

# STUDY OF ADDUCT FORMATION OF BIS(2,4-PENTANEDIONO)-COPPER (II) WITH PYRIDINE BASES

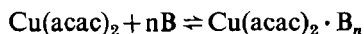
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Co-ordination equilibria involving  $\text{Cu}(\text{acac})_2$  and pyridine and several 2-, 3- and 4-substituted pyridine bases have been examined. According to our and related data in the literature there is no correlation between the stability constants and the electron releasing and withdrawing power of the base substituents.

Copper(II)  $\beta$ -diketonates behave as Lewis acids and react with nitrogen bases to form generally 1:1, rarely 1:2 adducts. These reactions are of the type



where **B** represents a molecule of base, and  $n=1$  or 2. The equilibria in non-aqueous solvents have been studied by using spectrophotometric [1–3], titrimetric [4,5], ESR and NMR [6,7] and several other techniques [8,9].

Since the formation constants published by several authors show controversy (see e.g. [1,10] and [9]), we have investigated the reaction of adduct formation between bis(2,4-pentanediono)-Cu(II) [ $\text{Cu}(\text{acac})_2$ ], and several 2-, 3- and 4-pyridines at room temperature in different solvents.

## Structure and other characteristics

The  $\text{Cu}(\text{acac})_2$  is extremely stable and electron diffraction studies are consistent with a planar structure in the vapour phase [11]. In the crystalline compounds there is a weak interaction between the copper atoms of one molecule and the  $\text{C}_3$  carbon atoms of the chelate rings of neighbouring molecules; the  $\text{Cu}-\text{C}_3$  distance is 3.08 Å [12–14]. The spectra of the adducts has been interpreted as indicating a square-pyramidal structure, this is confirmed by X-ray analysis of  $\text{Cu}(\text{acac})_2$ ·quinoline [15].

The magnetic moments of the parent compounds and that of the solid adducts are normal, in the range of 1.75–2.0 B. M. (see e.g. [1]).

Reflectance spectra of the  $\text{Cu}(\text{acac})_2$  and the solution spectra in non-donor solvents are similar; a broad doublepeaked band appears in the 14–19 kK region [16,17]. In the spectra of the adducts this band shifted to 14–15 kK. The assign-

ment of these band shows controversy. FUNCK AND ORTOLANO [18], GRADDON ET AL. resolved the solution spectra into four, three [20] and two [19] Gaussian components, *resp.* YOKOI [21] has given for the  $\text{Cu}(\text{acac})_2$  the  $x^2-y^2 > z^2 > xy > xz, yz$  one-electron orbital sequence.

### Experimental

The copper(II) complexes were prepared and purified according to literature procedures [1]. The pyridine and nitrogen bases were purified by either recrystallization or distillation prior to use. The solvent was freshly distilled before use. The adducts were prepared by crystallization of the  $\text{Cu}(\text{acac})_2$  in the pure bases. The adducts decomposed on exposure to the air, losing the base and leaving a residue of the  $\text{Cu}(\text{acac})_2$ .

The reflectance spectra were measured at room temperature on a Beckman DU spectrophotometer without dilution. The solution spectra were recorded at  $298 \pm 0.5$  K on a Specord UV VIS spectrophotometer.

The formation constants of the 1:1 adduct were obtained by the following equation [22]:

$$K_{ML} = \frac{(A - A_0)}{L(A_\infty - A) - \frac{M(A - A_0)(A_\infty - A)}{(A_\infty - A_0)}}$$

where  $A$  and  $A_0$  are the absorbances of the system and the  $\text{Cu}(\text{acac})_2$  only.  $A_\infty$  were found by calculating  $K_{ML}$  at several wavelengths for different values of  $A_\infty$ ;  $A_\infty$  for which the  $K_{ML}$  were most consistent was taken as the true value.  $L$  and  $M$  are the total concentrations of the base and the chelate, *resp.* At least ten experimental points were used in each system: The results are shown in Table I.

Table I.

Equilibrium constants\* for formation of adducts of  $\text{Cu}(\text{acac})_2$  with nitrogen bases at 298 K in chloroform and the  $\sigma_{\max}^{**}$  values measured in pure bases

Amine	$K_{LM}$	$\sigma_{\max}$	Amine	$K_{LM}$	$\sigma_{\max}$
pyridine	1.8	15.16	3-acetyl-pyridine	1.5	15.30
2- $\text{CH}_3$ -pyridine	0.5	15.28	3-CN-pyridine	1.0	15.60
2- $\text{C}_2\text{H}_5$ -pyridine	0.2	14.70	3- $\text{NH}_2$ -pyridine	1.9	14.30
2-acetyl-pyridine	~0.1	15.30	3-benzoyl-pyridine	0	15.15
2-CN-pyridine	~0.1	15.60	4- $\text{CH}_3$ -pyridine	2.4	15.02
2- $\text{NH}_2$ -pyridine	2.2	15.20	4- $\text{C}_2\text{H}_5$ -pyridine	1.9	14.70
2,4,6-collidine	0	15.05	4-acetyl-pyridine	1.7	15.40
3- $\text{CH}_3$ -pyridine	2.2	15.20	4-CN-pyridine	1.1	15.60
3- $\text{C}_2\text{H}_5$ -pyridine	1.8	14.70	4-benzoyl-pyridine	3.8	15.10

\*  $K_{LM} \pm 0.05$ ; \*\* in kK.

### Results and Discussion

The absorption of  $\text{Cu}(\text{acac})_2$  in indifferent solvents is considerably modified on addition of pyridine and other pyridine base, most noticeably by a progressive increase in extinction of the band at about 15 kK with increasing base concentration. The successive curves have a sharply defined isobestic point (Fig. 1) indicating the equilibrium between two different species.

It can be seen from Table I that the adducts formed are relatively weak and there is no correlation between  $K_{ML}$  and the substituent constants,  $\sigma$ . MAY AND JONES [8] have pointed out, that there is a definite correlation between the heat of adduct formation and the basicity of pyridines.

From dipole moment investigations [23] it was found that the electron donating groups have a large effect on increasing the electron density on the base nitrogen, whereas the electron withdrawing groups have approximately the same effect, regardless of the electron withdrawing power of the substituent. Thus the stronger bases are able to force a pair of electrons into the orbital of the square-planar copper(II) chelate. This effect reflects in the change of the heat of the adduct formation reactions [8], while such changes in  $K_{ML}$  values are not observable.

The stability constant of pyridine adduct is 1.8 which compares very well with GRADDON and WATTON's data [1]. In the presence of electron releasing and withdrawing substituent in the base molecules are the  $K_{ML}$  values relative to those of pyridine adduct higher and lower, *resp.* The higher stability of the 4-X-pyridine adducts relative to those of pyridine reflects the increased donor property of the nitrogen atom due to substitution. The lower stabilities observed for the adducts of 2-, 2,6- and 2,4,6- $\text{CH}_3$ -pyridine can be considered as a consequence of a steric interference. The high  $K_{ML}$  value (2.2) of the 2- $\text{NH}_2$ -pyridine adduct can be interpreted probably with the tautomerism of base molecule. Generally the  $K_{ML}$  values increase in the order of 2,6- $\text{X}_2$ - < 2-X- < H < 3-X- < 4-X-pyridines. It is interesting to note, that 3-benzoyl-pyridine forms no adduct, while the adduct of 4-benzoyl-pyridine is stable. The stability of adducts of the 4-X-pyridines are slightly greater than that of the 3-X-bases.

The results show, that the stability of the adducts increases in the following order of solvents:



This effect can be interpreted by decreasing attraction between solvent molecules and the copper atom of the chelates or by decreasing solvation energy of the bases. There is some evidence in favour of the latter alternative [24, 25].

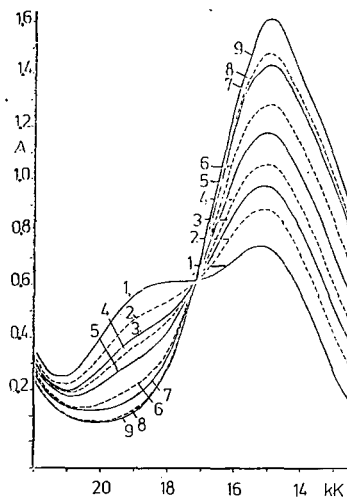


Fig. 1. Absorption spectra of  $\text{Cu}(\text{acac})_2$  in chloroform and with increasing concentration of 4- $\text{CH}_3$ -pyridine.  $[\text{chelate}] = 2.10 \cdot 10^{-2} \text{ M}$ ; [4- $\text{CH}_3$ -pyridine] 1: 0; 2: 9.15 M; 3: 18.30 M; 4: 27.44 M; 5: 45.74 M; 6: 91.48 M; 7: 182.95 M; 8: 274.43 M; 9:  $457.38 \cdot 10^{-2} \text{ M}$ .  $d = 1.00 \text{ cm}$ ;  $T = 298 \pm 0.5 \text{ K}$ .

The stabilities decrease linearly as temperature rises; the adduct dissociation must be much enhanced by the increase of thermal energy. The thermodynamic parameters are:  $-\Delta H=20-60$ ,  $-\Delta G=8-30$  kJ mol<sup>-1</sup> [9], and  $-\Delta H=6-15$ ,  $-\Delta F=4-8$  kJ mol<sup>-1</sup> [8].

The position of the main absorption bands differ only slightly; they appear in the 14.70—15.60 kK region. This band can be resolved into two Gaussian components. Depending on the bases the position of the band with lower ( $\nu_2$ ) and higher ( $\nu_1$ ) energy changes in a small and in higher extent, *resp.*

Since the visible absorption is attributable to the ligand-field around the Cu atom, we have evidence that the environment of the copper atom is the same in each of the three cases: a) in the solid adducts; b) in the 1:1 adducts formed in solution, and c) in solution in pure bases.

The limited solubility of the chelate in non-polar solvents kept us from examining the adduct formation in other solvents.

The solutions of Cu(acac)<sub>2</sub> in pyridine and in other bases are stable and no decomposition can be observed. This behaviour is different from that of the chelates of 3-alkyl- $\beta$ -diketonates.

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#### ИЗУЧЕНИЕ ОБРАЗОВАНИЯ ПРОДУКТОВ ПРИСОЕДИНЕНИЯ БИС (2,4-ПЕНТАДИЕНОЛ) ДВУХВАЛЕНТНОЙ МЕДИ И ПИРИДИНИЕВЫХ ОСНОВАНИЙ

Й. Часар и Н. М. Бизонь

Изучены равновесия реакций комплексообразования ацетилацетоната меди и нескольких 2-, 3-, и 4-замещенных пиридиниевых оснований. В соответствии с нашими и литературными данными не обнаружено корреляции между константами устойчивости и электродонорной или электроакцепторной силами заместителей пиридиниевых оснований.