Mono- and Di-pyridine Adducts of Bis(3-substituted 2,4-pentanedionato)Copper(II) Complexes

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Adduct formation constants, K_1, for equilibria of the type, $CuL_2 + py \rightleftharpoons CuL_2(py)$, where L = (MeCO·CR·COMe; R = Me, H, Cl, Ac, CO_2Et, CN, and NO_2) and py = pyridine, have been determined in benzene, acetone, and acetonitrile solution at 22 °C. The values of K_1 are correlated with the electronic nature of the substituent, R, and the dielectric constant of the solvent. In two cases, R = CN and NO_2, further equilibria of type $CuL_2py + py \rightleftharpoons CuL_2(py)_2$ have been observed at high pyridine concentrations and diadduct formation constants, K_2 have been determined.

THE equilibria between copper(II)–β-diketoenolate complexes and their adducts with Lewis bases in solution have been previously investigated by several workers.[1-7] Graddon and Watton[1,2] established that the copper acetylacetonate complex, $Cu(acac)_2$, [acac = $(CH_3COCHCOCH_3)^-$], formed 1 : 1 adducts with pyridine bases and that the adduct formation constant, K, for equilibrium (1) increased with decreasing polarity of the

$$Cu(acac)_2 + Base \rightleftharpoons Cu(acac)_2Base \qquad (1)$$

solvent, an effect they attributed to decreased solvation of the base by the less-polar solvents. They also found that K increased along the series of heterocyclic bases, 2,6-lutidine < α-picoline < pyridine < γ-picoline, an observation they explained in terms of a combination of electronic and steric effects. May and Jones[3] further investigated the equilibria in benzene solution with pyridine and substituted pyridines and determined ΔH, the enthalpy change, directly by using calorimetric methods and indirectly from the variation of K with temperature. Agreement between the ΔH values obtained was poor but the results did indicate that ΔH increased with increasing basicity of the substituted pyridine consistent with an increasing Cu–N bond strength. No direct correlation, however, was found between K and the basicity of the substituted pyridine due to relatively large variations in the entropy change, ΔS, with different substituents.

More recently, the equilibria (2) where L =

$$CuL_2 + \text{pyridine} \rightleftharpoons CuL_2\text{pyridine} \qquad (2)$$

$[CH_3COCRCOCH_3]^-$ and R = alkyl or substituted alkyl group have been examined.[7] This system was chosen in order to study the transmission of electronic effects through the co-ordinated β-dicarbonyl ring to or from the cupric ion. 3-Substitution of the ligand was not expected to cause as marked steric effects at the co-ordination site as would have been the case with substitution at the terminal carbons. It was found that, for a series of substituents, R, which were electron donating with respect to hydrogen, K decreased smoothly with increasing positive inductive effect of the substituent. These results indicated that the substituent was affecting the electron density on the copper ion and also suggested that any variation in ΔS on changing the substituent was small relative to the change in ΔH. This paper presents the results of an extension of this work to some substituents which are electron accepting, relative to H, namely, R = Cl, Ac, CO_2Et, CN, and NO_2.

EXPERIMENTAL

Preparative methods for the ligands and analytical data for the cupric complexes are given in Table 1. The complexes (with the exception of the nitro-compound)[14] were prepared by adding the substituted ligand to a saturated solution of copper acetate followed by at least two recrystallisations of the product. The nitro-compound was recrystallised three times from acetone before use.

TABLE 1

Microanalytical results and preparative methods for the complexes CuL_2

Compd. CuL_2 R =	Prep. method ref.	% C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found
Me	8	49·7	49·5	6·3	6·2		
H	9	45·9	45·9	5·4	5·4		
Cl	10	36·3	36·3	3·7	3·8		
Ac	11	48·6	48·3	5·3	5·3		
CO_2Et	12	47·3	47·0	5·5	5·6		
CN	13	46·2	45·9	3·9	3·8	9·1	9·0
NO_2	14	34·1	33·9	3·5	3·3	8·0	7·8

Other Materials.—Acetone and acetonitrile were dried over P_4O_{10}, benzene over sodium metal, and pyridine over KOH pellets; each was fractionally distilled before use.

Determination of Adduct Formation Constants.—All the copper β-diketoenolate–pyridine systems examined exhibited isosbestic points consistent with 1 : 1 adduct formation. At higher pyridine concentrations the 3-cyano- and 3-nitro-acetylacetonate complexes showed a second isosbestic point corresponding to 2 : 1 adduct formation.

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The K values were determined spectrophotometrically. The optical densities of the copper chelate solutions both with and without added pyridine were measured in 1 cm thermostatted cells using a Unicam SP 500 spectrophotometer. Wavelengths were chosen to provide the largest optical density range for each set of measurements and are given in Tables 3 and 4. At least 15 different pyridine concentrations were used to provide data for each determination. The values of K_1 were obtained from equation (3)

$$K_1 = \frac{(E_1 - E_2)(E_3 - E_2)}{(E_3 - E_1)\{[\mathrm{py}](E_3 - E_2) - [\mathrm{Cu}](E_1 - E_2)\}} \qquad (3)$$

where E_1 is the apparent molar extinction coefficient of the complex in the presence of a concentration of pyridine, [py] (mol l^{-1}), and E_2 and E_3 are the molar extinction coefficients of the complexes CuL_2 and $CuL_2(py)$ respectively. [Cu] is the molarity of copper present.

Since both E_3 and K_1 are unknown, the value of E_3 was varied until the most consistent values of K_1 for a given set of data (in terms of percentage standard deviation) was obtained. This procedure was computed on an IBM 360/44 computer using a locally written program. The K_1 values for the 3-cyano- and 3-nitro-complexes were obtained with [py] less than 0·05M. Copper concentrations of between 0·003 and 0·005M were used in all determinations. The reproducibility of the K_1 determinations was better than ±5% in all cases.

The determinations of K_2, where appropriate, were done in an analogous manner. The differences between K_1 and K_2 were sufficient to allow the approximation that the equilibria (4) and (5) occur exclusively at low and high

$$CuL_2 + py \rightleftharpoons CuL_2(py) \qquad (4)$$

$$CuL_2py + py \rightleftharpoons CuL_2(py)_2 \qquad (5)$$

pyridine concentrations respectively. K_2 Values were obtained with [py] greater than 2·5M; less than 1% CuL_2 is present at this concentration. The reproducibility of the K_2 values was estimated better than ±50%, the decreased reproducibility being largely due to (*a*) the restricted optical density range over which readings could be taken and (*b*) the instability of the complexes at high pyridine concentrations. The value of the molar extinction coefficient of CuL_2py was taken from the appropriate K_1 results.

The values of K_1 and K_2 are not absolute since no correction has been made for any solvent effect due to the pyridine. This may be appreciable especially in the case of the K_2 measurements where relatively high pyridine concentrations were used.

TABLE 2

Microanalytical results for some representative mono- and di-pyridine and quinoline adducts

Compound CuL_2B_2	% C Calc.	% C Found	% H Calc.	% H Found	% N Calc.	% N Found
$Cu(CO_2Etacac)_2(py)$	52·0	51·8	5·6	5·8	2·9	2·7
$Cu(CO_2Etacac)_2$-(quin)	56·1	55·9	5·5	5·5	2·6	2·4
$Cu(NO_2acac)(py)_2$	47·0	46·2	4·4	4·3	11·0	10·8
$Cu(NO_2acac)(quin)_2$	55·1	54·5	4·3	4·3	9·2	8·8

Preparation of Adducts.—Solid adducts can usually, but not always, be prepared by dissolving the complex CuL_2 in the minimum volume of hot base and allowing the solution to cool. The crystals of adduct were filtered off and stored in stoppered bottles to prevent loss of base. Analytical data for some of the prepared adducts are given in Table 2.

Thermogravimetric data were obtained in a nitrogen atmosphere using a Stanton Model TR-1 thermobalance at a heating rate of 2 °C per min. Reflectance spectra were determined with an SP 735 diffuse-reflectance attachment on a Unicam SP 700 spectrophotometer with a magnesium oxide reference.

RESULTS AND DISCUSSION

The adduct formation constants, K_1, for the mono-pyridine adducts, $CuL_2(py)$, in benzene, acetone, and acetonitrile solutions at 22 °C are given in Table 3. The low solubilities of the acetyl-, cyano-, and nitro-compounds in benzene precluded K measurements in this solvent. With the exception of the chloro-compound, K_1 values for all the complexes in acetone solution have been determined. The chloro-compound decomposed quite rapidly in benzene and acetone solutions; with the other complexes any decomposition in solution was too slow to significantly affect the accuracy of measurements. K_1 values for the 3-cyano- and 3-nitro-complexes in acetonitrile are also reported.

TABLE 3

Adduct formation constants, K_1, for the equilibria $CuL_2 + py \rightleftharpoons CuL_2(py)$ at 22 °C

	K_1 (mol^{-1} l)			
R =	Benzene	Acetone	Acetonitrile	$\lambda_{\mathrm{measurement}}$ (nm)
Me	2·0	2·0		630
H	7·4	4·1		475
Cl	30 [b]	*b*		650
A	*a*	8·5		680
CO_2Et	33	10·6		680
CN	*a*	42	39	730
NO_2	*a*	45	43	720

[a] Insolubility of complex prevented measurements. [b] Complex unstable in solution.

In both acetone and benzene solution there is a marked increase in K_1 on going from the system with R = Me to systems with more strongly electron-withdrawing substituents. This is interpreted as being largely due to an increasing Cu–N bond strength in the adduct: the decreasing electron donation by the ligand as R becomes a better electron acceptor increases the Lewis acidity of the copper ion. The correlation between K and the electron or acceptor properties of R in both this and previous work [7] suggests that any change in ΔS with change of substituent is small relative to the corresponding change in ΔH for the adduct formation.

The values of K_1 are, with the exception of R = Me, higher in benzene than in acetone. This type of behaviour has been previously ascribed to differences in solvation of the pyridine.[2] However, K also increases more rapidly with increasing electron-acceptor power of the substituent in benzene than in acetone. For example, on going from R = Me to R = CO_2Et, K increases by a factor of *ca.* 16 in benzene and only *ca.* 5 in acetone. This apparent difference in the sensitivity of the Cu^{2+} ion to the nature of R depending on the solvent is considered to be a field-effect phenomenon. The field-effect interaction[15] between R and Cu^{2+} ion although largely dependent on the 'dielectric constant' of the β-diketone ring will also depend on the dielectric constant of the solvent, ε; an increase in ε decreasing the interaction and *vice versa*. The more marked dependence of K on the nature of R in benzene solution is therefore proposed to be a consequence of the lower dielectric constant of benzene ($\varepsilon_{22^\circ} = 2{\cdot}28$) compared with acetone ($\varepsilon_{22^\circ} = 20{\cdot}7$).[16] This interpretation also explains the apparently anomalous result that K for the 3-methylacetylacetonate complex is the same, within experimental error, in both acetone and benzene solution. Although the greater solvation of pyridine by acetone compared with benzene tends to give lower K values in acetone, the positive inductive effect of the methyl substituent which also tends to lower K, is more effectively transmitted in benzene solution. It is proposed that these two effects largely cancel one another in the case of the 3-methylacetylacetonate complex.

With the strongly electron-withdrawing substituents, R = CN and NO_2, an isosbestic point corresponding to the formation of a 1 : 1 adduct occurs at low pyridine concentrations. At higher pyridine concentrations the absorbance is decreased and a second isosbestic point occurs. Computation of the data obtained in this concentration region confirmed that the diadduct $CuL_2(py)_2$ was being formed and K_2 values for the equilibria $CuL_2(py) + py \rightleftharpoons CuL_2(py)_2$ were determined and are given in Table 4.

TABLE 4

Adduct formation constants, K_2, for the equilibria $CuL_2(py) + py \rightleftharpoons CuL_2(py)_2$ at 22 °C

	K_2 (mol^{-1} l) *	
R =	Me_2CO	MeCN
CN	0·4	0·2
NO_2	0·5	0·3

* $\lambda_{measurement}$ = 700 nm.

The K_2 values are approximately two orders of magnitude lower than the corresponding K_1 values. The cupric ion is presumably unsaturated to such an extent, due to the relatively poor electron donation from these ligands, that it is capable of co-ordinating a second pyridine molecule. Diadducts have been reported for other copper β-diketoenolate complexes where the diketone $R^1CO{\cdot}CHR^3{\cdot}COR^2$ contains electron-acceptor groups R^1 and/or R^2, namely, trifluoroacetylacetone,[17] hexafluoroacetylacetone[18,19] and thenoyltrifluoroacetone[20] but this is the first example where $R^1 = R^2 =$ Me and R^3 is the electron-acceptor group. Investigation of the systems with R = Cl, CO_2Et, and Ac at high pyridine concentrations did not indicate that any significant diadduct formation was taking place. Apparently it is necessary to have powerful electron-acceptor groups such as CN and NO_2 as R^3 substituents to promote appreciable diadduct formation, whereas weaker electron-accepting groups such as CF_3 are sufficient if in the R^1 or R^2 positions.

The electronic absorption spectra of the complexes, CuL_2, in neat pyridine solution are, with the exceptions of R = CN and NO_2, very similar. They show broad asymmetric absorption bands with a maximum in the region 15,000—16,000 cm^{-1} and molar extinction coefficients of between 70 and 110. The absorption data for several systems are given in Table 5. The determined values of K indicate that these spectra are mainly due to the species $CuL_2(py)$ in all cases except the cyano- and nitro-complexes; for instance with R = Me a neat pyridine solution of CuL_2 will contain *ca.* 96% $CuL_2(py)$ and 4% CuL_2.

TABLE 5

The absorption maxima $\bar{\nu}_{max.}$ and molar extinction coefficients, E_m, of the complexes CuL_2 in neat pyridine at 22 °C

R	$\bar{\nu}_{max.}$ (cm^{-1})	E_m
Me	15,820	81
Et	15,870	85
$CH_2{=}CH_2{\cdot}CH_2$	15,850	85
$PhCH_2$	15,750	91
Pr·CH=CH	15,460	114
H	15,170	70
Cl	15,060	78
Ac	15,150	92
EtO_2C	15,170	96
CN	13,660	59
NO_2	13,510	63

[a] High value of E_m due to significant overlap with a higher frequency absorption band.

Funck and Ortolano[21] have resolved the absorption spectrum of the monopyridine adduct of cupric acetylacetonate into four Gaussian components which they have assigned in terms of C_{2v} symmetry of the Cu^{2+} ion. Attempts to resolve unambiguously the spectra of the $CuL_2(py)$ complexes described here into Gaussian components were unsuccessful.

The reflectance spectra of the dipyridine adducts of the cupric 3-nitro- and 3-cyano-acetylacetonates are given in Figure 1. These spectra are very similar to that previously reported[21] for the compound $Cu(hfaa)_2$-pyridine$_2$ (hfaa = hexafluoroacetylacetonate anion), which has absorption maxima at *ca.* 8000 and 14,000 cm^{-1}.

Dudley and Hathaway[22] have pointed out that the similarity of the electronic absorption spectra of

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$Cu(hfaa)_2py_2$ and the analogous bipyridyl adduct,[23] $Cu(hfaa)_2bipy$, indicates that the two pyridine molecules occupy *cis*-positions rather than *trans*-positions.[6] By similar reasoning the above results would indicate a *cis* arrangement of the pyridines in CuL_2py_2 ($R = CN$ and NO_2) and the similarities between the spectra in neat pyridine and in the solid state is consistent with the same pseudo-octahedral $CuL_2(py)_2$ species being present in both cases.

Figure 2 shows some representative thermogravimetric results obtained for mono- and di-adducts. No evidence for the formation of a solid monoadduct was obtained during the thermal decomposition of either the cyano- or the nitro-substituted diadducts. The nitro-complex combusted spontaneously between 200—210 °C. The thermal stabilities of the monoadducts varied considerably (see, for example, $R = CO_2Et$ and $PhCH_2$ in Figure 2) but in all cases a distinct break at the loss of one pyridine was observed.

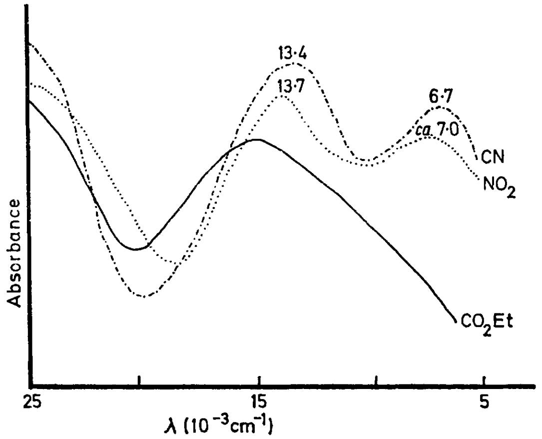

FIGURE 1 Reflectance spectra of the solid adducts $Cu(CNacac)_2(py)_2$, $Cu(NO_2acac)_2(py_2)$, and $Cu(CO_2Etacac)_2(py)$

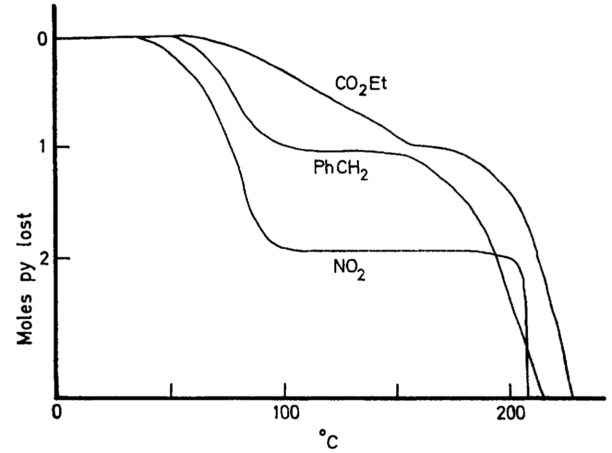

FIGURE 2 Thermograms showing loss of pyridine from the adducts $Cu(CO_2Etacac)_2(py)$, $Cu(PhCH_2acac)(py)$ and $Cu(NO_2acac)(py)_2$

Intramolecular electronic effects caused by 3-substitution of acetylacetonate complexes of Cr^{III}, Co^{III}, and Rh^{III} have been reported by Collman and his coworkers.[24] For example, bromination of $Cr(Clacac)_2(acac)$ occurs much more readily than bromination of the corresponding nitro-compound ($Cr(NO_2acac)_2(acac)$). It is apparent from the results presented above that 3-substitution also exerts a considerable electronic effect on the metal ion, Cu^{2+}, and can, in extreme cases, determine the stereochemistry of the adduct.

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