Thermochimica Acta, 117 (1987) 59–72
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOLID AND SOLUTION COMPLEXES OF COPPER(II) ACETATE WITH PYRIDINE: STOICHIOMETRY, SPECTRAL AND THERMODYNAMIC CHARACTERISTICS

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(Received 12 December 1986)

ABSTRACT

Solubility isotherms, ESR and electronic spectra have been measured for $Cu(O_2CCH_3)_2$–pyridine–chlorobenzene and $Cu(O_2CCH_3)_2 \cdot H_2O$–pyridine–chlorobenzene systems. The results, together with the measured heats of solution of the solid $Cu(O_2CCH_3)_2py_3$ and $Cu(O_2CCH_3)_2py_3 \cdot H_2O$, their ESR (powder) and reflectance spectra, have been interpreted in terms of the stoichiometry of the complexes formed and the solute–solvent interactions. The dependence of the calculated activity coefficients of the solution complexes on pyridine activity suggests strong solvation of the mononuclear but not binuclear compounds by pyridine. The solute–solvent interactions lead to ligand rearrangement in polar media.

INTRODUCTION

It is now clearly recognized that copper(II) carboxylates form a variety of structures with basic ligands (L), the most common being binuclear monoadducts, $Cu(O_2CR)_2L$, and mononuclear adducts, $Cu(O_2CR)_2L_n$ ($n \geqslant 2$). While the structure of the binuclear compound is well known [1] and does not substantially change with anionic or basic ligands, the stoichiometry of mononuclear complexes is very sensitive to the electronic and steric properties of coordinated molecules or ions. At the moment there is no clear understanding of the factors determining which of the possible structures, mononuclear or binuclear, will be adopted in the solid state by the complex with the given ligands [2]. Even for adducts formed with ligands of the same homologous series, as for adducts of copper(II) alcoxylates with pyridine derivative bases, no correlation between the properties of the ligands and the adopted structure has been found: the balance between various effects is so delicate that even small modifications of the crystals' preparation procedure

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may result in a different stoichiometry and/or stereochemistry of the precipitated products [3].

Typical examples of such behaviour are the Cu(II) acetate–pyridine adducts. Four different stoichiometries have been reported for the complex precipitating from pure pyridine: those with 1, 2, 3 and 4 pyridine (py) molecules per $Cu(ac)_2$ entity [1,2,4] (ac = acetate). The mono-adduct ($n = 1$) is the well-known green binuclear compound [1] stable in the air, the other three (blue) are mononuclear. Amazingly enough they were all obtained by the same procedure but with a different temperature of crystallization in some cases (for $n = 1$, $T \approx 253$ K [4]; for $n = 2$ [2] and $n = 3$ [4], T was not specified; for $n = 3.8$, $T \approx 293$ K [4]). These data may suggest that the stoichiometry of the pyridine adducts is strongly dependent on the temperature and on the activity of pyridine in the gas or liquid phase in equilibrium with the solid. It is also thought that adopting mononuclear structures may be stimulated by traces of water in the reaction medium [3].

For a detailed investigation of the coordinating ability of Cu(II) acetate towards the pyridine ligand in the solid state and in solution we measured solubility isotherms, ESR and electronic spectra for the $Cu(ac)_2$–pyridine–chlorobenzene and $Cu(ac)_2 \cdot H_2O$–pyridine–chlorobenzene systems, as well as the temperature at which the two solid phases identified [$Cu(ac)_2L$ and $Cu(ac)_2L_3$] coexist with saturated solutions in the $Cu(ac)_2$–pyridine–chlorobenzene system. Heats of solution of the solid $Cu(ac)_2py_3$ and $Cu(ac)_2py_3 \cdot H_2O$ complexes in the binary pyridine–chlorobenzene solvent have also been measured by calorimetry. Chlorobenzene, which was used as a diluent to control the pyridine activity in the solutions, seems particularly suitable for such studies because it is a much weaker donor than pyridine and it forms nearly ideal solutions with pyridine bases [5].

EXPERIMENTAL

Preparation of the solid complexes

$Cu(ac)_2py_3 \cdot H_2O$ (mononuclear) and $Cu_2(ac)_4py_2$ (binuclear) were prepared as described previously [6]. $Cu(ac)_2py_3$ (mononuclear) was obtained by dissolving the binuclear $Cu_2(ac)_4py_2$ complex in dry, freshly distilled pyridine at 330 K and cooling the solution to 290 K. The blue precipitate was stored in a desiccator over pyridine. The complexes were analysed for Cu, pyridine and water content [6]. Analysis (%): calculated for $Cu(ac)_2py_3 \cdot H_2O$: Cu, 14.54; Py, 54.3; H_2O, 4.12; found: Cu, 14.57; Py, 56.9; H_2O, 4.12; calculated for $Cu_2(ac)_4py_2$: Cu, 24.37; Py, 30.3; N, 5.36; H, 4.21; C, 41.45; found: Cu, 24.2; Py, 32.3; N, 4.81; H, 4.28; C, 41.66; calculated for $Cu(ac)_2py_3$: Cu, 15.17; Py, 56.66; found: Cu, 15.4; Py, 55.1.

Chlorobenzene and pyridine were purified as described in ref. 5.

Measurements

Reflectance and UV-VIS solution spectra were measured on Beckmann 5270 spectrophotometer at 298.2 ± 0.1 K. ESR spectra (X band) were recorded on a Radiopan Se/X-2542 spectrometer at 298 and 77 K in quartz capillaries [7]. Solubility measurements were performed by the column method [5] at 298.2 K. The temperature of the phase transition (solid compounds equilibrated with the saturated solution) was estimated visually by sharp changes in the colour and shape of the precipitate's surface. Equilibrium was attained by cooling the supersaturated (320 K) solutions in stoppered flasks thoroughly protected from moisture. The samples were equilibrated for 5–8 days with continual shaking at temperature intervals of about 2 K. Calorimetric measurements were performed in moisture-free conditions using a reaction calorimeter of the "constant temperature environment" type, as described previously [8]. The complex (~ 100 mg) was placed in a reaction ampoule and dissolved in ~ 90 g of solvent. The heat capacity of the calorimeter was measured electrically [8]. The accuracy of the calibration was ±0.2%. The temperature of the measurements was 298.2 K. Special precautions had to be made to prevent decomposition of the solid complex during weighing and processing of the sample. This was achieved by placing two drops of pure pyridine on the inside wall of the cover-glass of the reaction ampoule.

All manipulations were performed in a dry-box over P_2O_5.

The measured conductivity of the solutions studied was below 10^{-7} Ω^{-1} cm^{-1} at Cu concentrations of 10^{-3} mol l^{-1}.

RESULTS AND DISCUSSION

$Cu(ac)_2$-pyridine–chlorobenzene system

Solubility isotherms (298.2 K) for $Cu(ac)_2$–pyridine–chlorobenzene and $Cu(ac)_2 \cdot H_2O$–pyridine–chlorobenzene systems are shown in Fig. 1. The solid phase in equilibrium with the solutions containing $X_{py} < 0.6$ is the binuclear $Cu_2(ac)_4py_2$ while at higher pyridine activities mononuclear solid complexes are formed.

The steep increase in the first part of the solubility curve ($X_{py} < 0.6$) strongly suggests that binuclear $Cu_2(ac)_4py_2$ reacts with pyridine. It was found [6] that in such systems an equilibrium is established:

$$2Cu(ac)_2py_2 \rightleftharpoons Cu_2(ac)_4py_2 + 2py \tag{1}$$

This is evidenced by the dependence of electronic spectra measured for $Cu(ac)_2$–pyridine–chlorobenzene solutions on Cu concentration (Fig. 2). The spectra indicate the presence of binuclear ($\lambda_{max} = 722$ nm) and mono-

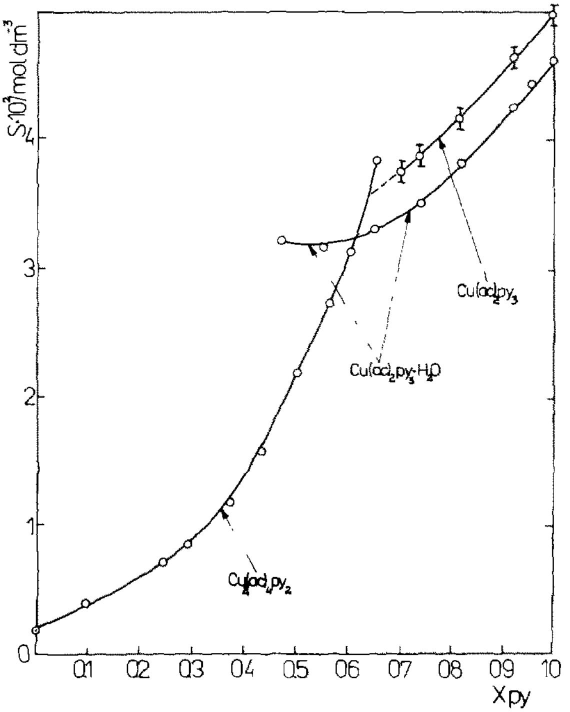

Fig. 1. Solubility isotherms for the systems $Cu(ac)_2$–pyridine–chlorobenzene and $Cu(O_2CCH_3)_2py_3 \cdot H_2O$–pyridine–chlorobenzene at 298 K. s = solubility calculated per atom of Cu.

nuclear complexes [6], the latter giving less intense absorption with $\lambda_{max} \approx$ 660 nm (in pure pyridine $\lambda_{max} = 658$, Fig. 3, curve 1). Small additions of water ($\sim 10^{-2}$ mol l^{-1}) do not appreciably influence the spectra. Even at $X_{H_2O} = 0.15$, changes in the spectrum are very small (compare Fig. 3, curves 1 and 3).

The second part of the solubility isotherm ($X_{py} = 0.6$–1) also shows a steep increase with increasing pyridine activity; this behaviour cannot, however, be discussed in terms of equilibria between mononuclear and binuclear forms of $Cu(ac)_2$–pyridine adducts because the electronic spectra of the saturated solutions containing $X_{py} > 0.6$ are typical of mononuclear solution complexes and they do not depend, within experimental error, on Cu concentration. However, the spectra show appreciable changes with increasing pyridine activity in the solutions (Fig. 3, curves 1 and 2). As the band at 658 nm is of the *d–d* type, it is not very sensitive to the medium effect. Hence the observed changes in spectra and in the solubility reflect either outer-sphere or inner-sphere interactions. The latter may involve competition between the pyridine molecules and one of the two oxygen atoms in the RCO_2 group for coordination sites around the Cu^{2+} ion.

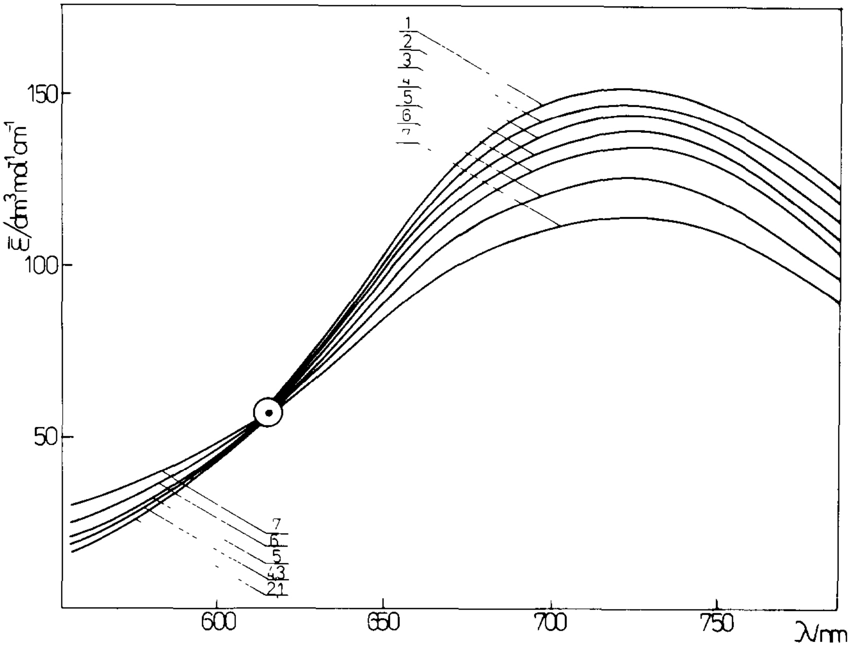

Fig. 2. Electronic spectra of $Cu(ac)_2$ in binary pyridine–chlorobenzene solvent at 298.2 K. $X_{py} = 0.120$; $c_{Cu} = 3.13 \times 10^{-3}$ mol l^{-1} (1); $c_{Cu} = 2.19 \times 10^{-3}$ mol l^{-1} (2); $c_{Cu} = 1.88 \times 10^{-3}$ mol l^{-1} (3); $c_{Cu} = 1.57 \times 10^{-3}$ mol l^{-1} (4); $c_{Cu} = 1.25 \times 10^{-3}$ mol l^{-1} (5); $c_{Cu} = 0.94 \times 10^{-3}$ mol l^{-1} (6); $c_{Cu} = 0.63 \times 10^{-3}$ mol l^{-1} (7).

Unfortunately neither solubility results nor IR solution spectra, which are perturbed by pyridine bands, are conclusive in this respect. ESR spectra of liquid and frozen $Cu(ac)_2$ solutions in the binary solvent are much more informative. They were measured in the mixed-solvent concentration range $X_{py} = 0.1$–1.0 in the X band. The recorded ESR spectra were characteristic of mononuclear complexes of Cu(II) acetate with pyridine derivatives which have no sterically hindering substituents [7] (the binuclear compounds, if present, do not absorb within the spectral range studied). The spin Hamiltonian parameters for $X_{py} = 0.1$ are: $g_0 = 2.150 \pm 0.005$, $a_0 = (-57 \pm 5) \times 10^{-4}$ cm^{-1}, $g_{\parallel} = 2.302 \pm 0.005$, $g_{\perp} = 2.057 \pm 0.002$, $A_{\parallel} = (-170 \pm 5) \times 10^{-4} cm^{-1}$, $A_{\perp} < 3 \times 10^{-4}$ cm^{-1}. They do not change with the composition of the mixed solvent and are close to those obtained for pure amine solutions [6]. A narrowing of the absorption bands and traces of developing superhyperfine structure in the perpendicular region of the spectrum can, however, be observed with increasing chlorobenzene content (Fig. 4). The shapes of the spectra suggest that there are no strongly coordinated pyridine ligands in the basal plane of the complex; consequently the pyridine molecules should occupy the apical positions and no more than two should occur in the first coordination sphere. Thus the ESR results strongly suggest

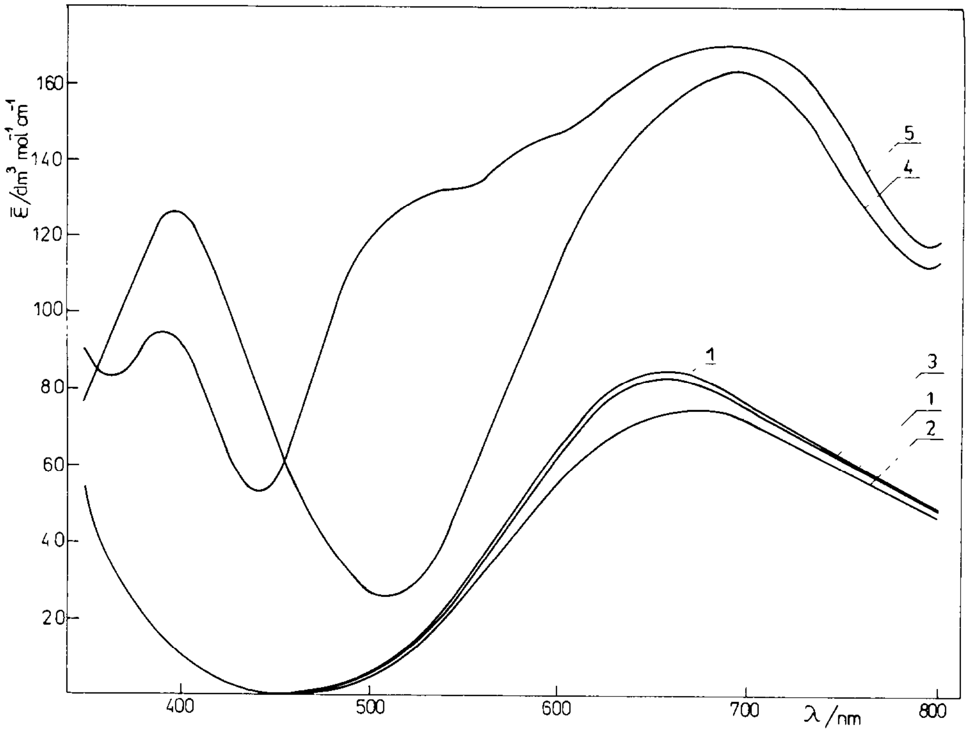

Fig. 3. Electronic spectra of (1) the $Cu(ac)_2$-pyridine-chlorobenzene system at 298.2 K, $c_{Cu} = 3.5 \times 10^{-3}$ mol l^{-1}, X_{py} 1.0; (2) the $Cu(ac)_2$-pyridine-chlorobenzene system at 298.2 K, $c_{Cu} = 3.5 \times 10^{-3}$ mol l^{-1}, $X_{py} = 1.0$; (3) the $Cu(ac)_2$-pyridine-H_2O system at 298.2 K, $c_{Cu} = 3.55 \times 10^{-3}$ mol l^{-1}; $X_{py} = 0.85$; (4) reflectance spectra of $Cu_2(ac)_4py_2$ (binuclear); (5) reflectance spectra of $Cu(ac)_2py_3 \cdot H_2O$.

that the mononuclear complex, present in the solutions in equilibrium with the solid $Cu(ac)_4py_2$ and $Cu(ac)_2py_3$ phases, has the stoichiometry $Cu(ac)_2py_2$.

With this information we can now calculate the constant of equilibrium (1) from solubility data. Taking solutions in pure pyridine as the reference state for ideal behaviour we may write:

$$K_{\text{therm}} = \frac{a_b a_{py}^2}{a_m^2} \approx \frac{s_b^0 a_{py}^2}{2\left(s - s_b^0\right)^2 \gamma_m^2} \tag{2}$$

where the indices b and m refer to binuclear and mononuclear species, respectively; $s_b^0 = 2a_b =$ constant is the solubility of $Cu_2(ac)_4py_2$ in pure chlorobenzene calculated per atom of Cu; s is the total solubility calculated per atom of Cu; γ_m is the activity coefficient of the mononuclear form. In equating $(s - s_b^0)$ to the concentration of the mononuclear form an assumption has been made that γ_b does not vary with the mixed solvent composition and, consequently, $\gamma_b = 1$ and $a_b = c_b = \frac{1}{2}s_b^0$. This assumption can be

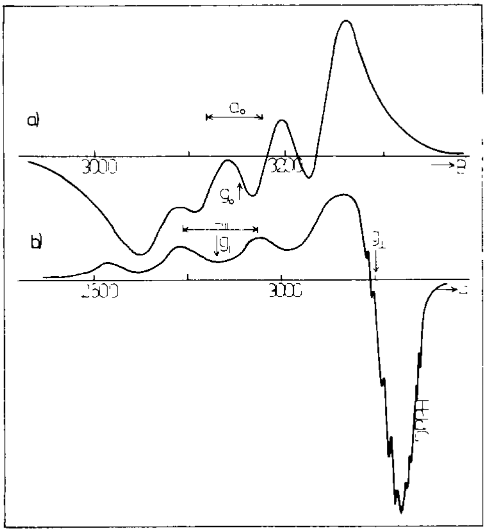

Fig. 4. ESR spectra of the $Cu(ac)_2$–pyridine–chlorobenzene system. $X_{py} = 0.10$, $c_{Cu} = 1.0 \times 10^{-3}$ mol l^{-1}; (a) 298 K, (b) 77 K.

verified by calculating the concentration of the binuclear complex in solutions saturated with $Cu_2(ac)_4py_2$ from the total solubilities and the c_b/c_m^2 ratio obtained by an independent (spectroscopic) method [6] (Table 1, columns 5, 4 and 3, respectively). As can be seen from the table the calculated concentration of the binuclear species does not substantially change over the concentration range $X_{py} = 0–0.6$, and it is practically equal to its solubility in pure chlorobenzene. However, γ_m cannot be assumed to be constant as is shown by the steep increase in solubility in the second part of the solubility isotherm ($X_{py} > 0.6$) where the solution contains mononuclear $Cu(ac)_2py_2$ complexes and the solid phase is $Cu(ac)_2py_3$. From this part of the isotherm we can, however, calculate the variation in γ_m with the mixed solvent composition down to $X_{py} \approx 0.63$ (Fig. 5, △). With the γ_m value for $X_{py} = 0.635$ (the triple point) and activities of pyridine in the binary mixture [9], we can calculate from eqn. (3) the value of $K_{therm} = 8.6 \times 10^{-2}$ and γ_m for solutions of mixed solvent composition $X_{py} < 0.6$. Figure 5 (△) shows that they rapidly decrease with increasing pyridine activity.

The results obtained from solubility data are compared with those derived from electronic spectra in Fig. 5, left ordinate (only the $K_{therm}\ \gamma_m^2$ product can be calculated from spectroscopic data). Although the scatter of experimental points is much greater for the spectroscopic data because of unfavourable measurement conditions [6], the agreement between the results obtained by the two independent methods is excellent.

In order to investigate the strength of the solute–solvent interactions revealed by variations in γ_m, we measured the heats of solution of the solid

TABLE 1

Solubilities (s) and equilibrium concentrations of binuclear (c_b) and mononuclear (c_m) Cu(ac)$_2$–pyridine complexes in pyridine–chlorobenzene mixed solvent (see text) (X_{py} = 0.0–0.65; T = 298 K)

X_L	a_{py}	c_b/c_m^2 [a] (l mol^{-1})	$s \times 10^2$ [b] (mol l^{-1})	$c_b \times 10^3$ [b,c] (mol l^{-1})	γ_b/γ_b^0 [d]
0.000	–	–	0.11	1.1 [e]	1.00
0.105	0.137	445	0.20	1.19	1.08
0.105	0.137	482	0.20	1.21	1.1
0.105	0.137	363	0.20	1.12	1.02
0.174	0.204	178	0.27	1.36	1.24
0.243	0.267	41	0.36	1.05	0.95
0.580	0.590	2.1	1.45	1.45	1.31
0.600	0.610	–	1.56	–	–
0.635	0.644	–	1.78	–	–
0.650	0.659	–	1.92	–	–

[a] From electronic spectra [6].
[b] Calculated per mol $Cu_2(O_2CCH_3)_4py_2$.
[c] Calculated from c_b/c_m^2 and s.
[d] Calculated from $c_b^0\gamma_b^0 = c_b\gamma_b$ = constant.
[e] Measured directly as solubility in pure chlorobenzene, $\frac{1}{2}s^0$.

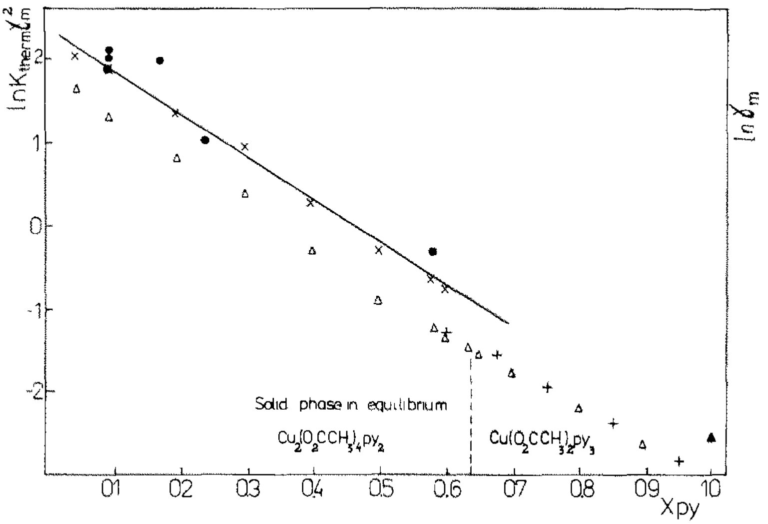

Fig. 5. Ln K_{therm} γ_m^2 (eqn. 2) vs. X_{py} (left ordinate): (×) Solubility method, (●) spectrophotometric method [6]; (▲) K_{therm} calculated from solubility data for X_{py} = 0.635. Ln γ_m vs. X_{py} (right ordinate), solubility method: (△) solutions equilibrated with Cu(ac)$_2$py$_3$; (+) solutions equilibrated with Cu(ac)$_2$py$_3 \cdot H_2O$.

TABLE 2

Solubilities (s) and heats of solution (ΔH_s) of $Cu(O_2CCH_3)_2py_3$ (solid) in pyridine–chlorobenzene mixtures, ΔG^0 and $T\Delta S^0$ of the reaction: $Cu(O_2CCH_3)_2py_3$ (solid) + solv $\rightleftharpoons$ $Cu(O_2CCH_3)_2py_2$(solv) + py(solv), and ΔH_{tr}, ΔG_{tr} and ΔS_{tr} of $Cu(O_2CCH_3)_2py_2$ from pyridine to the binary mixture pyridine–chlorobenzene ($x_{py} = 0.6–1.0$; $T = 298.2$ K)

X_{py}	a_{py}	$s \times 10^2$ (mol l^{-1})	ΔH_s[a] (kJ mol^{-1})	$-\Delta G^0$ (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔH_{tr} (kJ mol^{-1})	$-\Delta G_{tr}$ (kJ mol^{-1})	ΔS_{tr} (J mol^{-1} K^{-1})
1.00	1.00	4.98	38.0	7.44	152	0	0	0
0.910	0.910	4.57	42.5	7.88	169	4.5	0.44	17
0.867	0.868	4.37	44.0	8.11	175	6.0	0.67	23
0.775	0.780	4.01	46.0	8.59	183	8.0	1.15	31
0.670	0.678	3.65	46.5	9.17	187	8.5	1.73	35
0.650	0.659	3.60	48.0	9.27	192	10.0	1.83	40

[a] Error within 1 kJ mol^{-1}.

$Cu(ac)_2py_3$ in binary mixtures ($X_{py} = 0.6$–1), ΔH_s. The measured enthalpies of the reaction

$$Cu(ac)_2py_3(\text{solid}) + \text{solv} \rightleftharpoons Cu(ac)_2py_2(\text{solv}) + py(\text{solv}) \qquad (3)$$

are listed in Table 2 together with ΔG^0 calculated from the solubility measurements and ΔS^0 (ΔH_s^0 can be approximated by ΔH_s due to the strong dilution of the final solutions, $\sim 10^{-3}$ mol l^{-1}). The standard states are now: the solid state for the complex $Cu(ac)_2py_3$ and a binary solvent mixture of the given composition for $Cu(ac)_2py_2$. We can also approximate the functions of transfer of the mononuclear $Cu(ac)_2py_2$ complex from pure pyridine to the mixed solvent from the difference between pertinent values of the functions derived for reaction (3), because the transfer of pyridine between the given media contributes very little to the overall effects (for the pyridine–chlorobenzene system, ΔH^E and $\Delta G^E \approx 0.1$ kJ mol^{-1} [10,11]). The calculated ΔH and ΔS of transfer (Table 2), although indicating strong solute–pyridine interactions [12], are not typical of preferential solvation by pyridine because they rapidly change with small additions of chlorobenzene in the pyridine-rich region. Therefore, they reflect more radical changes than variations in the outer-sphere coordination.

A similar conclusion may be drawn from electronic spectra: the blue shift and increasing absorptivity coefficient of the *d–d* band of the mononuclear compound observed with increasing pyridine concentration suggest stronger tetragonal distortion and deviation from the centrosymmetric arrangement of the complex. Further changes in this direction occur when a pure pyridine solution of $Cu(ac)_2$ is diluted with small amounts of water (Fig. 3, curve 3). They are accompanied by changes in the ESR spectra of such solutions. At $X_{H_2O} = 0.1$ an SHF structure develops in the spectrum of the frozen solution and the spin Hamiltonian parameters differ appreciably from those derived for the spectrum of pure pyridine. The character of the observed changes strongly suggests that two pyridine molecules are now coordinated in the basal plane [7,13]. Such behaviour has been interpreted in terms of loosening of one of the Cu–O bonds in each of the COO groups with simultaneous shortening of the Cu–N distance (the complexes remain electrically neutral down to $X_{H_2O} \approx 0.2$; further additions of water result in monodentate coordination of the acetate anion and electrolytic dissociation [13]). It is quite possible that the effects observed on increasing pyridine concentration in the $Cu(ac)_2$–pyridine–chlorobenzene system reflect a gradual change from the structure of the complex adopted in weak polar media (two bidentate acetate groups in the basal plane) to that characteristic for polar media, as for pyridine–water mixtures at $X_{H_2O} \approx 0.1$, the situation in pure pyridine being an intermediate one. The structure of the electrically neutral complex in such polar media would be similar to that reported for $Cu(ac)_2py_3$ in the solid state [4] with two short Cu–O and two short Cu–N bonds in the basal plane and two oxygens loosely coordinated on the axis inclined to the plane of the complex.

The susceptibility of the mononuclear complexes to rearrangements in the first coordination sphere under the influence of increasing solute–solvent interactions (strong dependence of γ_m on X_{py}) is fully consistent with the known lability of the six-coordinate Cu(II) complexes. Such interactions seem to be much less effective in the case of the binuclear compound, as shown by the weak dependence of γ_b on X_{py}. This may be due to the rigidity of the binuclear compound which does not allow such modifications of the bond angles and lengths as would facilitate the solvation of the complex with changing medium.

$Cu(ac)_2 \cdot H_2O$–pyridine–chlorobenzene system

Small amounts of water, comparable with the Cu concentration in the saturated solutions ($\sim 10^{-2}$ mol l^{-1}), do not substantially affect either electronic or ESR spectra. However, the reflectance spectrum of solid $Cu(ac)_2py_3 \cdot H_2O$ apparently differs from that measured for its saturated solutions in pyridine [cf. Fig. 3, curves 5 and 1, which is identical to that obtained for solutions saturated with $Cu(ac)_2py_3 \cdot H_2O$]. Although its shape indicates that the sample must have been contaminated with the bimolecular compound (cf. curve 4) as a result of rapid decomposition of $Cu(ac)_2py_3 \cdot H_2O$ at low pyridine and water pressures, the absorption near 520 nm must be characteristic of the $Cu(ac)_2py_3 \cdot H_2O$ or $Cu(ac)_2py_3$ species, because such a band cannot be found either in the spectrum of binuclear compound or that of the mononuclear $Cu(ac)_2py_2$ complex in the solution (Fig. 3, curve 1). The position of this band strongly suggests increased tetragonality, as expected for the $Cu(ac)_2py_3$ complex which has a nearly planar stereochemistry [4].

To gain more information on the coordination of the H_2O molecule in the solid complex, we used ESR and calorimetric methods. The ESR powder spectrum of $Cu(ac)_2py_3 \cdot H_2O$ measured at 298 K (Fig. 6a) contains two broad lines which narrow at 77 K. The line positions at $g_1 = 2.047$ and $g_2 = 2.140$ are temperature-independent. The third line from parallel orientation is not resolved. It is also possible that $g_\perp = g_1$ and $g_\parallel = g_2$. This spectrum differs from the non-axial powder spectrum of $Cu(ac)_2py_3$ (Fig. 6c) which shows the line-width anisotropy resulting from magnetically non-equivalent copper(II) complexes in the crystal unit cell. The g factors for the $Cu(ac)_2py_3$ complex ($g_1 = 2.043$, $g_2 = 2.091$ and $g_3 = 2.302$) are also temperature-independent. They lead to the molecular local g factors of individual copper(II) complexes and an angle 2γ between differently oriented complexes in the crystal unit cell [14]: $g_\parallel = 2.345$, $g_\perp = 2.043$, $2\gamma = 56$. The line-width anisotropy and the line broadening at 77 K suggest a rather small exchange coupling between Cu(II) ions. The differences in the ESR spectra of $Cu(ac)_2py_3$ and $Cu(ac)_2py_3 \cdot H_2O$ suggest that the presence of the water molecule in the complex does influence its structure in the solid state.

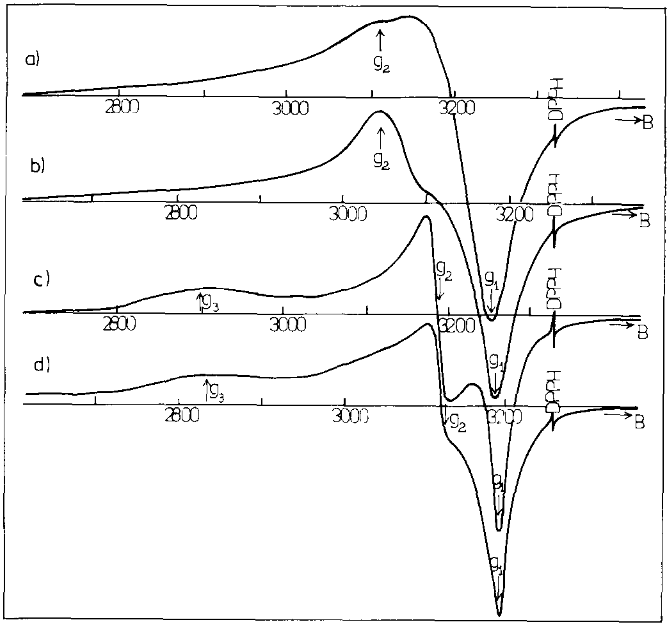

Fig. 6. ESR powder spectra of $Cu(ac)_2py_3 \cdot H_2O$ at (a) 298 K, (b) 77 K and those of $Cu(ac)_2py_3$ at (c) 298 K, (d) 77 K.

The measured calorimetric heats of solution of $Cu(ac)_2py_3 \cdot H_2O$ in pyridine ($+43.6$ kJ mol^{-1}) enabled us to estimate the heat of dissociation of H_2O molecule from the solid complex. As the spectra of solutions in equilibrium with solid $Cu(ac)_2py_3$ and $Cu(ac)_2py_3 \cdot H_2O$ are almost identical, we can assume that the solution complexes are the same. We can also assume that the dissociated water molecule is fully coordinated to the pyridine which is present in a large excess. The heat of the last interaction may be estimated from ΔH of mixing for the pyridine–water system [15]. We may thus write:

$$Cu(ac)_2py_3(solid) + py \overset{\Delta H_s}{\rightleftarrows} Cu(ac)_2py_2(solv) + py$$

$$\Delta H_s = 38 \text{ kJ mol}^{-1}$$

$$Cu(ac)_2py_3 \cdot H_2O(solid) + py \overset{\Delta H_b}{\rightleftharpoons} Cu(ac)_2py_2(solv) + py + H_2O(solv)$$

$$\Delta H_b = 43.6 \text{ kJ mol}^{-1}$$

$$H_2O(liq) + py \overset{\Delta H_c}{\rightleftharpoons} H_2O(solv); \Delta H_c = -2 \text{ kJ mol}^{-1}$$

$$H_2O(liq) \overset{\Delta H_d}{\rightleftharpoons} H_2O(gas) \qquad \Delta H_d = 10 \text{ kJ mol}^{-1}$$

and calculate the ΔH value of the reaction:

$$\mathrm{Cu(ac)_2py_3(solid)} + \mathrm{H_2O(gas)} \overset{\Delta H_4}{\rightleftharpoons} \mathrm{Cu(ac)_2py_3 \cdot H_2O(solid)} \tag{4}$$

as: $\Delta H_4 = \Delta H_a - \Delta H_b + \Delta H_c - \Delta H_d \approx -18$ kJ mol^{-1}. The very low heat of reaction (4) suggests that the water molecule enters the second coordination sphere. It also explains the fact that $\mathrm{Cu(ac)_2py_3 \cdot H_2O}$, although more stable in air than $\mathrm{Cu(ac)_2py_3}$, readily decomposes loosing water and, like $\mathrm{Cu(ac)_2py_3}$, transforms into the stable binuclear $\mathrm{Cu_2(ac)_4py_2}$.

As can be seen from Fig. 1, the presence of the water molecule in the solid complex decreases its solubility. It must, however, be noted that the equilibrium between the solid and liquid phases cannot be a true thermodynamic one, since this part of the solubility isotherm could be obtained only by saturating the mixed solvent with the solid $\mathrm{Cu(ac)_2py_3 \cdot H_2O}$ while attempts to precipitate this complex from the appropriate supersaturated solutions ($\mathrm{Cu/H_2O}$ ratio slightly above 1 : 1) were unsuccessful leading to the $\mathrm{Cu(ac)_2py_3}$ solid phase. Also the solution of the complex in equilibrium with the solid $\mathrm{Cu(ac)_2py_3 \cdot H_2O}$ behaves identically to that saturated with

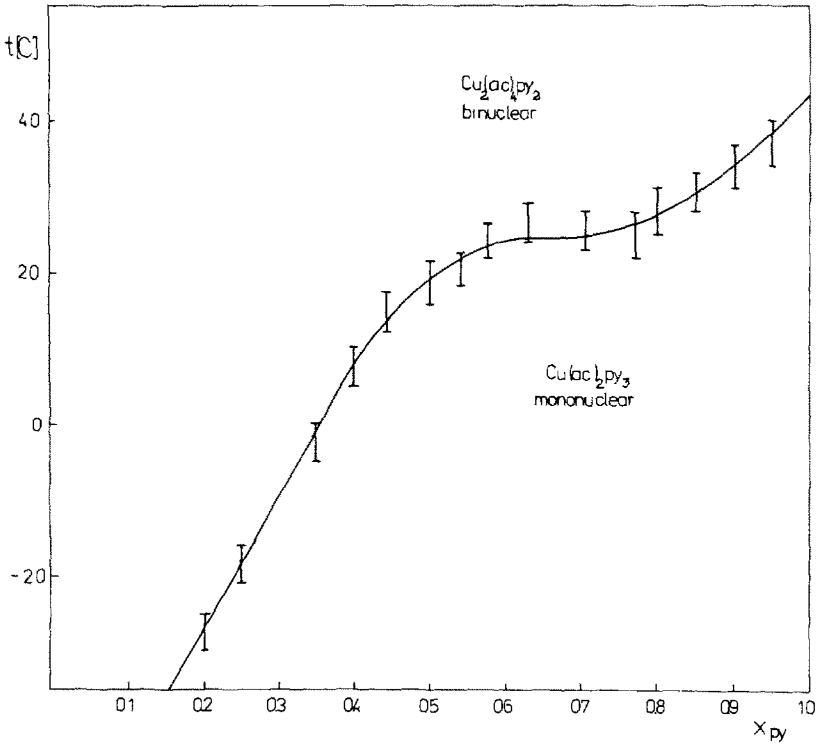

Fig. 7. Dependence of the temperature at which the three phases in equilibrium $\mathrm{Cu_2(ac)_4py_2}$, $\mathrm{Cu(ac)_2py_3}$ and the saturated solution in the $\mathrm{Cu(ac)_2}$ pyridine–chlorobenzene system coexist on the mixed solvent composition.

$Cu(ac)_2py_3$ (electronic spectra, activity coefficients), thus suggesting that the activity of water in such solutions is too low to allow the water to interact with the complex in solution.

Stability of the solid phase in equilibrium with pyridine and pyridine–chlorobenzene solutions

The temperature at which the three phases coexist [two solids: mononuclear $Cu(ac)_2py_3$ and binuclear $Cu_2(ac)_4py_2$, and the saturated solution] was measured as a function of amine activity in the saturated solutions (see Experimental section). In spite of the low precision of the method of measurement, the results obtained (Fig. 7) show that below 315 K only $Cu(ac)_2py_3$ is precipitated from pure pyridine solutions; above this temperature only the binuclear complex can be stable. At ambient temperatures the curve in Fig. 7 is almost horizontal over a comparatively wide range of solvent composition. This may explain the apparently contradictory reports on obtaining complexes of different stoichiometry by the same precipitation techniques. We did not, however, notice the appearance of the solid complex of the stoichiometry $Cu(ac)_2py_2$ at any proportion of pyridine in the solution.

ACKNOWLEDGEMENT

This work was done with the financial support of the Polish Academy of Sciences.

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