# Equilibria between Mono- and Bi-nuclear Complexes in $Cu(O_2CMe)_2$–Pyridine Derivative–Diluent Systems. The Influence of the Amine Ligand Basicity

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$Cu(O_2CMe)_2$–pyridine derivative (L) complexes [L = pyridine (py), 2-methylpyridine (2Me-py), 3,4-dimethylpyridine (3,4Me$_2$-py), and isoquinoline (i-quin)] have been studied by u.v. and e.s.r. spectroscopic methods. The results are interpreted in terms of the equilibrium $2[Cu(O_2CMe)_2L_2] \rightleftharpoons [Cu_2(O_2CMe)_4L_2] + 2L$. The relative stability of the binuclear complexes in solution strongly depends on the basicity and steric properties of the amine ligands, the tendency for adopting binuclear structures increasing in the order: 3,4Me$_2$-py < i-quin $\lesssim$ py < 2Me-py.

While a great deal of experimental and theoretical work has been focused upon the structure and magnetic behaviour of $Cu^{II}$ carboxylates in the solid state, the solution studies have been reported only briefly.[1–5] It was found by cryometric and spectroscopic methods that complexes of $Cu^{II}$ carboxylates retain the binuclear structure of the solid compound in such solvents as chloroform,[2] cyclohexane,[2] and benzene;[1,2] there is, however, some evidence from magnetic susceptibility measurements that copper(II) acetate complexes in pure pyridine are mononuclear.[6]

Our previous results have shown that solutions of $Cu(O_2CMe)_2$ in 3-chloropyridine contain electrically neutral mono- and bi-nuclear complexes in equilibrium.[7] It thus seemed interesting to investigate the factors influencing such equilibria, particularly those which involve electronic properties of the ligands.

In this work the influence of the basicity of the electrically neutral ligand on the stability of the structure adopted in solutions has been investigated for a series of copper(II) acetate complexes with the following pyridine derivatives: pyridine (py), isoquinoline (i-quin), 2-methylpyridine (2Me-py), and 3,4-dimethylpyridine (3,4Me$_2$-py) ($pK_a$ = 5.23, 5.40, 5.97, and 6.46 respectively). The data for 3-chloropyridine [7] (3Cl-py) are also included for comparison. The pyridine series is especially suited for such studies because of the easy control of the electron density on the donor atom without substantially changing the mechanism of the ligand–metal interaction. In order to control the amine activity in the solutions a mixture of the amine with a non-reacting solvent has been used. We have chosen chlorobenzene as the diluent because it forms nearly ideal mixtures with pyridine derivatives.[8]

## Experimental

*Preparation of Solid Complexes* $[Cu_2(O_2CMe)_4L_2]$.—(a) L = 2-*Methylpyridine*. $Cu(O_2CMe)_2{\cdot}H_2O$, recrystallized twice from water acidified with a few drops of acetic acid, was dissolved in pure 2-methylpyridine at 310 K and the almost saturated solution cooled to 265 K. The resulting blue precipitate, recrystallized from 2-methylpyridine, was dried over anhydrous $H_2SO_4$ *in vacuo* to yield green crystals {Found: Cu, 23.0. Calc. for $[Cu_2(O_2CMe)_4(2Me\text{-}py)_2]$: Cu, 23.15%}.

(b) L = *Pyridine or* 3,4-*dimethylpyridine*. Crystals were obtained by the above procedure and dried over $P_2O_5$ under reduced pressure {Found for L = py: Cu, 24.2. Calc. for $[Cu_2(O_2CMe)_4(py)_2]$: Cu, 24.35%. Found for L = 3,4Me$_2$-py: Cu, 22.0. Calc. for $[Cu_2(O_2CMe)_4(3,4Me_2\text{-}py)_2]$: Cu, 22.00%}.

(c) L = *Isoquinoline*. As cooling of a hot saturated copper(II) acetate solution in pure isoquinoline down to the m.p. of the amine (298 K) yielded only minor quantities of the precipitate, the complex was obtained by diluting the saturated solution with benzene. The resulting green precipitate was recrystallized by this procedure and dried over $P_2O_5$ {Found: Cu, 20.4. Calc. for $[Cu_2(O_2CMe)_4(i\text{-}quin)_2]$: Cu, 20.25%}.

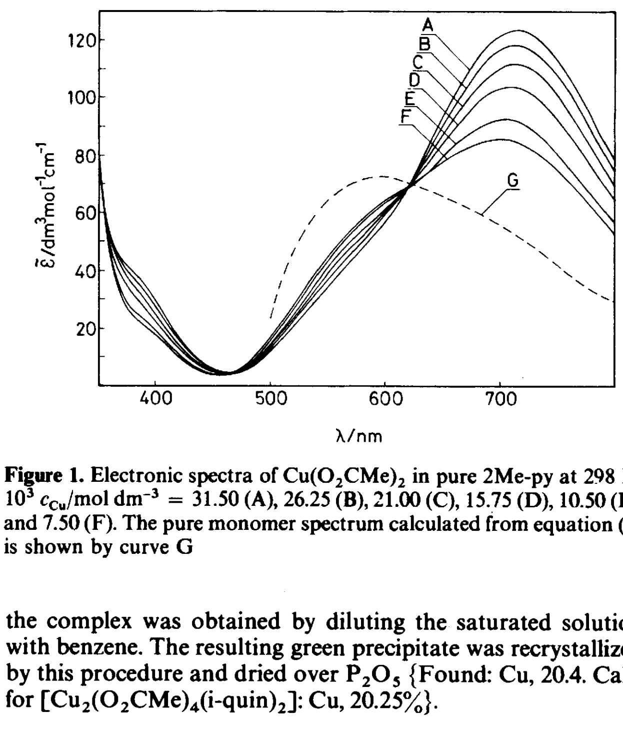

Figure 1. Electronic spectra of $Cu(O_2CMe)_2$ in pure 2Me-py at 298 K. $10^3\,c_{Cu}/mol\,dm^{-3}$ = 31.50 (A), 26.25 (B), 21.00 (C), 15.75 (D), 10.50 (E), and 7.50 (F). The pure monomer spectrum calculated from equation (3) is shown by curve G

*Materials*.—Chlorobenzene was purified as previously described.[7] The amines were dried by standing over KOH and distilled from molecular sieves (4A) *in vacuo*.

*Measurements*.—Electronic spectra (340—800 nm) were recorded on Perkin-Elmer 323 and Beckman u.v. 5270 spectrophotometers in thermostatted 0.5-, 1-, 2-, and 4-cm stoppered cells at 298 ± 0.1 K. E.s.r. (*X*-band) spectra (298 and 77 K) were measured on a Radiopan SE/X-201 spectrometer with diphenylpicrylhydrazyl (dpph) as a field calibrant. Density measurements and preparations of the solutions have been described elsewhere.[8] Copper analyses were obtained by the standard ethylenediaminetetra-acetate titration procedure. All manipulations were carried out in a dry-box, over $P_2O_5$. The measured[8] electrolytic conductivity of the solutions was less than $10^{-7}\,\Omega^{-1}\,cm^{-1}$ at Cu concentrations of $10^{-3}\,mol\,dm^{-3}$.

## Results and Discussion

*Electronic Spectra*.—(a) $Cu(O_2CMe)_2$–2-*methylpyridine*. The spectra of $Cu(O_2CMe)_2$ in pure 2-methylpyridine (Figure 1) show a marked dependence on the $Cu^{II}$ concentration (the range

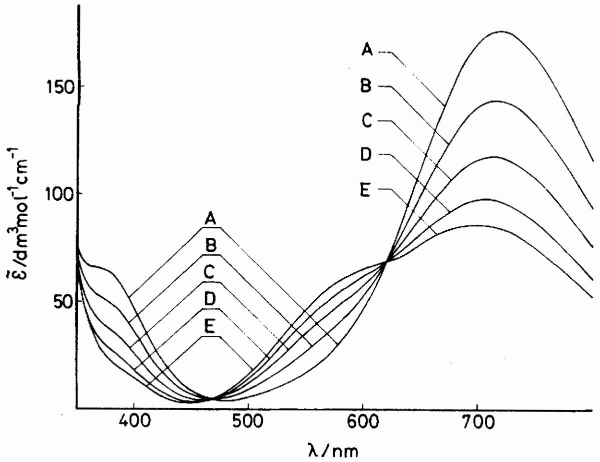

**Figure 2.** Electronic spectra of $Cu(O_2CMe)_2$ in mixed 2Me-py–chlorobenzene solvent at 298 K; $c_{Cu} = 7.50 \times 10^{-3}$ mol dm$^{-3}$. $x_{2Me\text{-}py}$ = 0.180 (A), 0.380 (B), 0.520 (C), 0.805 (D), and 1.000 (E)

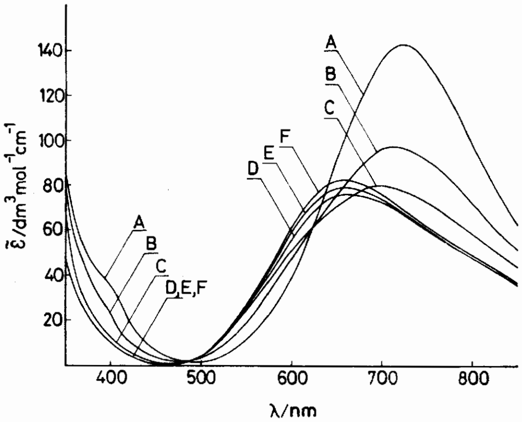

**Figure 3.** Electronic spectra of $Cu(O_2CMe)_2$ in mixed py–chlorobenzene solvent at 298 K; $c_{Cu} = 2.27 \times 10^{-3}$ mol dm$^{-3}$. $x_{py}$ = 0.123 (A), 0.240 (B), 0.351 (C), 0.680 (D), 0.835 (E), and 1.000 (F)

of concentrations studied was $1 \times 10^{-3}$—$3.15 \times 10^{-2}$ mol dm$^{-3}$; Figure 1 shows one set of solutions, in pure 2Me-py). This behaviour provides evidence for an equilibrium between complexes differing in the number of Cu atoms. Taking into account (*i*) the low probability of formation of higher polymers in the solutions containing low $Cu^{II}$ concentrations and (*ii*) the presence of only two absorbing species (clear isosbestic points at 340, 472, and 620 nm), we can assume that the equilibrium only involves mono- and bi-nuclear forms of the Cu complexes.

The bands which develop with increasing Cu concentration must arise from the binuclear species. This assignment is supported by the positions of the maxima ($\simeq$ 380 and $\simeq$ 720 nm) and their relatively high intensity, both being typical of binuclear carboxylate complexes.[3,9] Accordingly, the slight increase in absorption in the 472—620 nm region with decreasing Cu concentration must be due to the weakly absorbing centrosymmetric mononuclear species. As the very low conductivities of the solutions (Experimental section) imply that the solutes are electrically neutral, the complexes must contain two undissociated $O_2CMe^-$ groups per Cu atom. They should also co-ordinate amine molecules in the amine-containing solutions. If it is assumed[2,3] that both the mono- and bi-nuclear complexes complete their co-ordination spheres with two amine ligands, the equilibrium (1) can be written. If

$$2[Cu(O_2CMe)_2L_2] \rightleftharpoons [Cu_2(O_2CMe)_4L_2] + 2L \quad (1)$$

(1) is correct then increasing the amine activity in a mixed solution (pyridine derivative–chlorobenzene) should result in a shift of the equilibrium to the left which in turn should manifest itself in spectral changes analogous to those accompanying the decrease in Cu concentration. Figure 2 shows that this is indeed the case. Moreover, the clear isosbestic points evidence that, in spite of the known plasticity of the $Cu^{II}$ environment,[10] the stoicheiometry of the complexes remains unchanged over the whole range of the mixed-solvent compositions.

The equilibrium constant for equilibrium (1) may be given by equation (2) if we assume that activity coefficients of the

$$K = \frac{[Cu_2(O_2CMe)_4L_2]\cdot a_L^{\,2}}{[Cu(O_2CMe)_2L_2]^2} \quad (2)$$

complexes are equal to 1 (electrically neutral species, strongly diluted solutions). To calculate values of $K$ from the spectroscopic data [equation (3)] the molar absorption coefficients of the bi- and mono-nuclear forms ($\varepsilon_b$ and $\varepsilon_m$, respectively) must be known; $\bar{\varepsilon}$ represents the mean absorption coefficient of the solution, calculated per Cu atom, and $c$ is the total Cu concentration. As neither $\varepsilon_b$ nor $\varepsilon_m$ can be measured directly because pure amine and pure chlorobenzene solutions contain mixtures of both the mono- and bi-nuclear species, the values of $K$, $\varepsilon_b$, and $\varepsilon_m$ were calculated simultaneously by fitting the experimental $\bar{\varepsilon}$ and $c$ data to equation (3). The least-squares procedure of minimizing standard deviations has been employed to every set of solutions containing constant amine activity (6—10 solutions of different Cu concentrations in the set). The computed (Odra 1204) 'best' $K$ values (the average for three wavelengths) for the mixed-solvent compositions in the range $X_L \simeq 0.1$—1 are listed in Table 1. Table 1 contains $K_c$ as well as $K_x$ values, the latter being more appropriate for the final discussion because the assumption that $a_L = x_L$ seems to be a better approximation than $a_L = c_L$ (pyridine–chlorobenzene mixtures are nearly ideal on the mole fraction scale, $c_L$ values being only roughly proportional to $x_L$). The $\varepsilon_m$ and $\varepsilon_b$ values for $\lambda$ = 700 nm are also given for comparison in Table 2. The calculated spectrum of the mononuclear species is shown in Figure 1 (curve G); it is very similar to the measured absorption of $Cu(O_2CMe)_2$ in pure pyridine (Figure 3, curve F) which practically arises from the mononuclear species only [*cf.* section (*b*) below].

$$K = \frac{(\bar{\varepsilon} - \varepsilon_m)\,(\varepsilon_b - 2\,\varepsilon_m)}{c\,(\varepsilon_b - 2\,\bar{\varepsilon})^2}\cdot a_L^{\,2} \quad (3)$$

Reasonable agreement between the computed $K_c$ and $K_x$ values (Table 1) over the wide range of mixed-solvent compositions ($x_L$ varying from 0.08 to 1) strongly supports the reaction scheme (1).

(*b*) $Cu(O_2CMe)_2$–*pyridine*. The spectrum of $Cu(O_2CMe)_2$ in pure pyridine (Figure 3, curve F) appears as one very broad band of low intensity ($\varepsilon_{max.} \simeq 82$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at $\lambda_{max.}$ 660 nm). The parameters of the spectrum have been found to be independent of the Cu concentration (concentrations investigated: $10^{-3}$—$10^{-2}$ mol dm$^{-3}$). This fact together with the position and intensity of the band indicate that there are only mononuclear forms present in the solution. This conclusion is in accordance with the magnetic moment, 1.80 B.M. ($\approx 1.7 \times 10^{-23}$ J T$^{-1}$), reported for $Cu(O_2CMe)_2$ in pure pyridine.[6] Addition of chlorobenzene to the pyridine solutions results in more complicated spectroscopic changes than those observed for the $Cu(O_2CMe)_2$–2Me-py and $Cu(O_2CMe)_2$–3Cl-py[7] systems. The expected equilibrium between mono- and bi-

**Table 1.** Equilibrium concentration quotients, $K_c = c_b x_L{}^2/c_m{}^2$ and $K_x = x_b x_L{}^2/x_m{}^2$ [reaction (1)] for $Cu(O_2CMe)_2$–pyridine derivative (L) complexes in mixed L–chlorobenzene solvent at 298 K

| L = 2Me-py (p$K_a$ 5.97) | | | L = py (p$K_a$ 5.23) | | | L = i-quin[a] (p$K_a$ 5.40) | | | L = 3,4Me$_2$-py (p$K_a$ 6.46) | | | L = 3Cl-py (p$K_a$ 2.84) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $x_L$ | $K_c$/ dm$^3$ mol$^{-1}$ | $K_x$ | $x_L$ | $K_c$/ dm$^3$ mol$^{-1}$ | $K_x$ | $x_L$ | $K_c$/ dm$^3$ mol$^{-1}$ | $K_x$ | $x_L$ | $K_c$/ dm$^3$ mol$^{-1}$ | $K_x$ | $x_L$ | $K_c$/ dm$^3$ mol$^{-1}$ | $K_x$ |
| 1.000 | 19 ± 3 | 190 | 1.000 | ≃0 | ≃0 | 1.000 | ≃0 | ≃0 | 1.000 | ≃0 | ≃0 | 1.000 | 170 ± 20 | 1 800 |
| 0.819 | 21 ± 3 | 210 | 0.580 | ≃0.7 | ≃7 | 0.462 | 0.9 ± 0.3 | 8 | 0.092 | 0.2 ± 0.03 | 2 | 0.523 | 270 ± 60 | 2 800 |
| 0.423 | 23 ± 2 | 230 | 0.243 | 2.4 ± 0.5 | 24 | 0.185 | 2.0 ± 0.4 | 19 | | | | 0.096 | 150 ± 60 | 1 600 |
| 0.312 | 16 ± 3 | 160 | 0.174 | 5.4 ± 0.9 | 55 | 0.100 | 1.7 ± 0.4 | 17 | | | | 0.1[b] | 210 | 2 000 |
| 0.220 | 19 ± 3 | 190 | 0.105 | 4.0 ± 0.5 | 40 | 0.039 | 2.1 ± 0.3 | 20 | | | | | | |
| 0.187 | 17 ± 3 | 170 | 0.105 | 5.3 ± 0.6 | 53 | | | | | | | | | |
| 0.108 | 26 ± 6 | 260 | 0.105 | 4.9 ± 0.6 | 49 | | | | | | | | | |
| 0.1[b] | 20 | 200 | | | | | | | | | | | | |

[a] At 300 K. [b] Interpolated value.

**Table 2.** Spectroscopic characteristics[a] of mono- and bi-nuclear copper(II) acetate–pyridine derivative (L) complexes in L–chlorobenzene mixed solvent at 298 K

| L | | 2Me-py | py | i-quin | 3,4Me$_2$-py | 3Cl-py |
|---|---|---|---|---|---|---|
| $\lambda_{max.}$/nm | Mono | 600[b] | 658[c] | 660[c] | 660[b] | 650[b] |
| | Bi[b] | 723 | 722 | 722 | 725 | 710 |
| $\varepsilon_m$ at $\lambda_{max.}$ | | 73[b] | 82[c] | 95[c] | 78[c] | 84[b] |
| $\varepsilon_m$ at 700 nm[b] | | 55 ± 5 | 76 ± 6[d] | 84 ± 6[d] | 74 ± 5 | 81 ± 5 |
| $\varepsilon_b$ at 700 nm[b] | | 440 ± 30 | 450 ± 40 | 400 ± 40 | 430 ± 40 | 470 ± 10 |

[a] ε in dm$^3$ mol$^{-1}$ cm$^{-1}$. [b] Calculated from equation (3). [c] Measured in the pure amine solution. [d] The calculated $\varepsilon_m$ value increases slightly with increasing $x_L$.

nuclear forms can only be revealed (clear isosbestic points) at $x_{py} < 0.60$ (Figure 3). At higher pyridine concentrations the spectra do change with increasing amine activity, showing a small blue shift and slight increase in intensity; nevertheless the character of the band and the nearly constant value (independent of Cu concentration) of the mean molar absorption coefficient (at a constant amine activity) suggest that the equilibrium (1) is strongly shifted to the mononuclear forms.

As the low conductivities rule out the possibility of electrolytic dissociation, the medium effects observed at high pyridine activities ($x_L$ 0.6—1.0) should be explained by strong solute–solvent interactions influencing the molecular parameters (bond lengths and angles) of the complex or even its stoicheiometry (*e.g.* values of L greater than 2 cannot be excluded). Such interactions can be evidenced by solubility measurements[11] which reveal a rapid increase in the solubility of the mononuclear (m) complex $[Cu(O_2CMe)_2(py)_3]$ (solid phase in equilibrium with saturated solutions) on passing from $x_L = 0.6$ ($3.52 \times 10^{-2}$ mol dm$^{-3}$) to $x_L = 1.0$ ($4.98 \times 10^{-2}$ mol dm$^{-3}$). This means that the activity coefficient of the mononuclear species rapidly decreases with increasing pyridine activity and the assumptions made when approximating the true (thermodynamic) stability constant by the equilibrium concentration quotient [equation (2)] are no longer valid. This behaviour may account for the observed decrease in the value of the equilibrium concentration quotient at higher amine activities (it should decrease with the square of the activity coefficient of the mononuclear form), and for the fact that in pure pyridine this quotient is unmeasurable. The data in Table 1 show, however, that for $x_L < 0.2$ the values of $K$ are reasonably constant which may suggest that in this range of mixed-solvent composition the activity coefficients of the complexes do not vary appreciably. This conclusion may be, again, substantiated by the solubility measurements:[11] the increase in solubility of the binuclear (b) complex $[Cu_2(O_2CMe)_4(py)_2]$ (the solid phase in equilibrium with the saturated solutions below $x_L = 0.6$) from $2.10 \times 10^{-3}$ mol dm$^{-3}$ at $x_L = 0$ to $6.05 \times 10^{-3}$ mol dm$^{-3}$ at $x_L = 0.2$ can be fully rationalized in terms of the equilibrium (1) and the calculated values of $K$ for the range $x_L = 0.05$—$0.20$ shown to be constant ($K_x = 53 \pm 3$). This value is in good agreement with the mean value of $K_x$ for $x_L < 0.2$ obtained spectrophotometrically [equation (3)]. It must be noted here that conditions for measuring the equilibrium concentration constant at low amine activities by the spectrophotometric method are rather unfavourable (the equilibrium strongly shifted to the binuclear form at low Cu concentrations) which may result in comparatively large experimental errors [the errors given in Table 1 refer to the discrepancies within one series, *cf.* section (*a*) above].

(*c*) $Cu(O_2CMe)_2$–3,4-*dimethylpyridine.* The measured spectra are characteristic of the mononuclear complexes down to $x_L = 0.2$; even in solutions strongly diluted with chlorobenzene ($x_L = 0.1$) the calculated equilibrium constant is very low ($K_x \simeq 2$). This means that 3,4-dimethylpyridine shows a much stronger tendency to stabilize mononuclear structures than does a much weaker donor, *e.g.* pyridine.

(*d*) $Cu(O_2CMe)_2$–*isoquinoline.* The spectroscopic behaviour of this system shows a close analogy to that of the $Cu(O_2CMe)_2$–pyridine–chlorobenzene solutions. This fact can be easily recognized in view of the similarity of the donor properties of both amines. The slightly stronger basicity of isoquinoline seems to result in slightly lower values of the equilibrium constants (Table 1), the effect of increased $\pi$-acceptor ability of isoquinoline being of minor importance.

*E.S.R. Spectra.*—Only the spectra of the mononuclear forms can be resolved under the conditions of the measurements.[5c] Frozen solutions (77 K) of $Cu(O_2CMe)_2$ in pure py, 2Me-py, 3,4Me$_2$-py, or i-quin show typical axial spectra characteristic of tetragonally-distorted monomeric Cu$^{II}$ complexes (Figure 4). The differences between the spin-Hamiltonian parameters for the pure py, i-quin, and 3,4Me$_2$-py solutions are within experimental error, the values of the parameters for py being $g_\parallel = 2.30 \pm 0.005$, $g_\perp = 2.057 \pm 0.002$, $A_\parallel = (-172 \pm 5) \times$

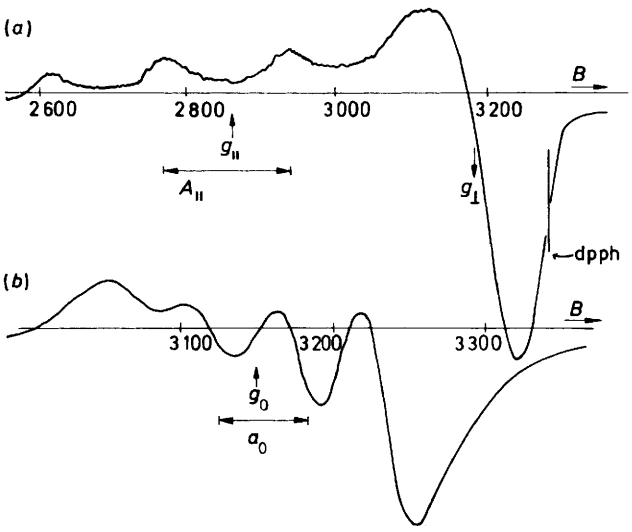

**Figure 4.** E.s.r. spectra ($B$/mT) of $Cu(O_2CMe)_2$ in pure py ($c_{Cu}$ = 1 × $10^{-3}$ mol $dm^{-3}$) at (a) 77 and (b) 298 K

$10^{-4}$ $cm^{-1}$; at 298 K, $g_0 = 2.150 \pm 0.005$, $a_0 = (-57 \pm 5) \times 10^{-4}$ $cm^{-1}$. The discrepancy between these values and those derived for pure 2Me-py solutions [$g_{\parallel} = 2.27 \pm 0.005$, $g_{\perp} = 2.051 \pm 0.002$, $A_{\parallel} = (-191 \pm 5) \times 10^{-4}$ $cm^{-1}$; at 298 K, $g_0 = 2.125 \pm 0.005$, $a_0 = (-70 \pm 5) \times 10^{-4}$ $cm^{-1}$] seems to reflect some changes in the molecular parameters of the complex, most probably caused by steric hindrance of the α-methyl group and/or weaker solute–solvent interactions. Comparison of the spin-Hamiltonian parameters measured for $Cu(O_2CMe)_2$–pyridine derivative complexes with the e.s.r. data derived for $[Cu(O_2CMe)_2(OH_2)_2]$ and $[Cu(O_2CMe)_2(MeOH)_2]$ solution complexes[5b] ($g_{\parallel}$ = 2.372, 2.345; $g_{\perp}$ = 2.087, 2.065; $A_{\parallel} = -137 \times 10^{-4}$ $cm^{-1}$, $-146 \times 10^{-4}$ $cm^{-1}$; $g_0$ = 2.178, 2.170, respectively) shows that the $g$ values increase and the hyperfine coupling decreases in the order: pyridines, methanol, water. This suggests that the apical ligand–metal interactions decrease in the same sequence.

## Conclusions

The results show that the structure adopted by $Cu^{II}$ acetate in solution strongly depends on the basicity and steric properties of the neutral ligand. Due to measurements carried out on solutions of varying amine activity we can determine the ability of the amines to stabilize the binuclear structures, even within those systems for which the thermodynamic equilibrium constant for reaction (1) with the activity coefficients standardized at $x_L = 1$ equals zero in the pure amine. Assuming that in the solutions strongly diluted with chlorobenzene the solute–solvent interactions are weak and, consequently, the activity coefficients of the complexes do not undergo appreciable variation with the mixed-solvent composition we can compare the equilibrium concentration constants determined for all the systems investigated at, *e.g.*, $x_L \simeq 0.1$. This comparison leads to the conclusion that the relative stability of the binuclear complexes in weakly coordinating solvent (chlorobenzene) increases in the sequence: $3,4Me_2$-py < i-quin ≲ py < 2Me-py < 3Cl-py, the respective $K_x$ values at $x_L \simeq 0.1$ being 2, 20, 50, 200, 2 000, approximately. As this is the order of decreasing p$K_a$ of the amines (except 2Me-py) the results obtained might suggest that the relative stability of the binuclear form is increased by removing electron density from the copper atoms. A similar tendency has been found for analogous solid binuclear copper(II) acetate complexes with pyridine oxide derivatives[12] and explained in terms of molecular orbital theory. This conclusion seems to contradict the widespread belief that stronger bonds and an increase in electronic charge on the copper atoms enhances Cu–Cu interactions.[13] The question of whether the increased basicity of the amine ligand really destabilizes the binuclear structure or merely stabilizes it less than the mononuclear form cannot be answered unless the true nature of the Cu–Cu interactions is revealed[14] or more experimental data are compiled. The unusually high $K$ values for the 2Me-py complexes and the marked deviation of its spin-Hamiltonian parameters from those derived for other pyridine derivatives, suggest that steric hindrance of the methyl group has a pronounced effect on the molecular parameters of the complexes in solution.

## References

1 E. Kokot and R. L. Martin, *Inorg. Chem.*, 1964, **3**, 1306.
2 D. P. Graddon, *J. Inorg. Nucl. Chem.*, 1961, **17**, 222.
3 M. Kato, M. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.
4 A. T. A. Cheng and R. A. Howald, *Inorg. Chem.*, 1968, **7**, 2100.
5 (*a*) H. Grasdalen and I. Svare, *Acta Chem. Scand.*, 1971, **25**, 1089; (*b*) H. Grasdalen, *J. Magn. Reson.*, 1973, **9**, 166; (*c*) *J. Chem. Soc., Faraday Trans. 2*, 1973, 462.
6 M. Kondo and M. Kubo, *J. Phys. Chem.*, 1958, **62**, 468.
7 M. Szpakowska and I. Uruska, *Pol. J. Chem.*, 1980, **54**, 1661.
8 I. Uruska and M. Szpakowska, *J. Chem. Soc., Faraday Trans. 1*, 1976, 2381.
9 L. Dubicki, *Aust. J. Chem.*, 1972, **25**, 1141.
10 J. Gažo, L. B. Bersuker, J. Garaj, M. Kabesova, J. Kohut, M. Langfelderova, M. Melnik, M. Serator, and F. Valach, *Coord. Chem. Rev.*, 1976, **19**, 253.
11 M. Szpakowska, I. Uruska, and S. Hoffmann, unpublished work.
12 D. Hibdon and J. M. Nelson, *Inorg. Chim. Acta*, 1973, 7, 629.
13 R. W. Jothan, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, 1972, 428.
14 M. Gerloch and J. H. Harding, *Proc. R. Soc. London, Ser. A*, 1978, **360**, 211.

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