Monomer and dimer complexes of copper(II) acetate with pyridine and picolines—II. Solution equilibria by…

2 authors, including:

A.Latif Abuhijleh

Birzeit University

19 PUBLICATIONS   **503** CITATIONS

MONOMER AND DIMER COMPLEXES OF COPPER(II) ACETATE WITH PYRIDINE AND PICOLINES—II.* SOLUTION EQUILIBRIA BY SPECTROPHOTOMETRIC AND NMR MAGNETIC MEASUREMENTS

A. LATIF ABUHIJLEH†

Chemistry Department, Birzeit University, P.O. Box 14, West Bank—Via Israel

and

I. Y. AHMED

Chemistry Department, The University of Mississippi, University, MS 38677, U.S.A.

Abstract—Equilibrium constants (K) for the reaction:

$$[Cu(OAc)_2 \cdot L]_2 + 2L \rightleftharpoons 2[Cu(OAc)_2 \cdot L_2],$$

where OAc is the acetate anion and L = pyridine (py), β-picoline (β-pic) or γ-picoline (γ-pic), were determined from spectrophotometric and variable-temperature magnetic measurements in chloroform solutions. Good agreement was found between the two methods. The small K values (0.01–0.45) found for the equilibria are consistent with the observed instability of the monomers in chloroform, and increase in the order: py < β-pic < γ-pic. The position of the β-picoline system, for which no crystalline monomer could be isolated, and the anomalous behaviour of α-picoline within this series are discussed in terms of crystal-packing requirements arising from the steric properties of these ligands. Thermodynamic parameters for the equilibria were obtained from the temperature dependence of K. The values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are in close agreement with those found for adduct formation of related copper(II) chelates with these ligands, and are discussed in terms of contributions from electronics and structural reorganization, bond formation and solvation effects.

Copper(II) carboxylate adducts with a large variety of ligands have been extensively investigated, and the results have been summarized in several reports.[1-4] Attention has been directed primarily at understanding the structural basis for the special magnetic and spectral properties of the dimeric mono-adducts. Some copper(II) carboxylates, on the other hand, tend to form monomeric bis- and tetrakis-adducts with these ligands.[5-9] There have been many studies to investigate the factors which influence dimer formation over monomer formation in copper(II) carboxylate solvate complexes.[3,6-8] It has been found, generally, that in-creasing acidity of the carboxylate groups and/or the basicity of the ligands increases the tendency towards formation of a monomeric adduct which is related to the electronic effects of the carboxylate groups and of the ligands.[6-8]

Previously,[9] we reported the preparation and characterization of some monomeric bis-adducts as well as the dimeric mono-adducts of copper(II) acetate with pyridine and picolines. Although the four dimeric adducts are converted to the monomeric complexes in solutions of their respective ligands, only in the cases of pyridine and α-picoline were crystalline monomeric bis-adducts isolated. In an effort to shed some light on the role of the addend in stabilizing either of the two structural types, we report herein the results of equilibrium measurements for the monomer–dimer interconversion.

---

* For Part I, see ref. 9.
† Author to whom correspondence should be addressed.

Because the two adducts have distinctly different spectral and magnetic properties and as a result of the relative instability of the monomers in most solvents, these systems are well suited for detailed examination by electronic and NMR spectral method. The utility of NMR spectroscopy to measure temperature-dependent magnetic properties and solution equilibria, where structural changes with concomitant changes in magnetic moments occur, has been amply demonstrated for several types of equilibria exhibited in solutions of transition metal complexes.[10-13] Solution magnetic studies of structural equilibria have the advantage of providing reliable thermodynamic parameters which are free from unpredictable lattice effects. The availability of a variable-temperature NMR probe permits the equilibrium constant to be determined over a wide range of temperatures and the thermodynamic parameters to be ascertained.

EXPERIMENTAL

Apparatus and measurements

Preparation of the complexes and characteristics of their solutions have been described previously.[9] Solution mixtures for equilibrium constant determination were prepared by the addition of varying amounts of the ligand to portions of a known fixed concentration of the dimer in chloroform solution. For NMR measurements, the latter solution contained 6% (v/v) cyclohexane as internal reference and 4% TMS for signal-locking. The ^{1}H NMR spectral measurements were recorded at 90 MHz on a Perkin–Elmer R-32 spectrometer in Wilmad co-axial tubes with movable glass spacers. The temperature calibration was monitored by methanol or ethylene glycol samples. The signal separation of the reference at each temperature was the average of at least four consecutive recordings which were further checked by comparison with the separation of chloroform signals averaged in the same manner. All other measurements and apparatus were as described previously.[9]

Procedure

According to the NMR technique proposed by Evans,[14] the corrected molar magnetic susceptibility, χ'_m, is related to the shift of the reference signal, δv, by the equation:

$$\chi'_m = \frac{3\delta v}{2\pi vC},\qquad(1)$$

where v is the oscillator frequency and C is the

concentration of the paramagnetic material in mol cm^{-3}. For a solution containing an equilibrium mixture of monomer (M) and dimer (D), the observed molar susceptibility per copper is the weighted average of contributions from the monomer and dimer magnetic susceptibility.[10]

It can be shown that the observed shift for a solution mixture is given by:

$$\delta v = [M]\Delta v_{(M)} + 2[D]\Delta v_{(D)},\qquad(2)$$

where Δv is the "molar shift" ($\delta v/c$) for pure monomer or pure dimer and can be determined separately from their respective solutions at various temperatures. The concentration of the monomer and dimer for each solution can then be determined from eq. (2) and also the known total copper concentration for each mixture.

RESULTS

Spectrophotometric measurements

Representative electronic spectra of equilibrium mixtures in chloroform of copper(II) acetate-γ-picoline complexes are presented in Fig. 1. Spectra of the mixtures show two isosbestic points, consistent with an equilibrium which involves two
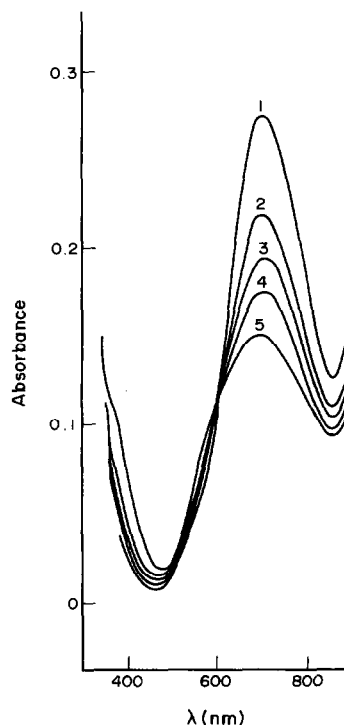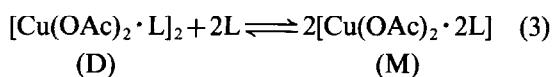

Fig. 1. Visible spectra of equilibrium mixtures in chloroform of copper(II) acetate-γ-picoline complexes, $[Cu^{2+}] = 1.916 \times 10^{-3}$ M, and γ-pic/Cu^{2+} = 25 (1), 50 (2), 76 (3), 101 (4), 239 (5), where the number in parentheses refers to the absorption curve in the figure.

absorbing species. The constant for the equilibrium:

$$[Cu(OAc)_2 \cdot L]_2 + 2L \rightleftharpoons 2[Cu(OAc)_2 \cdot 2L] \quad (3)$$
$$(D) \qquad\qquad\qquad (M)$$

was evaluated from absorptivities at the two wavelengths[9] (at the pure dimer maximum around 700 nm and at the pure monomer maximum around 650 nm), by common procedures[15] with the aid of a computer program. To further assess the degree of ligand participation in the equilibrium, the data were analysed graphically in terms of the equilibrium: $D + nL \rightleftharpoons 2M$, for which the equilibrium constant is given by:

$$K = \frac{[M]^2}{[D][L]^n}. \quad (4)$$

This can be rearranged in the form:

$$\log [M]^2/[D] = n \log [L] + \log K. \quad (5)$$

Plots of $\log [M]^2/[D]$ vs $\log [L]$ produced straight lines which are shown in Fig. 2. The value of n can be obtained from the slope, and was found to be two in all cases. The equilibrium constant values were found to be: $(1.2 \pm 0.2) \times 10^{-2}$, $(7.0 \pm 0.3) \times 10^{-2}$ and $(39 \pm 3) \times 10^{-2}$ for pyridine, β-picoline and γ-picoline, respectively. It should be pointed out that measurements of the β-picoline system were carried out at about 20°C to ensure complete conversion to the monomer in the neat ligand solutions, whereas data for the other two

systems were obtained conveniently at room temperature (30°C). For comparison, the K value for the pyridine system at 20°C was found to be 3.0×10^{-2}. It was not possible to evaluate an analogous equilibrium constant for the α-picoline system since traces of dimer persist even in its solutions in the neat ligand cooled to 0°C.[9] In addition, the electronic spectra of equilibrium mixtures of the α-picoline complexes show an anomalous shift to lower energies as the ligand concentration is increased. This is in contrast to the behaviour observed in the other systems, and makes evaluation of equilibrium constants from such data questionable.

NMR measurements

The effect of incremental addition of pyridine upon the NMR shift of the reference in chloroform solutions of the dimer at various temperatures is shown in Fig. 3. Similar behaviour was found at other concentrations and for the other systems. The plots demonstrate the exothermic nature of reaction (3) and the effect of the ligand on the equilibrium position. The equilibrium constant at each temperature was evaluated by solution of eq. (2). The temperature dependence of the equilibrium constants for the three systems is shown in Fig. 4. Analysis of the data by the least-squares method yielded the thermodynamic parameters for the equilibrium, which are summarized in Table 1.
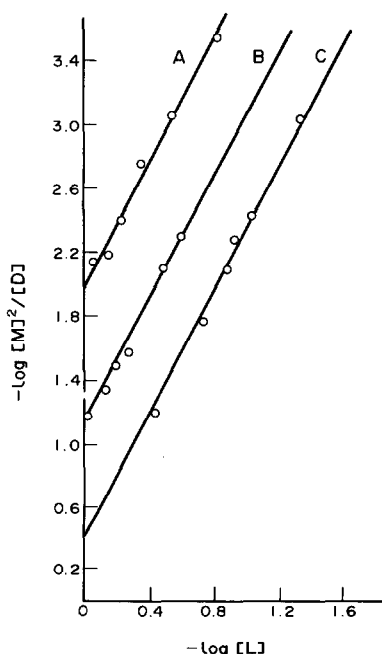
DISCUSSION

The results of this study are interesting in many respects. Equilibrium constant values, at room

Fig. 2. Graphic determination of K and n from eq. (5): (A) py, (B) β-pic and (C) γ-pic.
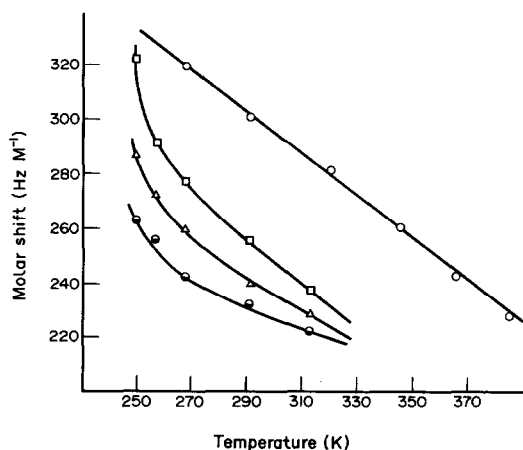

Fig. 3. Effects of temperature and pyridine concentration, 1.82 M ($\square$), 1.27 M ($\triangle$), 1.02 M ($\ominus$), on the NMR molar shift of the reference in the equilibrium mixtures; $\bigcirc$ represents the molar shift in solution of the pure monomer, $[Cu^{2+}] = 3.07 \times 10^{-2}$ M.
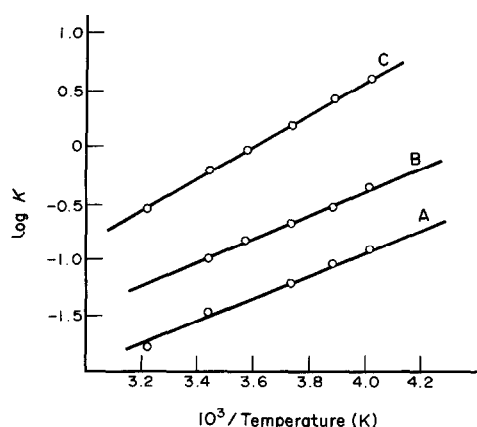
Fig. 4. Temperature dependence of the equilibrium constants: (A) py, (B) β-pic and (C) γ-pic.

temperature, measured by the NMR method agree reasonably well with those obtained spectrophotometrically, despite the inherent differences and experimental uncertainties associated with the two techniques. This confirms the validity of the equilibrium stoichiometry and the reliability of the NMR method for studying structural equilibria in solution. The small K values for the dimer–monomer conversion are consistent with the observed instability of the monomers in chloroform solutions.[9] The most obvious result, however, is that the relative formation constants of the monomeric complexes with these bases increase in the order: py $< \beta$-pic $< \gamma$-pic. This is the order of increased base strength and the order observed for the formation constants of their complexes with a large variety of Lewis acids.[16–19]

This study, on the other hand, demonstrates that the pyridine bis-adduct shows exceptional stability in spite of the smaller value of its formation constant in solution, whereas the β-picoline bis-adduct, with a higher formation constant in solution, could not be isolated as a crystalline solid. The apparent contradiction can be reconciled if one recognized

Table 1. Thermodynamic values at 298 K for the equilibrium:

Dimer $+ 2L \rightleftharpoons 2$ monomer

L	$K \times 10^{2a}$	$-\Delta H^{\ominus} \pm 0.5$ (kJ mol^{-1})	$-\Delta S^{\ominus} \pm 1$ (J mol^{-1} K^{-1})
Pyridine	2.5 ± 0.2 (1.2)	20.8	100
β-Picoline	8.4 ± 0.3 (7.0)	20.5	89
γ-Picoline	45 ± 2 (39)	27.6	98

^{a} Values in parentheses are from spectrophotometric measurements at $\sim 30°C$.
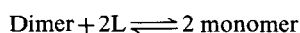
that the thermal stability of the solid may have little relationship with the solution formation constants. Factors related to crystal packing requirements which stem from symmetry properties of the ligand may account for the thermal instability of the β-picoline bis-adduct. This is further demonstrated in the case of α-picoline which has the same base strength as γ-picoline but fails to form a monomeric bis-adduct either in the crystalline state or in solution. The tendency to attain six-coordination with this ligand is suppressed by crowding around the central metal ion.[9,19] Steric interactions undoubtedly play a significant role in destabilizing the monomeric complex in the case of the α- and β-picolines.

The enthalpy and entropy values obtained for the equilibrium are not significantly different for the three systems, and are in close agreement with those found for adduct formation of related copper(II) chelates with these ligands.[16–19] The $\Delta H^{\ominus}$ values are in the range expected for copper–nitrogen bond formation[19] and increase in the order: py $\simeq \beta$-pic $< \gamma$-pic. Negative $\Delta S^{\ominus}$ values of the observed order of magnitude are to be expected in a system in which there is a net loss of translational freedom of two reactant species.

The observed thermodynamic values represent changes occurring in the total energy of the system upon monomer formation, and can be interpreted as the net result of contributions from electronic and structural reorganization, metal–ligand bond formation and solvation energy effects. However, the absence of thermochemical data for these systems does not allow a quantitative analysis of the various terms, but the significance of these contributions can be qualitatively assessed. Contribution from electronic rearrangement which accompanies monomer formation is evidenced by the fairly significant shift to higher energy in the electronic spectra (from around 700 nm in the dimer to around 650 nm in the monomer).[9] Structural reorganization within the dimer, whereby the four bridging acetate groups act as an essentially monodentate or asymmetric chelating ligand in the monomer, is expected to be extensive. The energy contribution of this term is expected to inhibit monomer formation by making a positive contribution to the enthalpy. However, the contribution of this term should be constant, or nearly so, in the three systems and is balanced by the negative contribution to the enthalpy as a result of formation of comparable copper–oxygen bonds in the monomer.

Formation of the additional copper–nitrogen bond should make a negative contribution to the enthalpy. In the absence of any steric effects, the

contribution due to bond formation depends on the availability of the electron pair on the nitrogen atom and, within a related series of ligands, is reflected by the relative order of their dipole moments, ionization energies and pK_a values.[17] On this basis the sequence of donor ability is well established to be: py $< \beta$-pic $< \alpha$-pic $< \gamma$-pic.

That contribution to the observed thermodynamic parameters from solvation effects must be significant is clearly manifested in the instability of the monomer in chloroform solution where it is quantitatively converted to the dimer. Whether the dimers are solvated to any extent in these solutions is not clear, but no large variations in the degree of solvation are expected among the four complexes. On the other hand, pyridine bases are known to interact strongly with chloroform, presumably via hydrogen bonding.[17,19,20] This interaction contributes a large exothermic ΔH(soln) term, which increases in the order: py $< \beta$-pic $< \alpha$-pic $< \gamma$-pic. Variations in the actual values of $\Delta H^\ominus$ and $\Delta S^\ominus$ are affected, no doubt, by differences in the solvation effects which may account for the lower than expected values found for the β-picoline system.

The thermodynamic parameters found for these systems are, in general, in accord with this analysis. While the electronic properties of the carboxylate group may be significant in affecting the stabilization of a particular structural type,[1] the steric and electronic properties of the addend also play an important role in this respect.[6-8] This view is supported by the structural results of the copper(II) acetate bis-adduct with collidine[6] in which, despite prohibitive steric crowding resulting from the two α-methyl groups, the superior donor ability of this ligand allows copper–nitrogen bond formation at the expense of disrupting the copper–acetate bonding. In addition, the importance of electronic properties of the addend are also demonstrated when basic ligands such as ammonia and imidazoles react

with copper(II) acetate in which only monomeric adducts are formed.[5,21]

REFERENCES

1. R. J. Doedens, *Prog. Inorg. Chem.* 1976, **21**, 209.
2. R. W. Jotham, S. F. A. Kettle and J. A. Marks, *J. Chem. Soc., Dalton Trans.* 1972, 428.
3. M. Melnik, *Coord. Chem. Rev.* 1981, **36**, 1.
4. M. Kato and Y. Muto, *Coord. Chem. Rev.* 1988, **92**, 45.
5. H. A. Henriksson, *Acta Cryst.* 1977, **B33**, 1947.
6. N. E. Heimer and I. Y. Ahmed, *Inorg. Chim. Acta* 1982, **64**, L65.
7. F. T. Greenaway, A. Pezeshk, A. W. Cordes, M. C. Noble and J. R. J. Sorenson, *Inorg. Chim. Acta* 1984, **93**, 67.
8. A. Latif Abuhijleh, *Polyhedron* 1989, **8**, 2777.
9. I. Y. Ahmed and A. L. Abuhijleh, *Inorg. Chim. Acta* 1982, **61**, 241.
10. T. H. Crawford and J. Swanson, *J. Chem. Educ.* 1971, **48**, 382.
11. D. F. Evans and T. A. James, *J. Chem. Soc., Dalton Trans.* 1979, 723.
12. R. H. Petty, E. V. Dose, M. F. Tweedle and L. J. Wilson, *Inorg. Chem.* 1978, **17**, 1064.
13. L. Rusnak and R. B. Jordan, *Inorg. Chem.* 1971, **10**, 2199.
14. D. F. Evans, *J. Chem. Soc.* 1959, 2003.
15. R. S. Drago, *Physical Methods in Chemistry*, pp. 88–93. Saunders, Philadelphia (1977).
16. J. J. Christensen, D. J. Eatough and R. M. Izatt, *Handbook of Metal Ligand Heats*, 2nd edn, pp. 306–338. Marcel Dekker, New York (1975).
17. B. L. Libutti, B. B. Wayland and A. F. Garito, *Inorg. Chem.* 1969, **8**, 1510; A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.* 1969, **91**, 866.
18. F. G. Herring and R. L. Tapping, *J. Phys. Chem.* 1974, **78**, 316.
19. D. P. Graddon, *Coord. Chem. Rev.* 1969, **4**, 1.
20. W. Libus, S. K. Hoffman, M. Kluczkowski and H. Twardowska, *Inorg. Chem.* 1980, **19**, 1625.
21. Y. A. Simonoo, A. U. Abloo and T. I. Molmoski, *Kristallografiya* 1963, **8**, 205.