Co-ordination State of Copper(II) Ion in $Cu(O_2CMe)_2$–Pyridine Derivative–Diluent Mixtures; the Steric Effect of the Amine Ligand

Irmina Uruska,* Jan Zielkiewicz, and Maria Szpakowska
Department of Physical Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Electronic spectra (360—800 nm) and electrolytic conductivities have been measured for the $Cu(O_2CMe)_2$–L–chlorobenzene systems (L = 2-chloro-, 2-methyl-, 2-ethyl-, 2,4-dimethyl-, or 2,6-dimethyl-pyridine) and K_{th} for the equilibrium $2[Cu(O_2CMe)_2L_2] \rightleftharpoons [Cu_2(O_2CMe)_4L_2] + 2L$ calculated. The results are compared with those obtained for non-α-substituted pyridines as ligands. A strong steric effect on the co-ordination equilibria as well as on the stereochemistry and solvation of the mononuclear $[Cu(O_2CMe)_2L_2]$ complexes has been evidenced and discussed.

Copper carboxylates are known to form a variety of structures even with ligands of the same homologous series, such as pyridine derivatives.[1] It is expected that ligand basicity and steric factors may play an important role in determining the structures of both the solid and solution complexes and particularly in their tendency to form mono- or bi-nuclear structures. However the arguments for the solid compounds are of a qualitative rather than quantitative nature because the parameters which may be taken as a measure of such tendencies (Cu–Cu distance, $2J$ value, *etc.*) are likely to be influenced by crystal-lattice effects.[1,2] The problem is much simpler to solve for the solution complexes because the relative thermodynamic stability of mono- and bi-nuclear forms may be measured quantitatively as the equilibrium constant corresponding to equation (1). The data for such equilibria show that the relative

$$2[Cu(O_2CR)_2L_2] \rightleftharpoons [Cu_2(O_2CR)_4L_2] + 2L \quad (1)$$

stability of the binuclear form in a weakly co-ordinating solvent (chlorobenzene) increases in the order of increasing pK_a of the anionic ligand[3] and with decreasing amine ligand basicity.[4] It was, however, found that complexes with 2-methylpyridine deviate from this regularity and their electronic and e.s.r. spectra apparently differ from those measured for amine ligands without steric hindrance.[4]

The aim of this work was to investigate the steric effect of the neutral ligand on the co-ordination pattern and spectra of the copper(II) ion in $Cu(O_2Me)_2$–pyridine derivative–diluent solutions. Complexes with 2-ethylpyridine (2Et-py), 2,4-dimethylpyridine (2,4Me_2-py), 2,6-dimethylpyridine (2,6Me_2-py), and 2-chloropyridine (2Cl-py) have been studied and the results compared with those obtained previously for analogous systems. The measurements were carried out at varying amine activities which made it possible to draw some conclusions about the solvation of the complexes in the solutions. As the diluent, which was used to control the amine activity in the mixed solvent, chlorobenzene was used because its mixtures with pyridine derivatives were shown to be nearly ideal.[5,6]

Experimental

Solid Complexes.—The binuclear compounds $[Cu_2(O_2CMe)_4L_2]$ (L = 2Et-py, 2Cl-py, 2,4Me_2-py, or 2,6Me_2-py) were obtained by methods described previously[3] and dried over anhydrous H_2SO_4 or P_2O_5 under reduced pressure. All products were green except for the complex with L = 2,6Me-py which was blue-violet {Found for L = 2Et-py: Cu, 20.9. Calc.: Cu, 22.0. Found for L = 2Cl-py: Cu, 21.4. Calc.: Cu, 21.55. Found for L = 2,4Me_2-py: Cu, 21.9. Calc.: Cu, 22.0. Found for L = 2,6Me_2-py: Cu, 21.9. Calc.: Cu, 22.0%}.

Solvents.—Pyridines (Fluka, pure grade) were shaken with KOH, distilled twice from KOH under reduced pressure, and stored in the dark in a dry-box. Chlorobenzene (Inter. Enzymes Ltd., pure) was purified by a standard method, dried over molecular sieves (A4), and distilled.

Measurements.—Solutions were prepared using weighted amounts of the solid compound and the solvent (the range of concentrations studied was 2×10^{-2}—10^{-4} mol dm^{-3}). The stock solutions were checked for copper concentration by the standard ethylenediaminetetra-acetate titration procedure (also used for copper analysis). Electronic spectra (30 000—12 500 cm^{-1}) were measured at 298.2 ± 0.1 K in stoppered quartz cells using a Beckman u.v. 5270 spectrophotometer. Electrolytic conductivity was measured as described previously.[5] All solutions were freshly prepared before measurements.

Calculations.—The thermodynamic equilibrium constant of equilibrium (1), K_{th}, is defined by equation (2) where γ_m and γ_b

$$K_{th} \equiv \frac{c_b}{c_m^2} \cdot \frac{\gamma_b}{\gamma_m^2} \cdot a_L^2 \quad (2)$$

are the activity coefficients of the mono- and bi-nuclear forms respectively, c_b and c_m the molar concentrations, and a_L is the amine activity. The equilibrium quotient $Q \equiv c_b/c_m^2$ at a given mole fraction of L in the mixed solvent (L + chlorobenzene) x_L can be calculated from the dependence of $\bar{\varepsilon}$ (mean molar absorption coefficient calculated per Cu atom) on the total copper concentration, c [see equation (3)]. As the molar absorption coefficients of the mononuclear (ε_m) or

$$Q = \frac{(\bar{\varepsilon} - \varepsilon_m)(\varepsilon_b - 2\varepsilon_m)}{c(\varepsilon_b - 2\bar{\varepsilon})^2} \quad (3)$$

binuclear form (ε_b) cannot be measured directly (except when L = 2Cl-py), the values of Q, ε_m, and ε_b were calculated simultaneously by fitting the set of c and $\bar{\varepsilon}$ data (6—10 solutions in the set) by equation (3) using the least-squares procedure of minimizing standard deviations. Calculations were performed for at least three wavelengths in the region of $\lambda_{max.}$ for the binuclear form. Average values of Q were used for calculation of the equilibrium constants. Where possible, a_L values were taken from the literature [py,[7] 2Me-py,[6] and isoquinoline (i-quin)[5]].

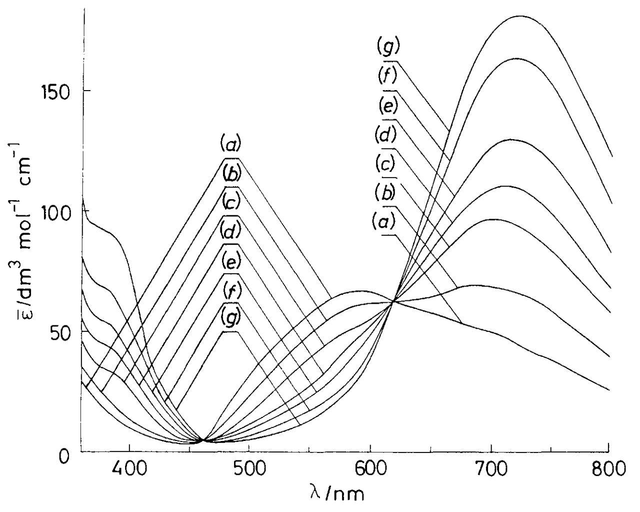

Figure 1. Electronic spectra of the $Cu(O_2CMe)_2$–2,6Me_2-py–chlorobenzene system. 10^4c_{Cu}/mol dm^{-3} ($x_{2,6Me-py}$ in parentheses) = 2.2 (1) (*a*), 5.80 (0.66) (*b*), 6.64 (0.387) (*c*), 2.72 (0.202) (*d*), 6.73 (0.202) (*e*), 19.8 (0.17) (*f*), and 10.1 (0.106) (*g*)

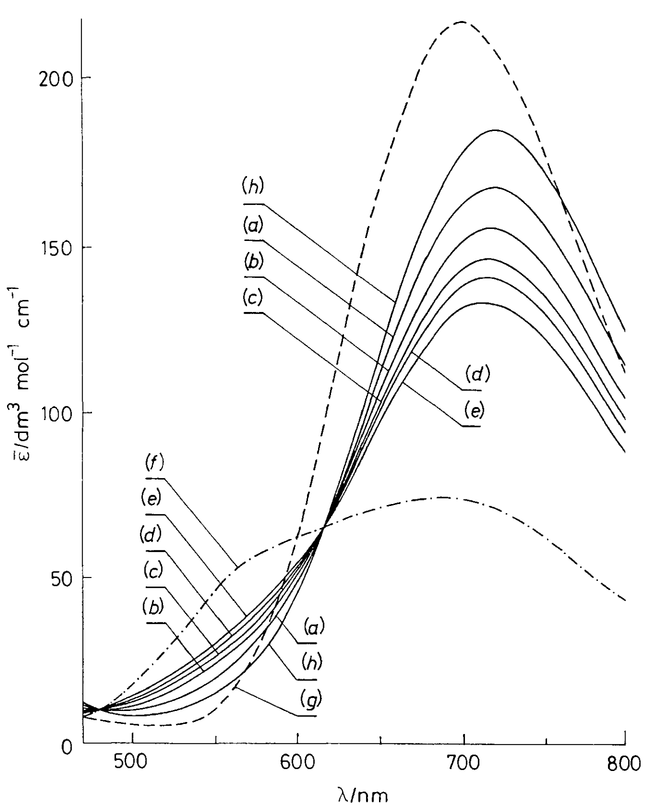

Figure 2. Electronic spectra of $Cu(O_2CMe)_2$ in pure amines (L) and mixed 2Et-py–chlorobenzene solvent. For L = 2Et-py, 10^3 c_{Cu}/mol dm^{-3} = 13.6 (*a*), 6.63 (*b*), 4.40 (*c*), 3.30 (*d*), and 2.64 (*e*). For L = 2Me-py or 2Cl-py 10^3 c_{Cu}/mol dm^{-3} = 5.54 (*f*) or 5.62 (*g*) respectively. For the $Cu(O_2CMe)_2$–2Et-py–chlorobenzene system (*h*), c_{Cu} = 2.64 × 10^{-3} mol dm^{-3} and x_{2Et-py} = 0.18

As the difference between activity and concentration of the pyridines, especially that expressed on the mole fraction scale, was very small we assumed that for the other mixtures $a_L = x_L$.

Results and Discussion

Conductivity Measurements.—The molar conductivities of freshly prepared solutions, even of those in pure amines of comparatively high dielectric constant (≈10), were very low (<1 Ω^{-1} cm^2 mol^{-1}) at the concentrations investigated. This indicates that the equilibria in the solutions do not involve ionic species.

Electronic Spectra.—Figure 1 shows the electronic spectra of $Cu(O_2CMe)_2$ in the mixed 2,6Me_2-py–chlorobenzene solvent of varying amine activity. They are typical of all the systems studied in this work. The spectra indicate an equilibrium between two copper acetate complexes in the solution. The position and intensity of the bands developing with decreasing amine activity (725 and 385 nm) are characteristic of binuclear copper carboxylates[8] while the weak band appearing for amine-rich solutions containing low copper concentrations can be ascribed to mononuclear species.[9,10] The strong dependence of the spectra on the amine activity suggests that the amine takes part in the dissociation of the binuclear form into mononuclear complexes. It is noted that all the spectra run through common isosbestic points. This may be an indication that the first co-ordination spheres of both types of the complexes remain unchanged regardless of amine concentration. The same behaviour is shown by all the systems investigated in this work (α-substituted pyridines) while for similar complexes of similar basicity studied previously (py, 3,4Me_2-py, and i-quin)[4] an apparent increase in the intensity of the band of the mononuclear complex has been observed for amine-rich solutions. The existence of the equilibrium between mono- and bi-nuclear forms can be additionally verified by the dependence of the spectra on the copper concentration at a constant mixed-solvent composition, as shown by Figure 2, curves (*b*)—(*f*) and Figure 1, curves (*d*) and (*e*). From the absorptions for such sets of solutions (varying c_{Cu}, x_L = constant) an equilibrium concentration quotient $Q = c_b/c_m^2$ can be calculated for the given mixed-solvent composition (see Calculations). For the pure amine (the standard state), Q is equal to the thermodynamic equilibrium constant, K_{th} of the equilibrium (1) in which we assume two amine molecules are co-ordinated to both the mono- and bi-nuclear compound.[3,11,12] This assumption can be verified by plotting the ln Q values *vs.* ln $a_L(x_L)$. Figure 3 shows that for L = 2Me-py, 2,4Me_2-py, or 2,6Me_2-py the value of the slope is close to 2 over the whole range of the mixed-solvent composition, in accordance with equilibrium (1). For L = 2Et-py the slope is *ca.* 2 only at high amine concentrations. It is unlikely that the deviation of the 2Et-py complexes from the rectilinear dependence could be ascribed to the changes in the first co-ordination sphere, because the character of the spectra of the $Cu(O_2CMe)_2$ solutions does not change from pure 2Et-py solutions to solutions with as low 2Et-py concentration as x = 0.02 [curve (*h*), Figure 2 shows, as an example, the spectrum for x_L = 0.18]. It appears to reflect the changes in outer-sphere co-ordination expressed by γ_b/γ_m^2 or the dependence of γ_L on x_L (no data in the literature for the latter).

Equilibrium Constants.—The calculated equilibrium constants for equilibrium (1) in the pure amines are listed in the Table together with those obtained previously for the ligands without an α substituent in the pyridine ring. The data reveal two strong factors influencing the relative stability of the binuclear form in the solutions: the basicity of the amine ligand and the steric factor. The first one is clearly seen if we compare the K_{th} values within the groups of ligands of the two types: (*a*) those without steric hindrance (K_{th} for 3Cl-py is much greater than that for py, i-quin, and 3,4Me_2-py), and (*b*) with the α substituent (K_{th} for 2Cl-py ≫ 2Et-py > 2,6Me_2-py > 2Me-py ≈ 2,4Me_2-py). The striking feature of the last sequence is the position of 2Et-py which is as basic as 2Me-py but shows a much stronger tendency to stabilize the binuclear form. This fact seems to indicate the importance of the bulkiness of the

Table. Equilibrium constants for equilibrium (1) and spectral characteristics[a] of mono- and bi-nuclear $Cu(O_2CMe)_2$ complexes with pyridine derivative ligands (L) at 298.2 K

			Binuclear		Mononuclear	
L	pK_a	K_{th}	$\lambda_{max.}$/nm	$\varepsilon_{max.}$	$\lambda_{max.}$/nm	$\varepsilon_{max.}$
py[b]	5.23	8.6×10^{-2}	722 ± 6	460 ± 30	658 ± 2[c]	82 ± 5[c]
2Me-py	5.97	19 ± 3[d]	723 ± 2	440 ± 10	595 ± 10	73 ± 8
2Et-py	5.97	260 ± 20	722 ± 2	450 ± 10	≈ 600	72 ± 8
2,4Me_2-py	6.63	15 ± 2	730 ± 4	450 ± 10	600 ± 10	74 ± 6
2,6Me_2-py	6.72	37 ± 5	728 ± 4	445 ± 10	595 ± 8	65 ± 6
3,4Me_2-py[e]	6.46	≈ 0	725 ± 5	430 ± 40	660 ± 5	78 ± 5
2Cl-py	0.72	$(10 \pm 3) \times 10^4$	700 ± 2[c]	440 ± 10[c]	*f*	*f*
3Cl-py	2.84	170 ± 20[e]	705 ± 4	480 ± 10[e]	650 ± 10[e]	84 ± 10[e]
i-quin[e]	5.40	≈ 0	722 ± 6	430 ± 30	660 ± 2[c]	95 ± 5[c]

[a] ε in $dm^3 mol^{-1} cm^{-1}$. Spectral data calculated from equation (3) unless otherwise stated. [b] Ref. 13. [c] Experimentally measured. [d] Ref. 3. [e] Ref. 4. [f] Not calculable.

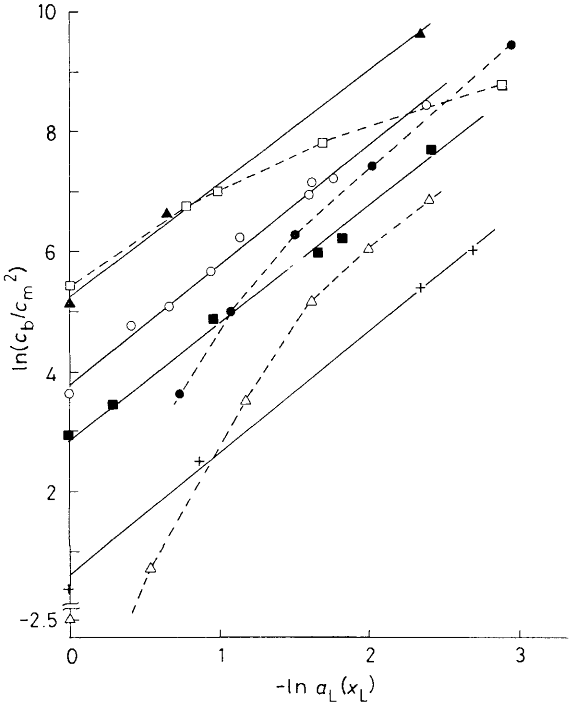

Figure 3. The dependence of the equilibrium concentration quotient $Q = c_b/c_m^2$ on the amine ligand activity (concentration) in the mixed amine (L)–chlorobenzene solvent. [L = 2,4Me_2-py (+), py (△), 2Me-py (■), 2Et-py (□), i-quin (●), 2,6Me_2-py (○), or 3Cl-py (▲)]

hindering group. Such an increased steric effect may also cause the peculiar behaviour of the ln *Q* *vs.* ln x_L dependence observed for 2Et-py complexes, discussed in the preceding section. It may be argued that K_{th} values corresponding to the solutions in pure amines represent media of different polarity, this factor also playing a substantial role in the stabilization of the two forms.[12,13] However the data show that the values of equilibrium concentration quotients calculated for low amine activities, where the polarity of the medium is primarily determined by the diluent, also follow the inverted order of amine basicities, *e.g.*, at $x_L = 0.098$ K_{th} decreases in the order; (*a*) 3Cl-py (18 000) ≫ i-quin (3 200) > py (950) > 3,4Me_2-py (24); (*b*) 2Cl-py (10^5) > 2,6Me_2-py (5 200) > 2Et-py (5 000) > 2Me-py (1 800) > 2,4Me_2-py (250). The unusual position of i-quin, 2,6Me_2-py, and 2Et-py in the above series may be most probably ascribed to the additional steric hindrance (bulky substituents and two α groups, respectively).

A question now arises as to which of the two forms is more strongly influenced by the steric effect; the fact that K_{th} values only measure the relative stabilities of the bi- and mono-nuclear forms must be taken into account. Stereochemical arguments suggest it is more likely that the less crowded five-co-ordinated binuclear complex will be less susceptible to steric hindrance than the flexible six-co-ordinated mononuclear compound. This supposition seems to be supported by the e.s.r. spectra of liquid solution complexes which indicate[14] different arrangements of carboxylate and amine ligands around the Cu^{II} in mononuclear complexes with pyridine derivatives with and without α substituents. In the former case the two amine molecules co-ordinate in the basal position together with two oxygens of the O–C groups at short distances, the other two Cu–O bonds being longer and directed out of the basal plane as in solid $[Cu(O_2CCH_2Cl)_2(2Me\text{-}py)_2]$[15] and $[Cu(O_2CMe)_2(2,6Me_2\text{-}py)_2]$.[1] In the mononuclear complexes of the second type (no steric hindrance at the pyridine nitrogen) the amine molecules occupy the apical sites, while the basal plane contains four oxygens from the two carboxylate bridges.

The two different stereochemistries of the mononuclear complexes suggested by the e.s.r. measurements are fully consistent with the electronic spectra calculated or directly measured for the systems listed in the Table: $\lambda_{max.}$ for the mononuclear complex with all the α-substituted ligands lies at ≈600 nm, while for the other amines it is situated at a much longer wavelength (≈660 nm). Here the increased tetragonality expected for the complexes with α-substituted derivatives manifests itself in the blue shift of this band. Unfortunately any attempts to correlate the band position with the basicity of the amine ligands are unreliable because in the systems where such a band may be measured fairly precisely (the equilibrium shifted to the mononuclear form) the amine ligand occupies the apical position and shows comparatively little influence on the spectra, while in complexes with basal amine ligands the spectra of the mononuclear complexes can only be calculated (the equilibrium is shifted to the binuclear form) and, in view of the broadness and low intensity of the band, the error in $\varepsilon_{max.}$ is too great to make any meaningful comparisons. A spectral shift suggesting weaker Cu–L bonds (an increase in tetragonality) seems to be observed only for a very weak base (3Cl-py).

As indicated by the data in the Table, the steric properties of the amine ligand do not apparently influence the spectra of the binuclear compounds. There is however a monotonic, roughly linear, decrease in $\lambda_{max.}$ for the binuclear complex with increasing pK_a of the amines (Figure 4), in accord with the expected strengthening of the apical Cu–L bond and the decreasing effective in-plane ligand field. The absence of the

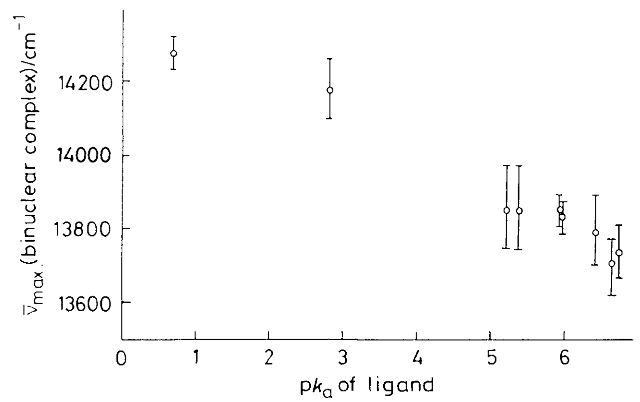

Figure 4. The dependence of the $\tilde{\nu}_{max.}$ of the electronic absorption band for the binuclear complex $[Cu_2(O_2CMe)_4L_2]$ on the pK_a value of the amine ligand (L)

steric effect on the spectra of the binuclear form is explicable by analogous rigid structures for all the $[Cu_2(O_2CMe)_4L_2]$ complexes {the known structure of the parent $[Cu_2(O_2CMe)_4(py)_2]$ compound}. An additional argument for the weak effect of the steric factor for this type of compound may be the nearly equal $\Delta H^\ominus$ values for formation of $[Cu_2(O_2CMe)_4L_2]$, with L = 2-, 3-, and 4-methylpyridine (−865, −853, and −869 kJ mol^{-1}, respectively).[16]

Solute–Solvent Interactions.—The rectilinear plots of ln Q vs. ln x_L in Figure 3 suggest that for these systems the $\gamma_b\gamma_L{}^2/\gamma_m{}^2$ factor in equation (2) is approximately equal to 1 over the whole range of the mixed-solvent composition. As the pyridine derivative–chlorobenzene mixtures behave approximately as ideal solutions ($a_L \simeq x_L$) and the activity coefficients of the binuclear copper(II) acetate complexes also seem to remain constant ($\gamma_b \approx 1$) down to low amine concentrations,[17] the γ_m values for complexes with 3Cl-py, 2Me-py, 2,4Me$_2$-py, and 2,6Me$_2$-py ligands should be ≈ 1 as well. This means that there is no preferential solvation of the solution complexes by the components of the mixed solvent. This is however not the case for py, i-quin and 2Et-py as ligands: the rapid decrease of the $\gamma_b\gamma_L{}^2/\gamma_m{}^2$ product in solutions diluted with chlorobenzene suggests preferential solvation of the mononuclear complexes with pyridine and isoquinoline while the opposite must be true for 2-ethylpyridine. As no changes in the character of the spectra of the 2-ethylpyridine complexes have been observed over the whole range of amine activity (Figure 2) the peculiar behaviour of the last system seems to be a further manifestation of the steric effect: not only does it influence the co-ordination of 2Et-py in the first co-ordination sphere, but it also hinders the solvation of the complex.

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