Solvent Effect on CuCl₂-Pyridine Derivative Complexes: UV-VIS and E.S.R. Study of the CuCl₂-2,4-Dimethylpyridine-Solvent Systems

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Summary. The electronic (400–800 nm; 298.2 K) and E.S.R. spectra (298 K; 77 K) have been measured for CuCl₂-2,4-dimethylpyridine(2,4-Me_2py)-solvent systems (solvents: aliphatic and aromatic hydrocarbons, carbon tetrachloride, chloroform, 1,1,2,2-tetrachloroethane). In all the media CuCl₂ forms electrically neutral strongly distorted six-coordinated complexes, the extent of tetragonality being greater than for analogous complexes with non-a-substituted pyridines. In contrast to aliphatic and aromatic hydrocarbons protic solvents and, unexpectedly, aprotic carbon tetrachloride solvate the CuCl₂-Me_2py complex comparatively strongly, most probably through interactions with the chlorine ligand. The results for 2,4-Me_2py were compared with those for pyridine, 4-ethylpyridine and isoquinoline and discussed in terms of steric effects on solvation. In particular, a-substitution seems to hinder the solvation of the complex by the amine.

Keywords. Solvent effect; Copper(II) chloride complexes; Pyridine derivative complexes.

Lösungsmitteleinfluß auf den Koordinationszustand des CuCl₂ in Lösungen.
Elektronen- und EPR-Spektren der CuCl₂-2,4-Dimethylpyridin-nichtwäßrigen Lösungsmittel-Systeme

Zusammenfassung. Es wurden die Absorptions-Elektronenspektren (400 − 800 nm; 298.2 K) und EPR-Spektren (298 K; 77 K) verschiedener CuCl₂-2,4-Dimethylpyridin(2,4-Me_2py)-Lösungsmittel(L)-Systeme gemessen und mit analogen CuCl₂-Pyridinbasen-L-Systemen verglichen (L = aliphatische und aromatische Kohlenwasserstoffe, Chloroform, Tetrachloromethan, 1,1,2,2-Tetrachlorethylen). In allen Lösungen bildet CuCl₂ mit Pyridinbasen neutrale, stark verzerrt oktaedrische monomere Komplexe. Die Verzerrung nimmt mit a-Substitution zu. Bemerkenswert ist, daß CCl₄ einen Mediumeffekt zeigt, der demjenigen der protischen Lösungsmitteln ähnlich ist; er solvatiert die Komplexe verhältnismäßig stark, möglicherweise an den Chloridliganden. Die Komplexe von a-substituierten Pyridinbasen sind gegenüber Solvatation weniger empfindlich als die übrigen.

Introduction

Our previous work on 2,4-dimethylpyridine (2,4-Me_2py) and 2-methylpyridine (2-$Mepy$) complexes of CuCl₂ [1] have shown that the presence of an *ortho*-substituent in the pyridine ring has a pronounced effect on the structure of the complexes not only in the solid state but also in the pure amine solutions. The different behaviour of adducts with sterically hindering ligands manifests itself in a temperature effect which is opposite to that observed for non-*ortho*-substituted com-

pounds such as pyridine (*Py*) [2], isoquinoline (*IQ*) [3] and 4-ethylpyridine (4-*Etpy*) [4]. The obtained results [1] indicate that steric factors may play a decisive role in the thermochromic effect, as was also shown for another series of the complexes of the same (4N + 2X) coordination type, with N-substituted derivatives of ethylenediamine as N-donors [5–7] (X = univalent anion).

The aim of this work was to investigate whether the *ortho*-substitution in the pyridine ring does influence solvation and to supply more information on the solute-solvent interactions. In view of the known lability of the Cu(II) coordination sphere [8], Cu(II) complexes are particularly suitable for the investigation of the medium effect. Such information for metal complexes in weakly polar solvents is rather scarce in the literature.

Electronic and E.S.R. (298 und 77 K) spectra have been measured for CuCl$_2$-2,4-*Me$_2$py*-diluent systems in the mixed-solvent (2,4-*Me$_2$py*-diluent) in the concentration range X_L = 0.01–1.0, where possible (X_L = mole fraction of 2,4-*Me$_2$py* in the mixed solvent). The diluents: *n*-heptane, cyclohexane, toluene, chloroform and 1,1,2,2-tetrachloroethane have been chosen as representatives of nonprotic aliphatic and aromatic solvents and protic ones. As the protic solvents used are chlorinated compounds, nonprotic carbon tetrachloride and chlorobenzene have been also included.

Experimental

Solid CuCl$_2$(2,4-*Me$_2$py*)$_2$ has been obtained as described in [1]. %Cu: found (*EDTA* titration) 18.18, calc. 18.214; %Cl: found (argentometric titration) 20.3, calc. 20.35.

2,4-Dimethylpyridine was dried by prolonged (a week) standing over KOH and distilled from over molecular sieves (A4). Solvents were purified as described previously [3, 4].

Solutions were prepared by weighing appropriate amounts of stock solutions and solvents. Stock solutions: weighted amounts of the solid complex were dissolved in an appropriate volume of the solvent. The Cu content was checked by *EDTA* titration; standard deviation for 8 samples ⩽ 0.4%. The solutions were prepared immediately before use. Densities were measured pycnometrically with the cathetometer readings. All manipulations were carried out in a dry-box over P$_2$O$_5$.

Electronic absorption spectra were measured on a Beckman u.v. 5270 spectrophotometer and a Perkin Elmer 323 spectrophotometer in thermostatted ($\pm$ 0.1 K) stoppered quartz cells. E.s.r. spectra were recorded with a Radiopan SE/X-201 spectrometer (X-band) at 298 and 77 K. The magnetic field was calibrated by using a Radiopan NMR gausmeter; the g values were determined by comparison with the diphenylpicrylhydrazyl (*dpph*) signal. Conductometric measurements were performed on a Beckman RC-18A bridge.

Results

Electronic Spectra

The spectra (340–800 nm) in pure 2,4-*Me$_2$py* show one broad asymmetric d-d band (λ_{max} = 686 nm, ε_{max} = 128; Fig. 1, curve 1). The position and the shape of the band do not depend on Cu concentration ($10^{-4} - 10^{-2}$ mol dm^{-3}).

a) Aprotic solvents. Dilution of pure amine solutions with chlorobenzene (X_L = 1 − 0.1) or toluene (X_L = 1 − 0.2) does not influence either the position or intensity of the band; addition of *n*-heptane and cyclohexane results in a slight decrease in the intensity (for *n*-heptane at X_L = 0.4 ε_{max} = 124; for cyclohexane at
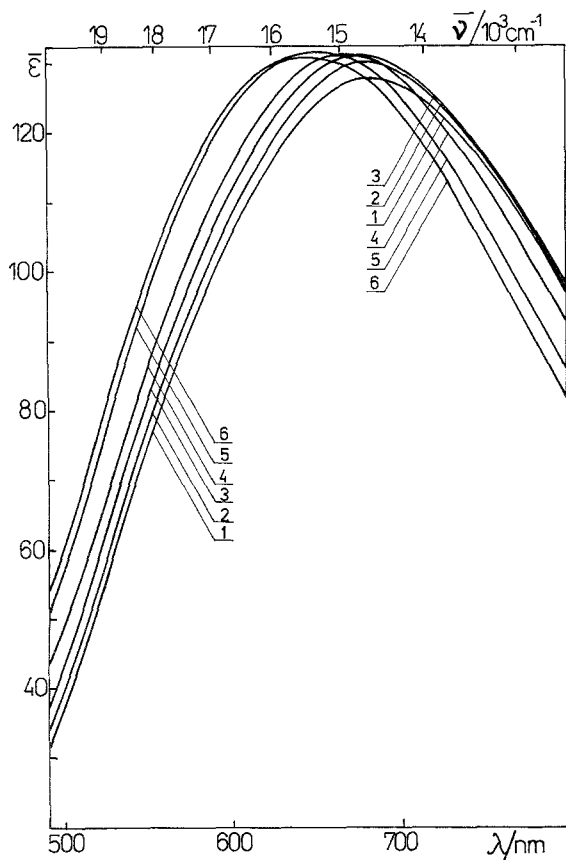
Fig. 1. Electronic spectra for the $CuCl_2$-2,4-dimethylpyridine(L)-carbon tetrachloride system, 298.2 K. $c_{Cu} = 4.35 \cdot 10^{-3}$ mol dm^{-3}; (1): $X_L = 1.0$; (2): $X_L = 0.869$; (3): $X_L = 0.782$; (4): $X_L = 0.557$; (5): $X_L = 0.261$; (6): $X_L = 0.177$
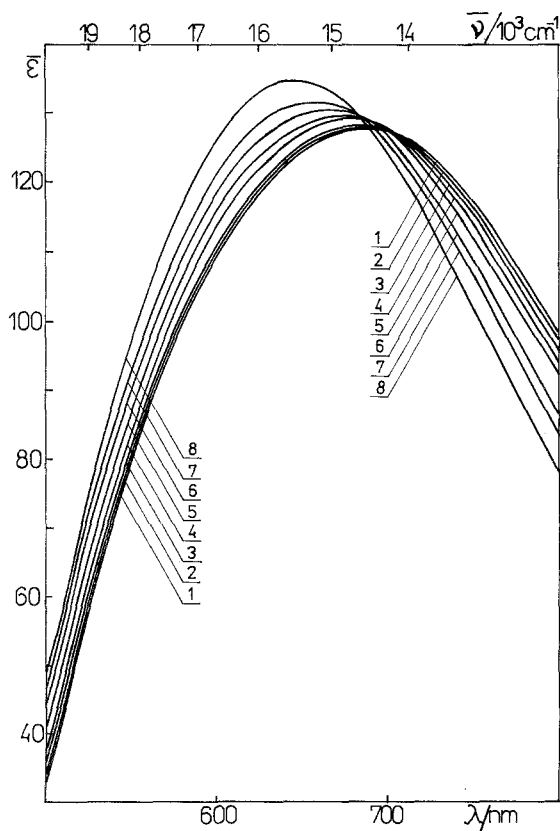

Fig. 2. Electronic spectra for the $CuCl_2$-2,4-dimethylpyridine(L)-chloroform system, 298.2 K. $c_{Cu} = 0.86 \cdot 10^{-3}$ mol dm^{-3}; (1): $X_L = 1.00$; (2): $X_L = 0.881$; (3): $X_L = 0.749$; (4): $X_L = 0.529$; (5): $X_L = 0.429$; (6): $X_L = 0.325$; (7): $X_L = 0.130$; (8): $X_L = 0.017$

Table 1. Solvent effect on the spin Hamiltonian parameters for $CuCl_2$-2,4-$Me_2py(L)$-solvent systems at 298 and 77 K

| Solvent	X_L	$\dfrac{c \cdot 10^3}{\mathrm{mol\,dm^{-3}}}$	g_0	$\dfrac{a_0 \cdot 10^4}{\mathrm{cm^{-1}}}$	g_{II}	$\dfrac{-A_{II} \cdot 10^4}{\mathrm{cm^{-1}}}$	$g_\perp$	$\langle g \rangle$
Pure 2,4-Me_2py	1.00	1.0	2.121	75	2.268	150	2.070	2.136
Chlorobenzene	0.60–0.18	1.0–1.1	2.121	75	2.268	150	2.070	2.136
Toluene	0.62	1.3	2.121	75	2.268	150	2.070	2.136
	0.37–0.20	1.0	2.121	75	2.268	150	2.070	2.136
n-Heptane	0.60–0.30	0.5	2.121	75	2.268	150	2.070	2.136
Cyclohexane	0.60–0.37	0.5	2.121	75	2.268	150	2.070	2.136
Chloroform	0.55	0.9	2.120	79	2.267	184	2.064	2.132
	0.129	0.9	2.119	80	2.250	172	2.059	2.122
	0.106	1.0	2.117	79	2.281	172	2.060	2.134
	0.084	2.0	2.114	77	2.283	171	2.072	2.142
	0.017	0.9	2.114	77	2.297	166	2.071	2.146
1,1,2,2-Tetrachloroethane	0.51	0.88	2.120	79	2.250	151	2.063	2.125
	0.19	0.87	2.120	79	2.242	162	2.053	2.116
	0.03	1.00	2.120	79	2.256	145	2.254	2.121
Carbon tetrachloride	0.78	0.70	2.118	75	2.264	160	2.070	2.135
	0.60	0.70	2.116	76	2.263	163	2.070	2.134
	0.40	0.70	2.115	78	2.261	171	2.071	2.134
	0.20	0.70	2.114	80	2.265	166	2.070	2.135
	0.10	0.70	2.113	81	2.264	152	2.071	2.135
		Error:	[±0.003]	[±5]	[±0.005]	[±4]	[±0.005]	
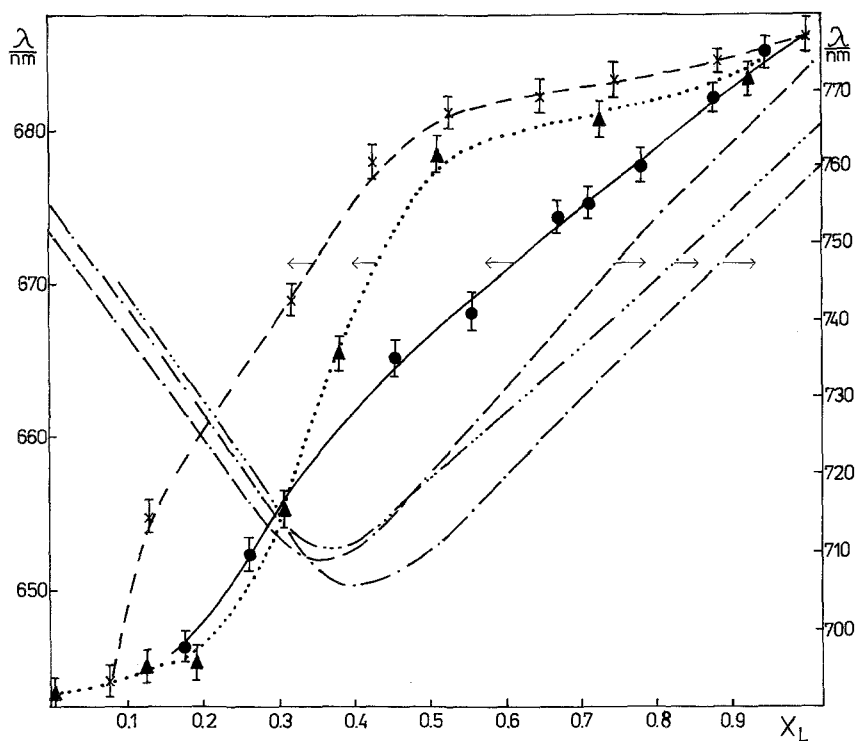
Fig. 3. Dependence of the λ_{max} of the d-d band for $CuCl_2$ solutions in mixtures of pyridine derivative (*L*) with protic solvents on the mixed solvent composition; 298.2 K. $L = $ 2,4-dimethylpyridine: (− × −) chloroform, (·· ▲ ··) 1,1,2,2-tetrachloroethane; (—●—) carbon tetrachloride; $L = $ 4-ethyl-pyridine: (—·—·) 1,1,2,2-tetrachloroethane; $L = $ isoquinoline (··· −) chloroform; $L = $ pyridine (− −·) chloroform [2]
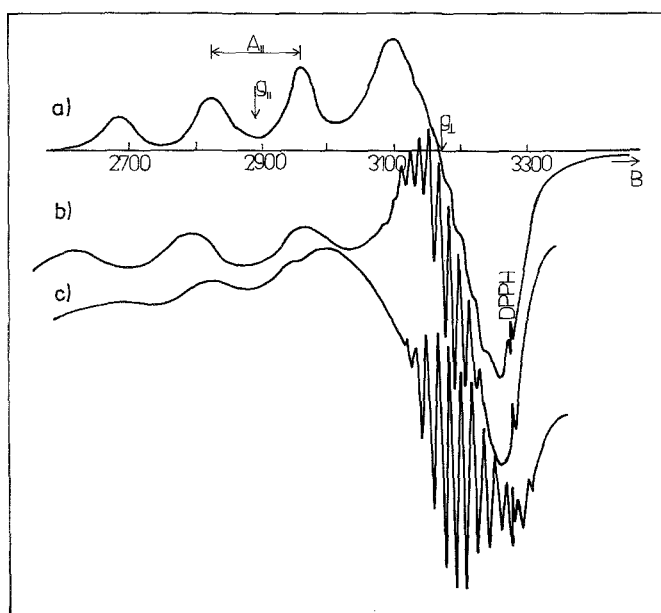

Fig. 4. Frozen solution E.S.R. spectra for $CuCl_2$ in the mixed 2,4-dimethylpyridine(*L*)-chloroform solvent (77 K); $c_{Cu} = 1.2 \cdot 10^{-3}\,mol\,dm^{-3}$; (a) $X_L = 1.00$; (b) $X_L = 0.529$; (c) $X_L = 0.130$

$X_L = 0.38$ $\varepsilon_{max} = 122$) leaving the band position unchanged. In contrast to this behaviour carbon tetrachloride does appreciably affect the spectra: a comparatively strong blue shift ($\simeq 40$ nm) and a slight increase in the ε_{max} value ($\Delta \varepsilon_{max} \simeq +3$) are observed at diluting the pure amine solutions down to $X_L = 0.177$ (Fig. 1).

b) Protic solvents. The effect of chloroform on spectra of $CuCl_2$-2,4-Me_2py solutions is analogous to that observed for carbon tetrachloride though the ε_{max} value increases more rapidly; at $X_L = 0.017$ the $\varepsilon_{max} \simeq +6$ (Fig. 2). A similar blue shift ($\simeq 40$ nm) is also observed for solutions diluted with 1,1,2,2-tetrachloroethane (Fig. 3) the ε_{max} value, however, first decreases to the value 121 for $X_L = 0.4$ and then increases to $\simeq 130$ at further dilution ($X_L = 0.032$).

E.S.R. Spectra

a) The spectra of liquid solutions consist of four broad hyperfine lines with a characteristic m_I–line-width dependence. The spin Hamiltonian parameters for the solutions studied are given in Table 1. They do not depend on the mixed solvent composition except for chloroform and carbon tetrachloride as diluents, where very small but systematic changes in a_0 and g_0 values could be observed by the method of comparison of the spectra recorded in strictly the same conditions of measurements.

b) Frozen solution spectra. Aprotic aliphatic (n-heptane, cyclohexane) and aromatic (benzene and chlorobenzene) solvents do not influence the shape or the spin Hamiltonian parameters characteristic of pure 2,4-dimethylpyridine solutions (Table 1). However the spectra of the solutions diluted with protic solvents or carbon tetrachloride show appreciable changes with the mixed-solvent composition. With increasing amount of chloroform a perturbation of the characteristic dependence of the line-width on m_I can be observed in the high-field part of the spectrum. Simultaneously nine lines of the shf structure begin to develop in the low-field region, which is clearly seen at $X_L \simeq 0.5$ (Fig. 4). Those changes are accompanied by an increase in A_{II} and decrease in g_{II} and $g_\perp$ values. At $X_L = 0.13$ an extra absorption line with well resolved superhyperfine structure appears in the spectrum (Fig. 4c). Further dilution with chloroform results in blurring the superhyperfine structure.

The spectra of mixed solvent solutions containing tetrachloroethane as the diluent undergo similar changes as do those diluted with chloroform. Here also the superhyperfine structure is best resolved at $X_L \simeq 0.5$.

It is interesting that carbon tetrachloride does not behave like other aprotic diluents. It influences the E.S.R. spectra in the same way as do the protic solvents: with an increase in CCl_4 concentration in the mixed solvent we observe narrowing of the band components and developing the superhyperfine structure in the low-field part of the spectrum while in the parallel region broadening of the lines takes place. This changes are accompanied by variation in the spin Hamiltonian parameters (Table 1).

Discussion

Solutions in Pure 2,4-Dimethylpyridine

The low conductivity ($\chi < 10^{-7} \Omega^{-1} cm^{-1}$ at Cu concentrations $\simeq 10^{-2}$ mol dm^{-3}) indicates that no electrolytic dissociation occurs even in comparatively polar pure

amine solutions. The position ($\lambda_{max} = 686$ nm) and intensity ($\varepsilon_{max} = 128$) of the d-d band (Fig. 1, curve 1) is consistent with the structure of strongly elongated tetrahedron, also suggested by E.S.R. measurements. The position and intensity of the d-d band are analogous to those exhibited by $CuCl_2$ solutions in the similar α-substituted pyridine base, 2-methylpyridine [1], but they markedly differ from the spectral characteristics of $CuCl_2$ in 4-ethylpyridine [4], pyridine [9] and iso-quinoline [3] (λ_{max} 760, 775 and 765 nm; ε_{max} 140, 140, 170, respectively).

From the E.S.R. and electronic spectra of $CuCl_2$ in 2,4-dimethylpyridine solutions it appears that Cu ion coordinates four amine ligands in the basal plane and two chlorines at the apical sites [1], the approach of the apical ligands being hindered by the α-methyl groups.

Aprotic Solvents

From the fact that aliphatic hydrocarbons (n-heptane, cyclohexane) and aromatics (toluene, chlorobenzene) do not show appreciable effects on electronic or E.S.R. spectra we can conclude that mere variations in the activity coefficients of the amine in the mixed solvent do not provoke substantial changes in the first coordination sphere of the Cu(II) ion. It is of interest that $2,4\text{-}Me_2py$ itself behaves differently in the mixtures with the two types of diluents: while the low ($\simeq 0$) heats of mixing of $2,4\text{-}Me_2py$ with aromatics [10] suggest nearly ideal mixtures and therefore comparable intermolecular interactions, much higher values of heats of solution of $2,4\text{-}Me_2py$ in aliphatics ($\Delta H^\infty \simeq 7$ kJ mol^{-1} [10]) indicate that amine-amine interactions are much stronger than those between the amine and the diluent. Thus in the mixtures with the aliphatics the activity coefficients of $2,4\text{-}Me_2py$ should vary strongly with amine concentration (for pyridine in its mixture with n-heptane $\gamma_{py} \cong 2.8$ at $X_{py} \cong 0.1$ [11]) while in aromatics they are most probably constant ($\gamma \simeq 1$). From these facts it may be concluded that 2,4-dimethylpyridine cannot strongly solvate the complex; if it did so then its varying activity in the solution should influence the ligand field of the flexible Cu(II) complex and hence influence the electronic and E.S.R. spectra.

With this respect the $CuCl_2\text{-}2,4\text{-}Me_2py$ aprotic diluent systems behave differently from analogous solutions containing pyridine derivatives without an α-substituent: dilution of $CuCl_2$ in 4-ethylpyridine [4] and isoquinoline [3] solutions with aprotic solvents results in an apparent decrease in ε_{max} of the d-d band. This effect does not, most probably, involve any drastic changes in the first coordination sphere of the complex because the position and the shape of the band remain essentially the same. It rather seems to reflect small variations in the bond parameters caused by changes in outer-sphere coordination, the last one being strongly influenced by amine activity in the solutions. The extent of the solvent effect observed for 4-ethylpyridine and isoquinoline as ligands depends on the kind of the aprotic diluent; it is interesting that it parallels the sequence found for ΔH of solution of the pure amines in these solvents [15]; aliphatic hydrocarbons > cyclohexane > benzene $\gtrsim$ chlorobenzene. It also shows nearly linear variation with the solubility parameter of the solvent, δ (Fig. 5). All these facts suggest that activity of the pyridine base in the solution plays a crucial role in solvating the complex when pyridine derivatives *without* an α-substituent are considered. However, for 2,4-dimethylpyridine such an effect is very small and only observed for aliphatic hydrocarbons. It is thus
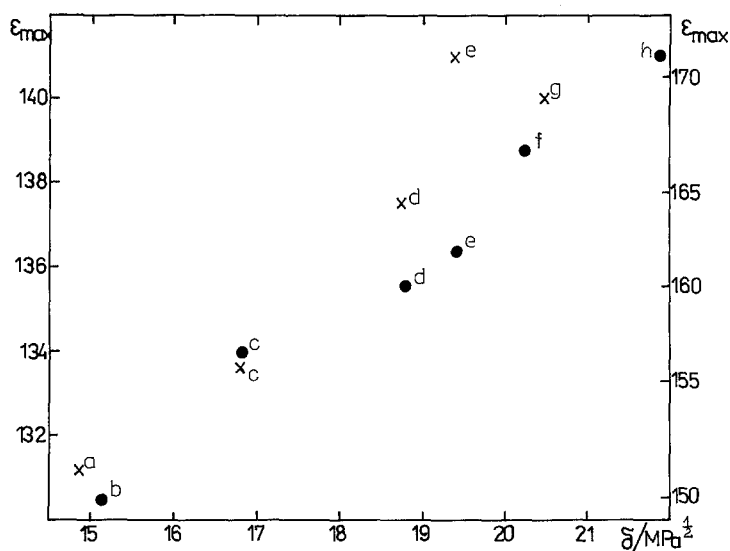
Fig. 5. Dependence of ε_{max} on the solubility parameter of the solvent, δ, for the visible spectra of the mixed solvent: pyridine base (L)-aprotic diluent; $X_L = 0.5$: ($\times$) $L = 4$-ethylpyridine (left ordinate); (●) $L =$ isoquinoline (right ordinate). Diluents: (a) n-hexane, (b) n-heptane, (c) cyclohexane, (d) benzene, (e) chlorobenzene, (f) *ortho*-dichlorobenzene, (g) 4-ethylpyridine, (h) isoquinoline (δ estimated as $\simeq \delta$ for quinoline)

highly possible that the a-methyl group not only hinders the interactions of the Cu ion with the apical ligands [1] but also the solvation of the complex by amine molecules.

Protic Solvents

The blue shift observed on dilution of the solutions of $CuCl_2$ in pure 2,4-dimethylpridine with chloroform and 1,1,2,2-tetrachloroethane strongly suggests that further elongation of the $CuCl_2(2,4\text{-}Me_2py)_4$ octahedra takes place. Indeed, loosening of the axial Cu-Cl bonds should result in lowering of the energy of d_{xz} and d_{yz} orbitals and, most probably, in shortening Cu-N distance in the basal plane; this in turn should rise the energy of the $d_{x^2-y^2}$ orbital. Both effects lead to an increase in the energy of the $d_{xz} \rightarrow d_{x^2-y^2}$ transition which is responsible for the maximum in the visible region of the electronic spectrum [12, 5].

The increased tetragonality evidenced by electronic spectra is supported by the E.S.R. results: we observe developing of the superhyperfine structure (9 lines) in frozen solutions of $CuCl_2$ in 2,4-Me_2py when the concentration of the protic diluent is increased (Fig. 4 b and c). This is what should be expected when the Cu-N distance in the basal plane decreases. The elongation of the axial bond should be accompanied by lowering of g_{II} and $g_\perp$ values [13, 14]. The data in Table 1 show that this is really the case when we dilute pure amine solution down to about $X_L \simeq 0.1$. At lower amine concentrations we observe, however, an increase in the values of g in the frozen solution spectra while the visible d-d band and g_0 values (298 K) seem to remain essentially unchanged. The inconsistency of the results obtained for the diluted solutions ($X_L < 0.1$) by the electronic and E.S.R. method

at 298 K and those for frozen solutions (E.S.R. spectra at 77 K) can be easily explained by the temperature effect on molecular parameters of the complex. The discrepancy between g_0 and $\langle g \rangle$ values (Table 1) indicate that such an effect really exists. As shown in [1], cooling the CuCl$_2$-2,4-Me_2py solutions results in shifting the d-d band to lower energies in full agreement with $\langle g \rangle$ values being greater than g_0. Both effects suggest an elongation of the Cu-N distance in the basal plane. A possible explanation for such behaviour may be hindering the motions of the ligands at lower temperatures which favours a closer approach of the axial ligand to the central ion and increases the repulsions in the basal plane where four a-substituted rings are coordinated.

The revealed temperature effect on electronic and E.S.R. spectra is just opposite to the solvent effect, observed on diluting pure 2,4-Me_2py solutions with protic solvents. It is conceivable that at low temperatures both effects operate, the latter prevailing at higher amine concentrations while the first one is effective in strongly diluted solutions. The disappearance of the superhyperfine structure in frozen solution spectra when X_L falls below 0.1 seems to support the suggestion that now the interactions between the Cu ion and basal amine ligands become weaker.

In discussing the coordination pattern of CuCl$_2$ in the mixtures of 2,4-Me_2py with protic solvents two assumptions seem to be applicable: (i) no exchange of the ligands for the solvent takes place on dilution, i.e. four amine molecules occupy the basal position of the complex, at least down to $X_L \simeq 0.1$ (nine lines in the frozen solution E.S.R. spectra); (ii) the solvation of the complex by $amine$ molecules is not strong enough to cause appreciable spectral changes (see the discussion on aprotic diluents). Thus the variation in the extent of tetragonality would, most probably, arise from the interactions between the complex and the protic solvent at apical sites, probably through a H$\cdots$Cl hydrogen bond.

Similar interactions are also conceivable in the case of complexes of CuCl$_2$ with pyridine bases which have no a-substituents, though here solvation by amine molecules cannot be neglected, as discussed before. Both effects should lead to tetragonal distortions in solutions diluted with the protic solvent. In fact, a blue shift, analogous to that observed for 2,4-Me_2py, appears for 4-ethylpyridine, pyridine [2] and isoquinoline complexes over the range of $X_L = 1 - 0.4$. On further dilution, however, the energy of the d-d band strongly decreases (Fig. 3) as also do the ε_{max} values. This behaviour may reflect the replacement of amine molecules in the outer coordination sphere by protic solvent which can form hydrogen bonds with the π-electron system of the pyridine ring.

Carbon Tetrachloride

Contrary to expectation, carbon tetrachloride does not behave like aprotic solvents – it seems to represent the way of interaction characteristic of chloroform and 1,1,2,2-tetrachloroethane, though the observed effects are less pronounced. No hydrogen bonds may however account for these interactions though carbon tetrachloride, like other protic solvents, acts as an electron acceptor using most probably its σ^* orbitals. As was shown by Gomel [16], Cl behaves like H towards typical electron donors, and in particular towards pyridine. By analogy, such interaction has been called "halogen bonding" [16]. There are also suggestions that outer sphere coordination of alkyl halides to MCl_2L_n complexes may involve

donor-acceptor interactions between the pair of halogen atoms [17]. Such a model seems to explain best the spectral effects observed for $CuCl_2$-2,4-dimethylpyridine solutions diluted with carbon tetrachloride, if, by analogy to protic solvents, we assume that carbon tetrachloride solvates the complex stronger than does 2,4-dimethylpyridine and the solvation sites are mainly chlorine ligands (see point c).

Acknowledgments

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