-058712) and the University of Texas.

Registry No. 1, 100228-85-1; 2, 100228-86-2; $\text{NiCl}_2(\text{PMe}_3)_2$, 19232-05-4; Ni, 7440-02-0.

Supplementary Material Available: Tables of general temperature factors and structure factors for 1 and 2 and least-squares planes and dihedral angles between planes for 2 (43 pages). Ordering information is given on any current masthead page.

(17) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(18) See paragraph at end of text regarding supplementary material.

Contribution from the Laboratoire de Chimie-Physique, Unité Associée au CNRS No. 405, ENSCS, Université Louis Pasteur, 67000 Strasbourg, France

Spectrophotometric Study of Copper(II) Chloride-Trimethyl Phosphate Solutions. Thermodynamic and Spectroscopic Properties of Copper(II) Chloro Complexes in Nonaqueous Solutions

Chisara Amuli, Max Elleb, Jean Meullemeestre, Marie-José Schwing, and François Vierling*

Received June 24, 1985

Copper(II) chloride complexes were investigated spectrophotometrically in trimethyl phosphate solutions. A large set of UV, visible, and near-IR optical density values were computed in the numerical treatment involving least-squares and Marquardt methods. Stability and individual electronic spectra were calculated for several different theoretical models. Four mononuclear chloro complexes are the best representation of the constitution of the trimethyl phosphate solutions, and their overall formation constants are respectively $\log \beta_1 = 7.3$, $\log \beta_2 = 12.4$, $\log \beta_3 = 16.8$, and $\log \beta_4 = 19.4$. Quantitative data obtained for the chlorocuprates in terms of equilibrium constants and extinction coefficients are compared to those we have calculated earlier in six aprotic dipolar solvents. The solvation properties of the copper(II) chloride compounds were generalized by considering both the stability and the electronic spectra of the individual copper(II) chloro complexes. The stabilization of the chlorocuprates in solution is an inverse function of the donor numbers of the solvents. The calculated electronic spectra in these six solvents render it possible to classify the complexes into two groups: the cationic and neutral species for which an original crystal field parameter sequence is found; the anionic species for which the spectra demonstrate less solvation than for the cations. The d-d transition bands indicate configurational changes of copper(II), which is square planar in the cationic and neutral species and flattened tetrahedral in CuCl_4^{2-} , characterized in these nonaqueous media.

Introduction

Copper(II) compounds are of great interest to chemists because of their important use as catalysts in organic synthesis and to theoreticians because of their particular behavior resulting from Jahn-Teller distortion. Copper(II) chloride compounds are so commonly present in synthesis and extraction reactions that the ligand ability of the chloride ion to complexation is often omitted. The determination of the stability, electronic spectra, and structure of the copper(II) chloro complexes would promote a better understanding of the behavior of these complexes, particularly in their interactions with different nonaqueous solvents.

The lack of quantitative data of nonaqueous copper(II) chloride systems has its origin in the difficulty both of handling the experimental procedure and in the interpretation of the measurements relative to a multicomponent equilibrium.

Usual electrochemical techniques are not easily practiced: either restricted copper and ligand concentration ranges would limit the complexation or uncontrollable interferences with the solvent, the supporting electrolyte, and the copper(II) or chloride ion indicating electrode are present. These difficulties have been solved in dimethyl sulfoxide¹ and in propylene carbonate² media where three

mononuclear copper(II) chloride species were identified.

Gutmann and co-workers³⁻⁶ have investigated the complexation of several transition metals such as Co^{2+} , Ni^{2+} , Cu^{2+} , and Cr^{3+} with the chloride ion in different nonaqueous solutions using spectrophotometric techniques. But in general the electronic spectra were interpreted only qualitatively with some estimates of the stability constants of mononuclear complexes.

Some attempts were made to compare the spectroscopic properties of the chlorocuprates in the solid state and in solution; the assignment of the CT and d-d transition bands were essentially given for the tetrachloro complex^{7,8} for which either D_{4h} or D_{2d}

(1) Foll, A.; Ledemzet, M.; Courtot-Coupez, J. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *35*, 41.

(2) Scharff, J. P. *Bull. Soc. Chim. Fr.* **1972**, *1*, 413.

(3) Gutmann, V.; Scherhauser, A.; Ozuba, H. *Monatsh. Chem.* **1967**, *98*, 619.

(4) Baaz, M.; Gutmann, V.; Hampel, G.; Masaguer, J. Rr. *Monatsh. Chem.* **1962**, *93*, 1416; **1963**, *94*, 822.

(5) Hubacek, H.; Stancie, B.; Gutmann, V. *Monatsh. Chem.* **1963**, *94*, 1118.

(6) Gutmann, V.; Hubner, L. *Monatsh. Chem.* **1961**, *92*, 1262.

(7) Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.

symmetry was postulated. But such band assignments are much more difficult to ascertain for ions in solution, because several equilibria are present in the mixture and the absorption changes either for CT or d-d transition bands corresponding approximately to an average absorption of several individual species. The identification of the copper(II) chloro complexes is usually supported by molar ratio considerations and is successful when the corresponding complex has a 100% degree of formation. But these conditions are seldom satisfied and explain consequently the confusion observed in the results published, particularly for the tri- and tetrachloro complexes.⁹

We have already reported the results of our investigation of the copper(II) chloride system in dipolar aprotic solvents such as DMF,¹⁰ Me₂SO and propylene carbonate,¹¹ in acetone,¹² and in nondissociating solvents such as tetrahydrofuran¹³ and acetic acid¹⁴ of very low dielectric constants where the chloro complexes are formal species.

We report here the copper(II) chloride system in trimethyl phosphate (TMP) using a spectrophotometric procedure with an original numerical method that ensures by numerical and chemical criteria the best representation of the constitution of the solution. We consider the complete absorption spectrum of copper(II) chloride solutions from the UV to the near-IR regions, and the numerical treatment concerns a large set of optical density values covering the whole investigated wavelength range. Two essential steps characterize our calculation method: first, the determination of the minimum number of absorbing species from the optical densities matrix rank analysis, based on a method described by Hugus et al.,¹⁵ second, the determination of stability constants and molar extinction coefficients of the individual complexes for each theoretical model compatible with the matrix rank analysis results. The second step of the interpretation is performed by an original program that combines least-squares and Marquardt methods.¹⁶

Compared to the previous solvents, trimethyl phosphate (TMP) has a donor number value (DN = 23) intermediate between the propylene carbonate and dimethylformamide values in the Gutmann's donor number scale.¹⁷ The value of its dielectric constant ($\epsilon = 20.6$) is at the lower limit for which the ion pairing effect could be neglected in the quantitative analysis of the TMP-copper(II)-chloride system.¹⁷

Quantitative data obtained in terms of equilibrium constants and extinction coefficients are compared to those calculated in other solvents.¹⁰⁻¹⁴ An attempt is made to generalize the solvation properties of the copper(II) chloride compounds by considering both stability and electronic spectra of the individual chloro-complexes.

Experimental Section

Reagents. Trimethyl phosphate (Merck) was used after several steps of purification according to the procedure indicated by Gutmann et al.¹⁸ The commercial product contains essentially phosphoric acids, traces of methanol, and some resulting esters of lower molecular weight than TMP. The solvent is heated by reflux in the presence of CaO, which transforms small amounts of phosphoric acids into the corresponding salts. After distillation under reduced pressure in a nitrogen atmosphere, the solvent is treated with Na₂CO₃ to destroy the esters that could not be removed by the first distillation. The final product is obtained by

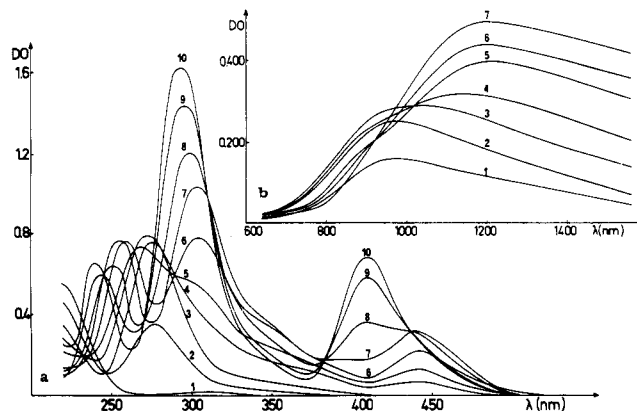


Figure 1. Absorption spectra of TMP-copper(II)-chloride solutions (C in M). (a) UV-visible: [Cu(II)] = 0.0005 M; $l = 0.5$ cm. Spectrum no./10⁴C: 1/0, 2/2.4, 3/5.9, 4/9.9, 5/11.9, 6/14.5, 7/20.0, 8/30.5, 9/59.4, 10/100.3. (b) Near-IR: [Cu(II)] = 0.001 M; $l = 4$ cm. Spectrum no./10³C: 1/0, 2/1.0, 3/2.2, 4/3.0, 5/4.0, 6/5.2, 7/11.4.

distilling the Na₂CO₃-solvent mixture under reduced pressure at around 60 °C and stored in an inert atmosphere. The Karl Fisher test indicates a water content less than 200 ppm. Copper(II) hexahydrate perchlorate (Alfa) was dried at 120 °C for 48 h and used without further purification. A solid copper(II) solvate was not prepared because of possible explosive mixtures. We prepared a 10⁻² M stock solution by mixing directly solid copper(II) perchlorate with the solvent; this solution was standardized as usual with EDTA and murexide as indicator. Storage of the stock solution in an inert atmosphere is necessary to keep a satisfactory copper(II) solvate solution for the period of time used to prepare the copper(II)-chloride mixtures. Tetraethylammonium salts were recrystallized in acetone and used because of its higher solubility than lithium or sodium salts in trimethyl phosphate. Tetraethylammonium perchlorate was added to the medium so that the ionic strength remains constant and equal to 0.1 M.

Copper(II) Chloride Solutions. The copper(II)-chloride-TMP mixtures were prepared in a nitrogen atmosphere (glovebox) in the following procedure: Different quantities of solid tetraethylammonium chloride were weighed directly in 20- or 50-mL flasks so that the chloride ion concentration changes from 5×10^{-4} up to 0.1 M. The copper(II) perchlorate solvate was added by dilution to obtain a constant Cu(II) analytical concentration of 5×10^{-4} M for the UV-visible experiments and 1×10^{-3} M for the near-infrared experiments. The ionic strength was maintained at a constant level of 0.1 M by the addition of tetraethylammonium perchlorate. After rapid mixing of reactants, the solution was transferred under inert atmosphere to the spectrophotometric cell. Zero time (t_0) is taken at the time of the addition of the solvent to the solid chloride. The absorption values corresponding to each sample were taken at different time intervals for 20 min after t_0 . The experimental absorption values corresponding to the Cu(II)-chloride equilibria were obtained by extrapolating at t_0 the absorption values at each wavelength taken at different times after the initial chloride ion-TMP interactions.

This procedure is necessary to eliminate or reduce to a negligible level the solvent-ligand interactions and obtain appropriate spectrophotometric data for a numerical treatment leading to correct thermodynamic and spectroscopic conclusions. Esters of the phosphoric acids will react with nucleophiles and undergo through a substitution mechanism phosphorylation or alkylation.^{19,20} Evidence for this type of interaction could not be found in our study; but looking at the absorption values of Cu(II)-chloride-TMP mixtures, we observed a regular intensity decrease with time, which could be estimated at approximately 10% after 30 min, depending upon the ligand ion concentration. This absorption decrease results clearly from the TMP-chloride ion interactions, related with the nucleophilic attack on the phosphorous atoms producing in the final state a certain amount of methyl chloride; consequently the chloride ion will be consumed and Cu(II)-chloride complexation regularly inhibited. Surprisingly, the TMP-chloride ion interactions were not mentioned in earlier spectrophotometric studies in TMP solutions concerning the complexation by chlorides of bivalent transition metals.⁴ These authors must admit that their conclusions are limited to a qualitative point of view for which evidently the TMP-chloride ion interactions can be neglected.

Apparatus. The absorption measurements were obtained with a Cary 17D spectrophotometer interfaced to a Periferic Zip 30SR printer and

(8) Furlani, C.; Morpurgo, G. *Theor. Chim. Acta* **1963**, *1*, 102.

(9) Katzin, L. I. *J. Chem. Phys.* **1962**, *36*, 3034.

(10) Elleb, M.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *Inorg. Chem.* **1980**, *19*, 2689.

(11) Elleb, M.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *Inorg. Chem.* **1982**, *21*, 1477.

(12) Amuli, C.; Meullemeestre, J.; Schwing, M. J.; Vierling, F., submitted for publication.

(13) Amuli, C.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *Inorg. Chem.* **1983**, *22*, 3567.

(14) Khan, M. A.; Meullemeestre, J.; Schwing, M. J.; Vierling, F. *Polyhedron* **1983**, *2*, 489.

(15) Hugus, Z. Z.; El Awady, A. A. *J. Phys. Chem.* **1971**, *75*, 2954.

(16) Elleb, M.; Meullemeestre, J.; Thomann, J.; Vierling, F. to be submitted for publication.

(17) Gutmann, V. "Coordination Chemistry in Nonaqueous Solutions"; Springer-Verlag: New York, 1968.

(18) Gutmann, V.; Hampel, G. *Monatsh. Chem.* **1963**, *94*, 830.

(19) Clark, V. M.; Todd, A. R. *J. Chem. Soc.* **1950**, 2030.

(20) Thuong, N. T. *Bull. Soc. Chim. Fr.* **1971**, *3*, 928.

puncher. The wavelength ranges were investigated between 220 and 550 nm in the UV-visible region and between 600 and 1500 nm in the near-infrared region. The data were taken each 10 nm in the UV-visible region and each 20 nm in the near-IR region. The differential spectroscopy method implies a reference solution that was always the same during the experiments: 0.1 M tetraethylammonium perchlorate was chosen in order to avoid the chloride ion interaction with the solvent.

Results and Discussion

(1) Experimental Spectra of Copper(II)-Chloride-TMP Solutions. The electronic spectra represented in Figure 1 are related to copper(II)-chloride-TMP mixtures with a constant total solvated copper(II) concentration and a ligand concentration increase up to 0.01 M. Over that ligand concentration value no significant absorption change is observed. The absorption values were corrected as indicated in the Experimental Section in order to minimize the ligand-solvent interactions. The ligand:metal ratio varied from 1 to 20 in the UV-visible range and from 1 to 11 in the near-IR range.

Spectrum 1 (Figure 1) corresponds in both wavelength ranges to solvated copper(II) perchlorate: a small absorption appears at 310 nm comparable to that observed in analogous propylene carbonate solutions;¹³ the d-d transition band is centered at 980 nm, and this appears at higher wavelengths (more than 200 nm) than in most other solvents. When the chloride concentration is increased up to 5.5×10^{-4} M, the absorption maxima shift to 277 nm and correspond probably to the first chloro complex (spectra 2 and 3).

Afterward, the UV absorption band is split into two maxima located around 270 and 305 nm; in the visible region a small absorption appears at 445 nm and increases regularly (spectra 4-7). In this low chloride ion concentration range, absorption spectra 4-6 intersect at 234.5, 265, and 290 nm and define in a primary approximation isosbestic points: consequently, only one equilibrium of two species intermediate of the first and last complexes can be considered.

For the highest chloride ion concentrations, the absorption is characterized by three bands that correspond to the highest coordinated chloro complex: the maxima are located around 240 nm for the lowest and 295 nm for the highest intensity absorption band in the UV range and at 410 nm in the visible range. In the range of ligand concentrations studied, five isosbestic points can be distinguished at 245, 271, 310, 383, and 436 nm (spectra 7-10).

The absorption variation in the near-IR region (Figure 1b) is characterized by a regular bathochromic shift of the maxima with the chloride ion increase. Essentially two absorption zones can be recognized, corresponding to the lower (spectra 1-3) and higher (spectra 4-7) ligand concentration ranges. The experimental near-IR absorption spectra show good evidence of the presence of more than two chlorocomplexes with different copper(II) inner-sphere configurations.

(2) Number and Stability Constants of the Chloro Complexes. The numerical treatment was performed for 384 experimental optical density values obtained from 16 solutions and 24 wavelengths in the UV-visible range and for 209 values obtained from 11 solutions at 19 wavelengths in the near-IR range. The matrix rank treatment^{15,16} applied to these two sets of data indicates the presence of a minimum of four absorbing species corresponding to the copper(II) solvate and three chlorocomplexes.

Consequently, the determination of the stability constants was performed for two theoretical models: [1,2,3] and [1,2,3,4] which concern three and four successive mononuclear complexes respectively and differ only by the addition of the tetrachlorocomplex in the second model. The results reported in Table I show clearly that [1,2,3,4] leads to better numerical results. The standard deviation value calculated for 593 optical density values is significantly lower than the [1,2,3] $\langle \sigma \rangle$ value.

(3) Calculated Electronic Spectra. The individual electronic spectra of the copper(II) chloro complexes in TMP solutions calculated for the [1,2,3,4] model are represented in Figure 2; the spectra are a result of computed extinction coefficients at 24 wavelengths in the UV-visible and at 19 wavelengths in the near-IR range.

Table I. Logarithms of the Overall Stability Constants of the Copper(II) Chloro Complexes in TMP Solutions, Calculated for Two Theoretical Models [1,2,3] and [1,2,3,4]^a

	models	
	[1,2,3]	[1,2,3,4]
CuCl^+ , $\log \beta_1$	5.8	7.3
CuCl_2 , $\log \beta_2$	9.4	12.4
CuCl_3^- , $\log \beta_3$	12.7	16.8
CuCl_4^{2-} , $\log \beta_4$		19.4
$\sigma_{\text{UV-vis}}$	0.220	0.063
$\sigma_{\text{near-IR}}$	0.065	0.048
$\langle \sigma \rangle$	0.170	0.057

^a $\sigma_{\text{UV-vis}}$ and $\sigma_{\text{near-IR}}$ are standard deviations calculated from the UV-vis and near-IR data; $\langle \sigma \rangle$ is the quadratic mean for all data.

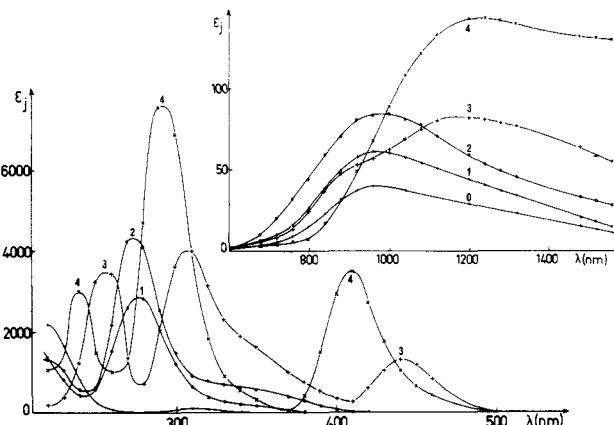


Figure 2. Individual electronic spectra of copper(II) chloro complexes in TMP: $\text{Cu}^{2+}_{\text{solv}}$ (0), CuCl^+ (1), CuCl_2 (2), CuCl_3^- (3), CuCl_4^{2-} (4).

Solvated Copper(II) (Curve 0, Figure 2). The uncomplexed solvated copper(II) in TMP obtained experimentally from a copper(II) perchlorate solution exhibits a spectrum with a maximum located around 215 nm ($\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$), which is slightly hidden by the solvent absorption interfering under 220 nm.

The small band at 310 nm ($\epsilon = 100 \text{ M}^{-1} \text{ cm}^{-1}$) was previously recognized in propylene carbonate solution:¹¹ this is not really surprising as the carboxy and phospho groups probably have comparable solvating properties toward metal ions.

In the near-IR region, the absorption maximum at 980 nm ($\epsilon = 40 \text{ M}^{-1} \text{ cm}^{-1}$) appears at a quite different wavelength than in other solvents (generally 790 nm), but the copper(II) configuration is still square planar (D_{4h} symmetry).²¹

CuCl^+ (Curve 1, Figure 2). This complex has an important absorption band at 277 nm ($\epsilon = 2880 \text{ M}^{-1} \text{ cm}^{-1}$) similar to that calculated in THF medium.¹³ The d-d transition band is characterized by a broad maximum at 980 nm ($\epsilon = 60 \text{ M}^{-1} \text{ cm}^{-1}$) consistent with a copper(II) configuration similar to that of the copper(II) solvate.

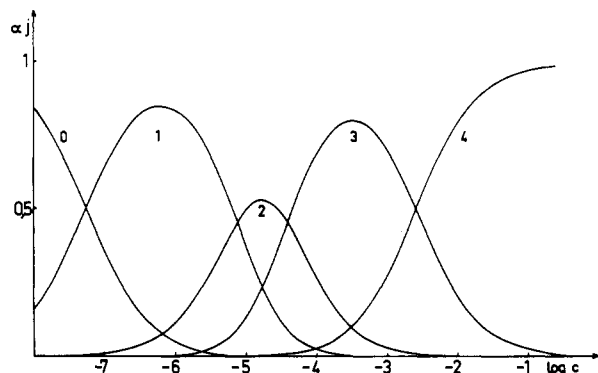
CuCl_2 (Curve 2, Figure 2). A intense absorption maximum at 274 nm ($\epsilon = 4280 \text{ M}^{-1} \text{ cm}^{-1}$) characterizes CuCl_2 in TMP. We observe also for this complex an extended shoulder of feeble intensity around 360 nm. In the near-IR region, the d-d transition band is located at 1000 nm ($85 \text{ M}^{-1} \text{ cm}^{-1}$), but this small bathochromic shift, compared to that of CuCl^+ , is not large enough to imply a configurational change of copper(II) in this complex.

CuCl_3^- (Curve 3, Figure 2). The trichloro complex presents two absorption maxima with similar intensities in the UV, at 257 nm ($\epsilon = 3440 \text{ M}^{-1} \text{ cm}^{-1}$) and 310 nm ($\epsilon = 4060 \text{ M}^{-1} \text{ cm}^{-1}$); this second band is not completely Gaussian, as a slight shoulder (around 350 nm) alters its symmetry. This particularity was also observed in propylene carbonate.¹¹ The complex has another less intense absorption maximum at 440 nm ($\epsilon = 1420 \text{ M}^{-1} \text{ cm}^{-1}$) sometimes observed in the solid state.²² In the near-IR region, we find two

(21) Smith, D. W. *Coord. Chem. Rev.* 1976, 21, 93.

Table II. Logarithms of Overall Stability Constants of the Copper(II) Chloro Complexes in Different Solvents

com- plexes	solvent; DN					
	CP; 15	Me ₂ CO; 17	THF; 20	TMP; 23	DMF; 26.6	Me ₂ SO; 29.8
CuCl ⁺	12.0	8.4	10.7	7.3	4.4	3.4
CuCl ₂	22.7	14.5	20.3	12.3	9.0	5.2
CuCl ₃ ⁻	29.0	19.9	23.9	16.4	12.0	7.3
CuCl ₄ ²⁻	34.0	21.5	25.7	19.4	12.9	7.9

**Figure 3.** Degree of formation of uncomplexed copper(II) (curve 0), the copper(II) mono- to tetrachloro complexes (curves 1-4) in TMP. *C* is the free ligand concentration.

maximums: one is the 890-nm shoulder and the other corresponds to a broad maximum near 1200 nm ($\epsilon = 83 \text{ M}^{-1} \text{ cm}^{-1}$). Again, this particularity was already observed for the tris complex in propylene carbonate¹¹ and could reflect a configurational equilibrium of CuCl_3^- with D_{4h} and D_{2d} symmetry.

CuCl₄²⁻ (Curve 4, Figure 2). The tetrachloro complex has three Gaussian-like absorption band maxima in the UV-visible range with quite different intensities at 241 nm ($\epsilon = 2980 \text{ M}^{-1} \text{ cm}^{-1}$), 293 nm ($\epsilon = 7580 \text{ M}^{-1} \text{ cm}^{-1}$), and 410 nm ($\epsilon = 3500 \text{ M}^{-1} \text{ cm}^{-1}$). The d-d transition band is characterized by a broad maximum at 1220 nm ($\epsilon = 144 \text{ M}^{-1} \text{ cm}^{-1}$). The bathochromic shift compared to the absorption maxima of the lower coordinated complexes is consistent with a configurational change of the copper(II) ion with a flattened-tetrahedral structure in CuCl_4^{2-} .

(i) The validity of the choice of the [1,2,3,4] model is illustrated by the comparison of experimental and calculated isobestic points. Two ligand concentration ranges show the possible existence of experimental isobestic points: between 0.59×10^{-3} and $1.45 \times 10^{-3} \text{ M}$ (spectra 4-6, Figure 1), the absorption curves intersect at 234.5, 265 and 290 nm; at higher chloride ion concentrations, $2 \times 10^{-3} \text{ M} < C < 10^{-2} \text{ M}$, evidence of five isobestic points is found (spectra 7-10, Figure 1) and defines an equilibrium between the two highest coordinated complexes.

The comparison of the calculated coordinates of the isobestic points in the case of the [1,2,3] and [1,2,3,4] models with the experimental data indicates clearly the better correlation in the case of the [1,2,3,4] model.

(ii) The formation curves calculated for the [1,2,3,4] model (Figure 3) indicates incomplete formation of each chloro complex and the presence of several species over the free ligand concentration range investigated. The lower degree of formation of CuCl_2 compared to CuCl^+ and CuCl_3^- can be correlated to the fact that the ionizing and dissociating properties of TMP favor ionic complexes more than neutral species. In the nondissociating solvent THF the results are exactly the opposite, with 100% formation of the dichloro complex and less than 60% of the bis and tris complexes.¹³

The formation curves indicate also that the assumption of a unique equilibrium between CuCl_2 and CuCl_3^- , implying a possible isobestic point in the lower ligand concentration range, is not really exact: in fact, nearly 10% of the other species are always formed

(Figure 3, $-4.4 < \log C < -3.6$). On the contrary, in the highest ligand concentration range, the α_3 and α_4 values justify the existence of the five isobestic points corresponding to the CuCl_3^- and CuCl_4^{2-} equilibrium.

(4) Solvent Effects and Copper(II) Solvation. The results obtained from the copper(II) chloride-TMP solutions, joined to our previously published results¹⁰⁻¹³ are used to study the solvent effects upon the stabilities, the electronic spectra, and the structures of copper(II) chloro complexes in different nonaqueous media. We next will discuss the quantitative data relative to the copper(II) species investigated in our laboratory and listed in decreasing values of the Gutmann donor numbers from Me_2SO (DN = 29.8) to propylene carbonate (DN = 15).¹⁷ The corresponding dielectric constants of the solvents except for THF are intermediate between 20 and 40: these values are consistent with a possible presence of ion pairs in the solution but are high enough to justify the assumption of a negligible ion-pairing effect upon the numerical values of the stability constants or the individual electronic spectra of the chlorocuprates.

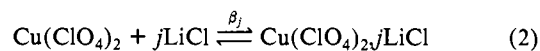
(i) Stability of the Copper(II) Chloro Complexes. The most important parameter calculated with the absorption data is the overall apparent stability constant β_j of the complex of rank *j* in the following complexation reaction:



We mention also three numerical resolution problems of spectrophotometric data that explain the lack of quantitative data in these multicomponent equilibria in the literature: the interdependence of both the parameter β_j and extinction coefficient ϵ_j of the *j* complex, the statistical discrimination of several theoretical models compatible with the experimental observation, and a good procedure to define the β_j 's uncertainties. These difficulties are partly overcome in our work by using an original numerical procedure created by two of us (J.M., F.V.) in which essentially the ϵ_j values are considered as β_j functions.¹⁶

In DMF and Me_2SO media, we demonstrated in previous papers^{12,13} that the [1,3,4] and [1,2,3,4] models were equivalent by considering the numerical results; the absence of the dichloro-complex in the [1,3,4] model was related to comparable donor number of both the ligand and the solvent, promoting autocomplex formation of the mono- and trichloro complexes as postulated by Gutmann.¹⁷ But the CuCl_2 electronic spectrum calculated for the [1,2,3,4] model in DMF and Me_2SO is very similar to those calculated in the other solvents. We used, consequently, this equivalent [1,2,3,4] model calculated in each DMF and Me_2SO medium and allowed an exhaustive discussion of the thermodynamic and spectroscopic properties of the four mononuclear complexes.

In the nondissociating THF solvent, the complexes are molecular and the multicomponent equilibrium can be written



In this complexation reaction, the molecular complexes are found to be ionic aggregates because of the low dielectric constant value of the solvent, also mentioned in anhydrous acetic acid solutions by Popov.²³ This particular organization of the ions in these solvents is even amplified as we maintained an identical environment of the copper(II) species by using constant electrolytic concentrations (0.1 M ($\text{LiCl} + \text{LiClO}_4$)). We may also assume that one or two LiClO_4 molecules will separate in the complexation reactions represented in footnote 27. In fact the β_j values show

(23) Popov, A. I. "The Chemistry of Nonaqueous Solutions"; Lagowski, J. J., Ed.; Academic Press: New York, 1970; Vol. III, 252.

(24) Khan, M. A.; Meullemeestre, J.; Vierling, F., unpublished data.

(25) Parker, A. J. *Q. Rev., Chem. Soc.* **1962**, *16*, 163.

(26) See statement at the end of this article regarding supplementary material. Absorption maxima coordinates in Tables III-VII provide structural conclusions; if the d-d transition bands of the cationic and neutral species are considered, an original spectrochemical sequence for Dq is obtained.

little difference with those obtained for the complexation reactions represented in (2); this can be related to different associations due to the inclusion or exclusion of LiClO_4 .

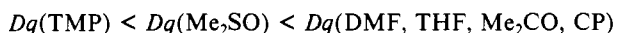
The overall stability constants calculated for the [1,2,3,4] model in the aprotic solvents under investigation are reported in Table II. The stability of copper(II) chloro complexes in these different solvents is an inverse function of the donor number. This result is remarkably correlated by decreasing donor strength of the solvents. Approximated to a linear variation, the $\log \beta_j$ (DN) function is the better verified with the more chloride ions coordinated to copper (II). Deviations to that linearity are observed for the stabilities in THF and in acetone: the THF results can be related to the nondissociating property of that solvent, which should be classified separately in the Gutmann donor numbers scale. Steric factors also interfere and could produce higher stabilization of the complexes.¹⁷ On the contrary, the lower stability of copper(II) chloro complexes in acetone results from the fact that the solvent absorption under 320 nm forbids a good identification of the absorption bands corresponding to the monochloro complex. The simultaneous β_j determination in the [1,2,3,4] model leads to too small a β_1 value and diminishes also the β_j values of the higher coordinated species.

(ii) Electronic Spectra. The individual electronic spectra of solvated copper(II) and the four chloro complexes were characterized by the absorption bands over the whole wavelength range, limited in the lower UV region by the solvent absorption. The d-d transition bands (over 600 nm) provide structural informations about the copper(II) configuration as they depend upon the electrostatic field of the coordinated ligand estimated by the crystal field parameters. Comparison of their shifts enables the ordering of donor solvents in a spectrochemical sequence.

Uncomplexed Copper(II). The spectra obtained from solvated copper(II) perchlorate solutions are very different in the UV region but show similarities in the near IR region (Figure 4, Table III).²⁶

Two absorption bands of very different intensity characterize copper(II) in the UV region: is one located around 208 nm and is partly hidden by the solvent absorption interfering close to 200 nm. The second absorption band, intense (DMF, Me_2SO), very broad (THF), or very low (TMP, CP), is good evidence for the copper(II) solvate in each solvent. The unicity of each electronic spectrum is clearly established, but there is no simple correlation between the solvent macroscopic properties and the copper(II) solvate absorption.

In the near-IR region, the d-d transition bands are the same except in Me_2SO and in TMP where bathochromic shifts of 30 and 190 nm, respectively, are observed. The copper(II) configuration is square planar in all solvents; the crystal field parameter sequence can be written as



Copper(II) Monochloro Complex. CuCl^+ or $\text{Cu}(\text{ClO}_4)\text{Cl}$ in the case of THF has a unique absorption band in the UV-visible as well as in the near-IR region. The CT band is located between 274 (CP) and 292 nm (Me_2SO) (Figure 5, Table IV).²⁶ The very small wavelength shift (18 nm) indicates that the Cu-Cl bond does not produce significant differences for the CT bands, which would permit one to discriminate the solvent effects.

The d-d transition bands are located between 820 and 970 nm, in all cases under 1100 nm. Thus, the copper(II) configuration is square planar in this complex as predicted by ligand field theory.²¹ The spectrochemical sequence induced by the square-

planar monochloro complex is similar to that of uncomplexed copper(II):



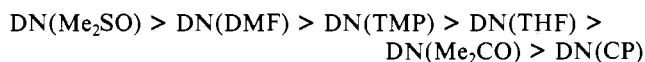
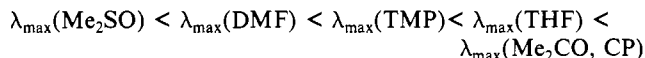
However, the λ_{max} difference observed in the near-IR region in TMP compared to those obtained in the other solvents could also be related to a possibly different structure of the complex in this solvent: this possibility can also be assumed for the TMP-copper(II) solvate described before.

CuCl_2 . In the UV-visible region the electronic spectrum has essentially one absorption peak either around 270 nm (CP, DMF, TMP) or around 300 nm in the case of Me_2SO or THF (Figure 6, Table V). The absorption maximum intensity is nearly solvent-independent. CuCl_2 is also characterized by a small shoulder around 350 nm. Secondary maxima distinguish propylene carbonate from the other solvents.

In the near-IR region, the spectra present a unique maximum with a broad extension in the case of acetone. The shifts of the absorption maxima with the solvents do not indicate configuration changes of copper(II), which is square planar as for the previous cationic species: the crystal field parameter sequence is still the same:



Copper(II) Trichloro Complex. CuCl_3^- or LiCuCl_3 in the case of THF, is characterized by three main absorption bands in the UV-visible region, at 255 nm, around 310 nm, and at 440 or 470 nm for the third maximum (Figure 7, Table VI).²⁶ Little shifts of the second UV (310 nm) and visible (440-470 nm) absorption bands are directly solvent-dependent; the corresponding λ_{max} sequence is correlated by an inverse function of the solvent donor numbers:



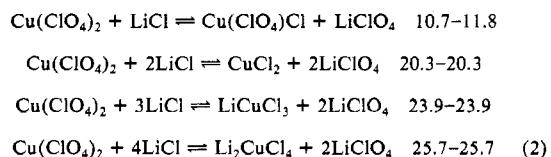
The calculated electronic spectra of CuCl_3^- show in the near IR region a regular evolution correlated with the solvent donor numbers: in CP, Me_2CO and THF ($15 < \text{DN} < 20$), CuCl_3^- has similar d-d transition bands with a well-defined maximum at 880 nm and a broad secondary maximum at 1150 nm, in TMP ($\text{DN} = 23$) the absorption maximum at 880 nm becomes negligible and the 1150 nm one increases slightly, and in DMF and Me_2SO ($\text{DN} = 26.6$ and 30), only one absorption maximum characterizes the d-d transition bands. Consequently, the copper(II) configuration is intermediate between D_{4h} and D_{2d} symmetry.

The similarities of the CuCl_3^- electronic spectra are obtained both in the CT and d-d transition band positions or in their slight but regular shifts depending upon the solvent donor number values. Consequently the solvent effect is less important in the absorption bands of this complex and confirms, as predicted, less solvation for the anions than for the cations or CuCl_2 .

Copper(II) Tetrachloro Complex. This tendency to identical spectra depending upon the solvent is much better observed for the electronic spectrum of CuCl_4^{2-} (or Li_2CuCl_4 in THF) unsolvated in the solvents under investigation. Three major CT bands characterize this anion, an intense one at 294 nm and two others of half-intensity at 241 and 410 nm (Figure 8, table VII).²⁶ A secondary absorption maximum is at 475 nm in acetone and at a minor level in THF. The nondissociating property of THF produces hypsochromic shifts of 11, 17, and 35 nm of the three maximums at 241, 294, and 410 nm respectively: these CT bands were already observed in aqueous solutions with copper(II) perchlorate in 10 M HCl.²⁴

In the near-IR region, the calculated electronic spectra are mainly solvent-independent. Little deviations are observed in THF and also in Me_2CO for which a secondary broad maximum at 900 nm is obtained. The d-d transition bands are comparable for the tetrachloro complex with an absorption intensity over $100 \text{ M}^{-1} \text{ cm}^{-1}$ consistent with a noncentrosymmetric structure.²¹ It cor-

(27) If the LiClO_4 molecule is assumed to separate from the ionic aggregates, the reactions and corresponding log of the stability constants are as follows:



responds to a flattened-tetrahedral configuration of copper(II) with D_{2d} symmetry.

Minor solvation for the anions than for the cations is remarkably confirmed in the unsolvated CuCl_4^{2-} species; similarity of the CT and d-d transition bands in all solvents is quantitatively described.

Summary

Copper(II) complexation by the chloride ion was investigated in trimethyl phosphate solutions, and quantitative conclusions upon the stability and the electronic spectra of CuCl^+ , CuCl_2 , CuCl_3^- , and CuCl_4^{2-} were obtained by using an original calculation method for spectrophotometric data.

The solvent effect on the stability, the electronic spectra, and the structure of copper(II) chloro complexes is discussed for the [1,2,3,4] model in six aprotic dipolar solvents. A good correlation with the solid-state results is obtained in the absorption bands assignment and in the copper(II) configuration, especially for the tetrachloro complex.

The stabilization of the chlorocuprates in solution is an inverse function of the solvent donor numbers (Table II). This effect increases with higher coordination of chloride atoms to copper(II). Complexes are less stable in better solvating solvents: this well-known property is verified quantitatively for the first time for successive mononuclear complexes identified in a large set of aprotic solvents.

The calculated electronic spectra provide the possibility to classify the chlorocuprates into two groups, the first one containing cationic and neutral species, i.e. uncomplexed copper(II) mono-

and dichloro complexes, and the second one the anionic species, i.e. the tri- and tetrachloro complexes.

(i) The first group species have two main absorption bands, in the UV region between 260 and 310 nm and in the near-IR region between 790 and 1000 nm. Little shifts of the CT bands, where uncomplexed copper(II) is progressively substituted to CuCl_2 , are observed but do not correlate with macroscopic properties of the solvents; however, regular bathochromic shifts of the d-d transition bands define for the crystal field parameter Dq an original sequence:



(ii) The electronic spectra variations of the anionic species are less solvent-dependent: this confirms the fact that, in the solvents under investigation, the solvation is less important for the anions than for the cations.²⁵ This property is very well satisfied for the unsolvated CuCl_4^{2-} ion for which the CT and d-d transition bands are remarkably solvent-independent.

(iii) When the ligand concentration increases, the bathochromic shifts of the d-d transition bands indicate configuration changes of copper(II): the structure is square planar for the cationic and neutral complexes and becomes flattened tetrahedral for the tetrachloro complex.

Registry No. Trimethyl phosphate, 512-56-1.

Supplementary Material Available: Complete electronic spectra (CT and d-d transition bands) of uncomplexed copper(II) (Figure 4) and individual copper(II) chloro complexes (Figures 5-8) calculated in six aprotic solvents and absorption maxima coordinates (Tables III-VII) (8 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Physical Chemistry, Hebrew University of Jerusalem, Jerusalem 91904, Israel, and Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Bonding in Zinc Proto- and Mesoporphyrin Substituted Myoglobin and Model Compounds Studied by Resonance Raman Spectroscopy

Jehuda Feitelson[†] and Thomas G. Spiro*[‡]

Received September 24, 1985

Resonance Raman spectra are reported for myoglobin reconstituted with zinc protoporphyrin and mesoporphyrin and for imidazole complexes of zinc protoporphyrin in methylene chloride. The bands are assigned with reference to previous studies of iron protoporphyrin and mesoporphyrin complexes. Coordination of zinc protoporphyrin by imidazole produces a downshift of the porphyrin core size marker frequencies, consistent with the core size expansion observed in five-coordinate zinc porphyrin crystal structures. The five-coordinate frequencies are observed for zinc myoglobin, implying coordination by the proximal histidine residue. The zinc-imidazole bond stretching frequency has been detected in the low-frequency region of the spectra, at 190, 183, and 177 cm^{-1} , for zinc protoporphyrin adducts with imidazole, 4-methylimidazole, and 2-methylimidazole, respectively. The 6- cm^{-1} difference between the last two values is an expression of the steric influence of the 2-methylimidazole ligand. All of these values are significantly below those observed for iron(II) protoporphyrin, implying a significantly weaker bond from imidazole to zinc than to iron. The proteins show a much weaker zinc-imidazole band, at a lower frequency, 148 cm^{-1} . Thus the zinc-imidazole bond in the myoglobin samples appears to be significantly weaker than normal zinc-imidazole bonds, presumably due to geometric constraints in the heme binding pocket.

Introduction

The substitution in metalloenzymes of metals other than the one contained in the native protein provides an opportunity to test the flexibility and restraints of the protein environment in the metal binding pocket. In this study we use zinc proto- and mesoporphyrin as probes of the heme binding pocket of myoglobin (Mb). This oxygen carrier contains iron(II) protoporphyrin in a cavity with a number of noncovalent contacts, the iron ion being coordinated by the imidazole side chain of the proximal histidine, His-93. There is also a distal histidine (His-64) whose imidazole residue is too far to coordinate to the iron but is in a position to

form an H-bond to the outer atom of bound dioxygen.

The heme group is readily extracted from Mb and can be replaced by a variety of metalloporphyrins.¹ In this study we have reconstituted apo-Mb with ZnPP (PP = protoporphyrin IX) and ZnMP (MP = mesoporphyrin IX) and have examined the resonance Raman (RR) spectra of these artificial zinc proteins, as well as of imidazole adducts of zinc protoporphyrin IX dimethyl ester (ZnPPDME) in CH_2Cl_2 solution. The resonance Raman bands of iron porphyrin complexes and of native Mb have been studied extensively.²⁻⁴ The higher frequency porphyrin skeletal

* To whom correspondence should be addressed.

[†] Hebrew University of Jerusalem.

[‡] Princeton University.

(1) Leonard, J. J.; Yonetani, T.; Callis, J. B. *Biochemistry* **1974**, *13*, 1460-1464.

(2) Choi, S.; Spiro, T. G.; Langry, K. C.; Smith, K. M.; Budd, D. L.; LeMar, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 4345-4351.

(3) Choi, S.; Spiro, T. G. *J. Am. Chem. Soc.* **1983**, *105*, 3683.