Solute–Solute–Solvent Interactions in $Cu(O_2CR)_2$–Pyridine–Diluent Systems; the Influence of the Carboxylate Ligand

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Electronic spectra (350–800 nm) have been recorded for $Cu(O_2CR)_2$–pyridine–chlorobenzene systems [R = Et, $(CH_2)_4CH_3$ and partly Me] and the equilibrium concentration quotients c_b/c_m^2 {b = binuclear $[Cu_2(O_2CR)_4(py)_2]$, m = mononuclear $[Cu(O_2CR)_2(py)_2]$} for varying pyridine concentrations have been calculated. No dependence of $c_b a_{py}^2/c_m^2$ (a = activity) on R has been observed in contrast to similar $Cu(O_2CR)_2L_n$ complexes where L is an α-substituted pyridine derivative. At higher a_{py} (>0.6) an equilibrium between two mononuclear forms $[Cu(O_2CR)_2(py)_2]$ and $[Cu(O_2CR)_2(py)_3]$ is postulated. The determined solubility isotherms for the system $Cu(O_2CEt)_2$–pyridine–chlorobenzene and for analogous acetate complexes reveal a dramatic increase in solubility accompanying the addition of a CH_2 group in the alkane chain. The activity coefficients of the bi- and mono-nuclear complexes in solution are discussed.

Previous results[1] on $Cu(O_2CR)_2$ complexes with 2-methylpyridine (2Me-py) and 2,6-dimethylpyridine (2,6Me$_2$-py) ligands in mixed amine–chlorobenzene solutions have shown that the tendency to form binuclear structures, measured by the equilibrium constant, K_b, of reaction (1), is comparatively

$$2[Cu(O_2CR)_2L_2] \underset{}{\overset{K_b}{\rightleftharpoons}} [Cu_2(O_2CR)_4L_2] + 2L \quad (1)$$

strongly influenced by the basicity of the parent carboxylic acid (*e.g.* for L = 2Me-py, and R = H, Me, Et or Pr^i, K_b is 0.14, 19, 31.5 and 35 mol dm^{-3}, respectively). However both 2Me-py and 2,6Me$_2$-py ligands show a strong steric effect (α substituents) which influences the solute–solvent interactions[2] and even the stereochemistry[3] of the mononuclear complexes in solution. To eliminate the steric effect on the equilibria we have now investigated a series of $Cu(O_2CR)_2$ complexes R = Me, Et or $(CH_2)_4CH_3$ with pyridine (py), a ligand from the same family but having no steric hindrance. We used chlorobenzene as the diluent controlling the amine activity because pyridine–chlorobenzene mixtures behave as nearly ideal ones.

Experimental

Solid Complexes.—The binuclear compounds $[Cu_2(O_2CR)_4L_2]$ were obtained by methods described previously[1] and dried over anhydrous H_2SO_4 or P_2O_5 [Found for R = Me: Cu, 24.30; py, 30.40. Calc.: Cu, 24.40; py, 30.30. Found for R = Et: Cu, 21.90; py, 27.55. Calc.: Cu, 22.00; py, 27.40. Found for R = $CH_3(CH_2)_4$: Cu, 17.0; py, 21.30. Calc.: Cu, 17.05; py, 21.20].

Solvents.—Pyridine (POCh, pure grade) was shaken with KOH and distilled from molecular sieves (4A). Chlorobenzene (Inter Enzymes, pure) was purified by a standard method, dried over molecular sieves (4A) and distilled.

Measurements.—Solutions were prepared using weighed amounts of the solid compound and the solvent (concentrations 10^{-2}–10^{-4} mol dm^{-3}). Electronic spectra (350–800 nm) were measured at 298.2 ± 0.1 K in stoppered quartz cells using a Beckman 5270 spectrophotometer. Electrolytic conductivity was measured as described previously.[4]

Solubility measurements were performed by the column method[4] at 298.2 ± 0.2 K and checked by a static method (solutions saturated at ≈303 K, allowed to equilibrate in a constant-temperature bath for several days). The solutions were saturated with the solid phase in equilibrium, as determined by preliminary measurements. Weighed samples of the saturated solutions were shaken with water and titrated with ethylenediaminetetraacetate (edta). The data presented in Fig. 4 are mean values of at least three measurements; the reproducibility was within 2%. The pyridine content in the solid samples was determined spectrophotometrically at 255.5 nm, after dissolution in acidified water. The stoichiometry of the solid phase agreed with the composition of the solid phase indicated in Fig. 4 within 2%.

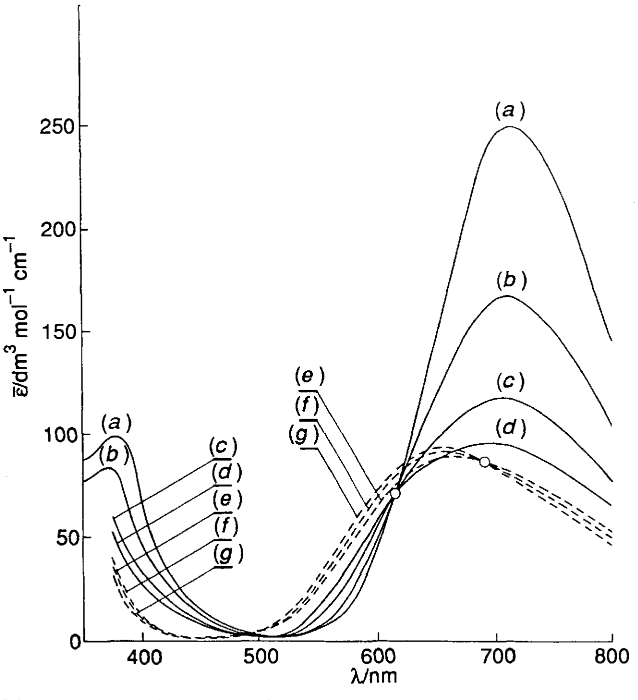

Fig. 1 Electronic spectra of $Cu(O_2CEt)_2$ in mixed pyridine–chlorobenzene solvent at 298.2 K; c_{Cu} = 3 × 10^{-3} mol dm^{-3}; x_{py} = 0.002 (*a*), 0.124 (*b*), 0.220 (*c*), 0.325 (*d*), 0.513 (*e*), 0.678 (*f*) or 0.950 (*g*)

Results and Discussion

Conductometric Measurements.—The measured molar conductivities of all freshly prepared solutions investigated in this work, including pure pyridine solutions, were below 1 S cm^2 mol^{-1}. This indicated that ionic equilibria in the solutions can be neglected.

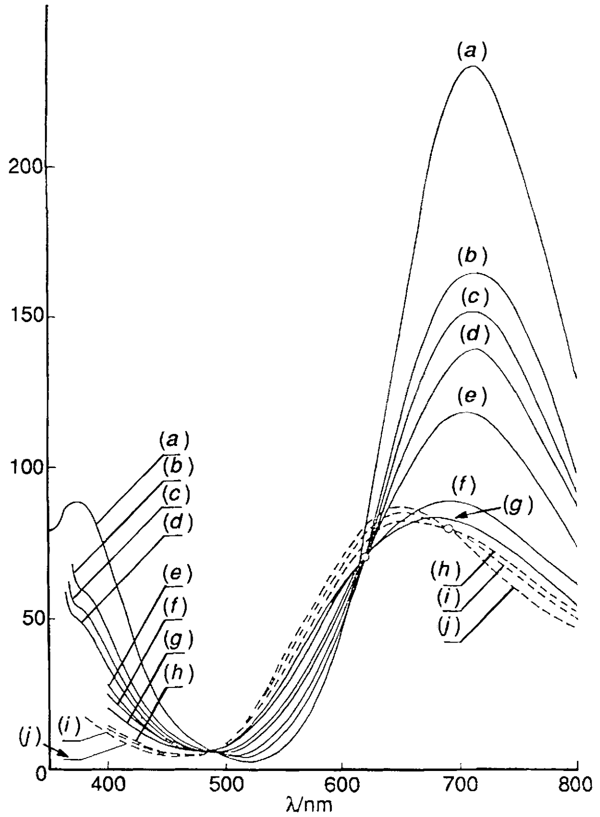

Fig. 2 Electronic spectra of $Cu[O_2C(CH_2)_4CH_3]_2$ in mixed pyridine–chlorobenzene solvent at 298.2 K: $x_{py} = 0.053$, $c_{Cu} = 4.3 \times 10^{-2}$ (*a*); $x_{py} = 0.252$, $c_{Cu} = 1.5 \times 10^{-2}$ (*b*), 0.96×10^{-2} (*c*), or 0.28×10^{-2} (*e*); $x_{py} = 0.124$, $c_{Cu} = 0.099 \times 10^{-2}$ (*d*); $c_{Cu} = 0.04 \times 10^{-2}$ mol dm^{-3}, $x_{py} = 0.215$ (*f*), 0.327 (*g*), 0.421 (*h*), 0.584 (*i*), or 1.00 (*j*)

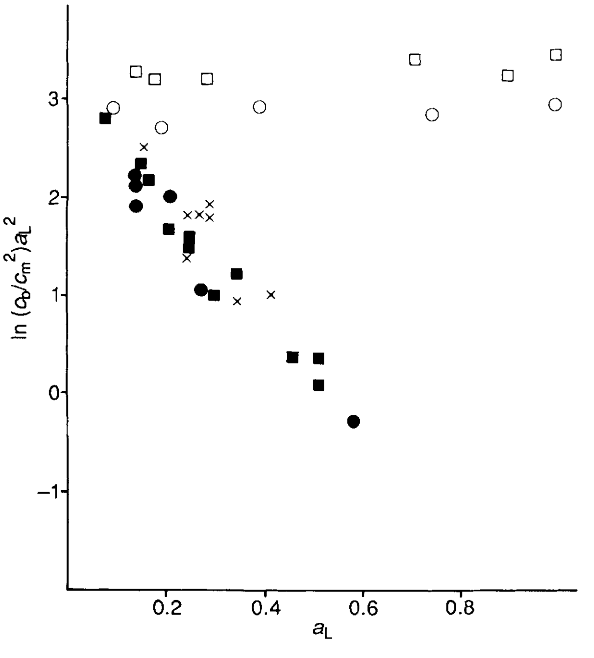

Fig. 3 Dependence of ln $(c_b/c_m^2)a_L^2$ on a_L (a_L based on the mol fraction scale) for $Cu(O_2CR)_2$–L–chlorobenzene systems: R = Me, L = py (●);[2] R = Et, L = py (■); R = $(CH_2)_4CH_3$, L = py (×); R = Me, L = 2Me-py (○);[1] R = Et, L = 2Me-py (□)[1]

Electronic Spectra.—Fig. 1 shows typical spectra of $Cu(O_2CR)_2$ in pyridine–chlorobenzene solutions of varying pyridine activity. Two sets of spectra, each with a common isosbestic point, are observed.

The set characteristic of solutions containing lower amine activities [mol fraction x_L from 0 to 0.5, curves (*a*)–(*d*)], with the isosbestic point at 618 nm, corresponds to the equilibrium between the mono- and bi-nuclear complexes[1] [equation (1)]; the band developing with decreasing amine activity (λ_{max} 714 nm) is characteristic of the binuclear compound.[1]

Equilibrium (1) is supported by the strong dependence of the spectra corresponding to this concentration range of the amine (x_L 0–0.5) on the total copper concentration [Fig. 2, curves (*b*), (*c*) and (*e*)].

The other set of spectra developing at $x_L > 0.5$ [Fig. 1, curves (*e*)–(*g*), isosbestic point at 685 nm] show no dependence of the mean molar absorption coefficient, $\bar{\varepsilon}$, on the copper concentration. This fact, and the comparatively low value of $\bar{\varepsilon}$, indicates that they correspond to mononuclear copper complexes. It is to be noted that such sets of mononuclear spectra do not appear in the electronic spectra of $Cu(O_2CR)_2$ complexes with pyridine derivatives of very low basicity[2] or those containing sterically bulky α substituents.[1] The last systems exhibit a strong tendency to form binuclear structures and they have been shown to form only one mononuclear complex $[Cu(O_2CR)_2L_2]$ in solution.[1,2]

As the solid phase in equilibrium with the solutions exhibiting mononuclear spectra ($x_L > 0.5$) is mononuclear $[Cu(O_2CR)_2(py)_3]$ (R = Me or Et), we postulate for such solutions an equilibrium between two mononuclear forms [equation (2)].

$$[Cu(O_2CR)_2(py)_2] + py \xrightleftharpoons{K_m} [Cu(O_2CR)_2(py)_3] \quad (2)$$

Thus the band developing at shorter wavelengths (below 685 nm) should arise from $[Cu(O_2CR)_2(py)_3]$. Its increased absorption coefficients may reflect lower symmetry of the complex. The equilibrium is strongly influenced by temperature, as shown by the spectra: λ_{max} of the band of $Cu(O_2CEt)_2$ in pure pyridine shifts from 664 nm at 313 K to 592 nm at 284 K with increase in $\bar{\varepsilon}$ by about 8%.

Equilibria.—For solutions with spectra running through the common isosbestic point at 618 nm [equation (1)] we can calculate the equilibrium concentration quotient c_b/c_m^2 at a given amine activity, a_L, by measuring the mean absorption coefficient $\bar{\varepsilon}$ as a function of the total copper concentration, keeping a_L constant [equation (3)]. Here c is the total copper

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

concentration in mol dm^{-3} calculated per atom Cu; the absorption coefficients ε_b and ε_m refer to the bi- and mononuclear forms, respectively.

Unfortunately, we cannot immediately calculate the thermodynamic constant [equation (4)] because the spectra only

$$K_{th(b)} = \frac{c_b}{c_m^2} \cdot \frac{\gamma_b}{\gamma_m^2} \cdot a_{py}^2 \quad (4)$$

supply the concentrations. Nor is it possible to calculate K_{th} for the standard state $x_{py} = 1$, $\gamma_b = \gamma_m = \gamma_{py} = 1$, because at $x_{py} = 1$ the equilibrium is strongly shifted to the mononuclear forms and not observable at the concentrations appropriate for spectral measurements. We can, however, plot the calculated $c_b a_L^2/c_m^2$ values against a_L and try to extrapolate them to $a_L = 1$. Fig. 3 shows that the values of $c_b a_L^2/c_m^2 = (\gamma_m^2/\gamma_b)K_{th(b)}$ strongly depend on the amine activity. As the spectra in the range x_L 0–0.6 indicate only one equilibrium involving copper(II) complexes in solutions (sharp isosbestic points), the variation of $(\gamma_m^2/\gamma_b)K_{th(b)}$ with x_L should be ascribed to changes in the preferential solvation of one or both types of complexes by one of the mixed solvent components. Also Fig. 3 shows that the dependence of $c_b a_L^2/c_m^2$ is approximately the same for acetate,[2] propionate and caproate (hexanoate) complexes. This fact suggests that equilibrium (1) is practically not influenced by

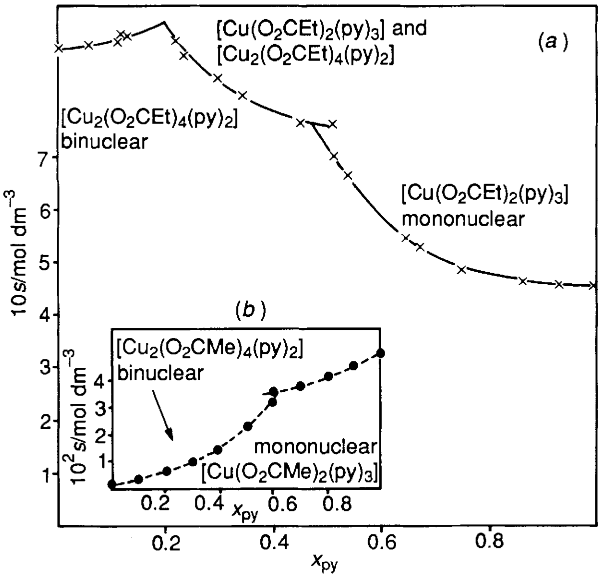

Fig. 4 Solubility isotherms for $[Cu_2(O_2CR)_4(py)_2]$–pyridine–chlorobenzene systems, at 298.2 K: (*a*) R = Et (this work); (*b*) R = Me.[6] Solid phases in equilibrium are indicated

the length of the hydrocarbon chain in the copper(II) carboxylate complexes with pyridine. This behaviour is in contrast with the dependence of K_{th} on R exhibited by $Cu(O_2CR)_2$ complexes with α-substituted pyridines.[1] Another difference between the two groups of complexes (with and without steric hindrance in the pyridine ligand) is that the first (with hindrance) do not show preferential solvation by solvent components (pyridine and chlorobenzene) as illustrated by the nearly horizontal dependence of $(\gamma_m{}^2/\gamma_b)K_{th(b)}$ *vs.* a_L for L = 2Me-py (Fig. 3).

The similarity of the plots of $c_b a_L{}^2/c_m{}^2$ *vs.* a_L for acetate, propionate and caproate complexes with pyridine suggests a common value of $K_{th(b)}$ (≈ 0.08;[1] extrapolation to $a_L = 1$). It is also of note that the spectral characteristics (Table 1) of the three systems investigated are also similar: the increase in the length of the alkane chain (R) results in a very small IR shift of the two characteristic bands (Table 1) while the calculated ε_m and ε_b values remain the same within experimental error.

The constant of the equilibrium between the two mononuclear forms [equation (2)] can only be roughly estimated because the dependence of $\bar{\varepsilon}$ on a_L is very weak over the range of pyridine concentrations x_L 0.6–1, and information about the activity coefficients of both forms is lacking. Assuming that $\gamma \approx 1$, K_m is estimated to be of the order 10^{-1} dm^3 mol^{-1} and the ε_m value for $[Cu(O_2CR)_2(py)_3]$ at $\lambda = 652$ nm as $\approx 130 \pm 30$ dm^3 mol^{-1} cm^{-1}.

Solubility Measurements.—Fig. 4 shows the solubility isotherm (298.2 K) for the copper(II) propionate–pyridine–chlorobenzene system. The dashed line represents the solubility of the analogous copper(II) acetate–pyridine complex.[6] The striking feature is a dramatic increase in the solubility of copper(II) proprionate in comparison with its acetate analogue (0.9 mol dm^{-3} and 2×10^{-3} mol dm^{-3} in chlorobenzene, 0.45 mol dm^{-3} and 5×10^{-2} mol dm^{-3} in pure pyridine, respectively). Moreover, the solubility isotherms of the two systems have different shapes in spite of the fact that the systems are similar and the equilibria occurring in solution [equations (1) and (2)] are the same. The increase in the solubility corresponding to the first part of the solubility curves {solid-phase $[Cu_2(O_2CR)_4(py)_2]$} can be explained by the formation of mononuclear structures, which are favoured by increasing amine activity. For this part of the solubility isotherm, not only is the activity of the binuclear complex constant, but also its concentration, c_b. The last conclusion can be drawn from spectrophotometric measurements which yield for the propionate complex c_b = 0.450, 0.446, 0.448, 0.444 and 0.446 mol dm^{-3} at x_L = 0, 0.14, 0.13, 0.17 and 0.20, respectively, and for the acetate complex $10^3 c_b$ = 1.1, 1.16, 1.20, 1.08 and 1.12 mol dm^{-3} at x_L = 0, 0.1, 0.15, 0.20 and 0.40, respectively. This allows us to assume that the activity coefficient of the binuclear form in solutions saturated with $[Cu_2(O_2CR)_4(py)_2]$ is approximately constant and close to 1. Consequently the variation of $(\gamma_m{}^2/\gamma_b)K_{th(b)}$ with a_L (Fig. 3) should be due to the preferential solvation of the mononuclear forms [the spectrophotometric results show that practically there is only one equilibrium, (1), in solutions in the range x_L 0–0.6].

The much smaller relative increase in the solubility observed for the propionate complexes (4%) in the first part of the solubility isotherm (x_L 0–0.2) in comparison with the acetate complexes (200% rise in *s* over the same range of x_L) can be explained by the striking difference in the concentration of the binuclear form in the saturated solutions (0.45 mol dm^{-3} and 1.1×10^{-3} mol dm^{-3}, respectively); it can be shown that $s_0{}^{-1}(\partial s/\partial a_L)_{\gamma_b = \text{const}} \approx c_b{}^{-\frac{1}{2}}K_{th(b)}{}^{-\frac{1}{2}}\gamma_m{}^{-1}$, the $K_{th(b)}$ and γ_m values for the two systems being the same within experimental error.

For $x_L > 0.6$ there is an even more dramatic difference in the shapes of the curves: here, the solubility of $[Cu(O_2CEt)_2(py)_3]$ decreases while that of $[Cu(O_2CMe)_2(py)_3]$ increases, in spite of the fact that the dependence of *s* on a_L is governed by the same equilibria. According to equations (1) and (2) the saturated solutions can contain mononuclear $[Cu(O_2CR)_2(py)_3]$ and $[Cu(O_2CR)_2(py)_2]$ as well as the binuclear $[Cu_2(O_2CR)_4(py)_2]$. However in the case of acetate complexes we can neglect the presence of binuclear structures in the saturated solutions because at $x_L > 0.6$ equilibrium (1) is fully shifted to the left due to the very low total copper(II) concentration (0.035–0.05 mol dm^{-3}; with $K_{th(b)} \approx 0.08$, c_b is of the order 10^{-5} mol dm^{-3}). Consequently only equation (2) should be taken into account, from which (5) follows. Here the activity of $[Cu(O_2CR)_2(py)_3]$

$$K_{th(m)} = \frac{a_{Cu(O_2CR)_2(py)_3}}{c_{Cu(O_2CR)_2(py)_2}\gamma_{Cu(O_2CR)_2(py)_2}a_L} \qquad (5)$$

is constant and rather low ($K_m \approx 10^{-1}$ dm^3 mol^{-1}) so the increase in solubility should primarily be due to the increase in concentration of $[Cu(O_2CR)_2(py)_2]$ in the saturated solution, even if $\gamma_{Cu(O_2CR)_2(py)_3}$ does change with a_L. Such an increase can easily be explained by the strong preferential solvation of mononuclear complexes (a rapid decrease in γ_m) which has been revealed for solutions of $x_L > 0.6$ and it is very probable for higher amine concentrations.

In the case of copper(II) propionate complexes we must take into account non-negligible amounts of the binuclear compound in the saturated solutions. This is because the ratio a_b/a_m rapidly increases (at constant a_L) with the total copper(II) concentration, which is much higher for propionate (0.7–0.5 mol dm^{-3}) than for acetate complexes. From equations (1) and (2) it follows that for solutions saturated with $[Cu(O_2CR)_2(py)_3]$, a_b decreases with the fourth power of a_L. Now, if we take into account that γ_b is not likely to depend strongly on a_L (see discussion above), we can expect a rapid decrease in c_b with increasing a_L. This effect should overcompensate the much lower increase in c_m caused by preferential solvation of mononuclear complexes with pyridine; indeed, for propionate complexes the calculated values of c_b and c_m vary as 0.15–0.01 (0.3–0.02 per atom Cu) and 0.2–0.4 mol dm^{-3}, respectively, when x_L increases from 0.6 to 1.

In contrast to binuclear $[Cu_2(O_2CEt)_4(py)_2]$ which is very stable in air (no changes after 2 years) the mononuclear dark blue propionate complex $[Cu(O_2CEt)_2(py)_3]$ decomposes rapidly yielding a light green binuclear compound. Similar behaviour is observed for the acetate complex $[Cu(O_2CMe)_2(py)_3]$. The real thermodynamic equilibrium between the solid $[Cu(O_2CR)_2(py)_3]$ and its saturated solution is not so readily obtainable for propionate complexes as it is for acetate because of supersaturation effects. The tendency to form supersaturated solutions is so strong for caproate complexes that it is difficult to measure reliable solubility isotherms.

Table 1 Equilibrium concentration quotients c_b/c_m^2, activity coefficient quotients $(\gamma_m^2/\gamma_b)K_{th}$ and spectral characteristics for bi- and mono-nuclear copper(II) carboxylate complexes in the system $Cu(O_2CR)_2$–pyridine–chlorobenzene at 298.2 K

$Cu(O_2CEt)_2$					$Cu[O_2C(CH_2)_4CH_3]_2$				
x_{py}	a_{py} (ref. 5)	c_m^{-2}/ dm^3 mol^{-1}	$(\gamma_m^2/\gamma_b)K_{th}$	Spectral characteristics	x_{py}	a_{py} (ref. 5)	c_m^{-2}/ dm^3 mol^{-1}	$(\gamma_m^2/\gamma_b)K_{th}$	Spectral characteristics
0.051	0.075	3000	16.9	$\lambda_{max(b)}$ 714,	0.124	0.156	510	12.4	$\lambda_{max(b)}$ 712,
0.107	0.140	520	10.2	$\varepsilon_{max(b)}$ 500	0.216	0.243	103	6.1	$\varepsilon_{max(b)}$ 490
0.124	0.160	370	8.9		0.216	0.243	68.7	4.1	
0.176	0.206	130	5.2	$\lambda_{max(m)}$ 665,	0.252	0.275	86.0	6.5	$\lambda_{max(m)}$ 662,
0.220	0.246	80.8	4.9	$\varepsilon_{max(m)}$ 83	0.258	0.286	85.2	7.0	$\varepsilon_{max(m)}$ 85
0.220	0.246	76.0	4.3	$\lambda_{max(m')}$ <654	0.258	0.286	78.0	6.4	
0.274	0.300	31.2	2.7		0.327	0.344	22.0	2.6	$\lambda_{max(m')}$ <650
0.325	0.342	29.3	3.4		0.400	0.413	16.2	2.8	
0.444	0.455	6.85	1.4						
0.500	0.511	4.1	1.1						
0.514	0.525	4.9	1.3						

Subscripts b and m refer to bi- and mono-nuclear complexes, respectively; m = $[Cu(O_2CR)_2(py)_2]$, m′ = $[Cu(O_2CR)_2(py)_3]$. The standard error in (c_b/c_m^2) is $<15\%$ except for values below 5 and above 500 where it can rise to 30%. Standard errors: λ ± 1 nm; $\varepsilon_b \pm 10$, $\varepsilon_m \pm 2$ dm^3 mol^{-1} cm^{-1}.

Conclusion

There is no appreciable dependence of the tendency to form binuclear structures in $Cu(O_2CR)_2$–pyridine–chlorobenzene systems and of the variation of the activities of the complexes in the solutions on the length of the alkane chain (R). The striking differences in the solubilities and in the shapes of the solubility isotherms for copper(II) acetate and propionate complexes with pyridine can mainly be ascribed to the stronger solvation of the binuclear propionate complex though the solvation of the mononuclear forms must also be higher. The solute–solvent interactions seem to be enhanced by the presence of the aromatic ring. This follows from the comparison between the measured solubilities of $[Cu_2(O_2Et)_4(py)_2]$ in benzene and chlorobenzene and those in hexane, cyclohexane and carbon tetrachloride (about 1 and 10^{-2}–10^{-3} mol dm^{-3}, respectively). The presence of the pyridine ligand without steric hindrance in the first co-ordination sphere strongly favours the solubility: the solubility in chlorobenzene strongly decreases when pyridine (L) is replaced by 2Me-py and 2,6Me$_2$-py in $[Cu_2(O_2CEt)_4L_2]$ (about four and forty times, respectively) and it is of the order of 10^{-3} mol dm^{-3} for anhydrous $[Cu_2(O_2CEt)_4]$.

Acknowledgements

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