

SPECTROSCOPIC STUDY OF SECONDARY AMINES AND THEIR COPPER(II) COMPLEXES

By

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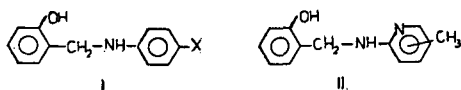
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The u.v. spectra and the complex-forming behaviour of secondary amines produced in the reduction of Schiff bases were studied. The changes observed in the spectra of the copper(II) complexes in pyridine solution can be interpreted in terms of the transformation $[\text{Cu}(\text{amine})(\text{acetate})]_2 \rightarrow \text{Cu}(\text{amine})(\text{acetate})(\text{py})$.

Similarly to the corresponding Schiff base, the secondary amines of N-aryl-hydroxybenzylamine type are potentially bidentate chelating agents. Many authors discuss the reduction of aromatic Schiff bases by different methods [e.g. 1—4] and two earlier papers [5, 6] describe the preparation and spectral investigation of several secondary amines of N-aryl-o-hydroxybenzylamine and N,N'-polymethylene-o-hydroxybenzylamine type. These amines gave rise to mixed chelates of the type $\text{Cu}(\text{amine})(\text{acetate})$, where amine represents the phenolate anion of the amine.

We report here the synthesis and spectral properties of a series of 4-X-aniline (I) and pyridine (II) derivatives and of their copper(II) complexes.



Experimental

Reduction of Schiff bases to amines (I and II) was achieved using sodium borohydride in anhydrous methanol [3]. After the initial reaction the mixture was refluxed for ten minutes. The amines were liberated on addition of water; the crude products were recrystallized from water-ethanol 1:1. The analytical data and the melting points are listed in Table I.

The copper(II) chelates were prepared by mixing the amine solutions in methanol with a warm aqueous solution of copper(II) acetate in 1:1 molar ratio. The dark-green crystals were recrystallized from chloroform; the composition was checked by Cu and C analysis.

Table I
Analytical data on several secondary amines studied

X	M.p.*	C %		H %	
		Calcd.	Found	Calcd.	Found
N(C ₂ H ₅) ₂	68.7	75.52	75.48	8.20	8.16
N(CH ₃) ₂	95.5	74.35	74.29	7.49	7.41
3,4-(OCH ₃) ₂	116.7	69.48	69.41	6.61	6.57
3,4,5-(OCH ₃) ₃	119.7	66.42	66.34	6.62	6.60
OC ₂ H ₅	98.5	74.05	74.00	7.04	7.06
COCH ₃	145.2	79.22	79.19	6.33	6.27
NHCOCH ₃	163.7	70.29	70.22	6.29	6.21
2-NH ₂ -py**	107.2	71.98	71.90	6.04	6.00
2-NH ₂ -3-CH ₃ -py	101.6	72.87	72.81	6.59	6.50
2-NH ₂ -4-CH ₃ -py	144.9		72.78		6.54
2-NH ₂ -5-CH ₃ -py	134.0		72.85		6.49
2-NH ₂ -6-CH ₃ -py	95.6		72.85		6.56

* Uncorrected values; ** py=pyridine.

The u.v. and visible spectra were measured at 298 K on a SPECORD UV VIS spectrophotometer in spectroscopically pure solvent, using quartz cells.

The transformation in pyridine was followed spectrophotometrically at 298 K, using 1 cm quartz cells. The first-order rate constants were calculated from the measured E_t and extrapolated E_0 and E_∞ values, via the formula $kt = \log \frac{E_\infty - E_0}{E_\infty - E_t}$.

Results

U.v. spectra of amines. The u.v. spectral data on the aniline and pyridine derivatives are given in Tables II and III, respectively.

The data in Table II, together with the earlier observations [3], show that these compounds may be characterized by two main bands, in the ranges 200–220 and 240–260 nm, respectively. These bands can probably be assigned to $\pi^* \leftarrow \pi$ transitions. In 0.1 mol/dm³ acidic solution the positions and intensities of the first bands remain almost unchanged, but the second band shifts toward longer wavelength (270–280 nm) and the intensity decreases. This longer-wavelength band is characteristic of the protonated form of the amines.

In alkaline solution (0.1 mol/dm³ NaOH) the spectra also contain two bands, at 240–260 and 290–300 nm; this spectral structure is characteristic of the ionized form resulting from the action of NaOH.

The spectra of methylpyridine derivatives are more complicated (Table III, Fig. 1). In methanol, four bands can be measured in the ranges 200–205, 245–250, 275–285 and 300–320 nm, respectively. Variation in the position of the methyl substituent does not alter the spectral character significantly. In contrast with the former group, the spectra of pyridine derivatives show no significant change in acidic or in basic media.

Table II

U.v. spectral data on aniline derivatives measured in different media

X	Solvent	nm and log ϵ						
N(C ₂ H ₅) ₂ N(CH ₃) ₂ 3,4-(OCH ₃) ₂ 3,4,5-(OCH ₃) ₃ OC ₂ H ₅ COCH ₃ NHCOCH ₃	MeOH	203(4.56)	~225	260(4.18)				
		203(4.56)	~220	259(4.25)	317(2.73)			
		208(4.58)		247(4.03)	~275	~305		
		215(4.67)		252(4.15)	~277			
		203(4.58)		243(4.18)	~275	310(3.43)		
		202(4.45)	~220	~240		331(4.41)		
		203(4.53)	~220		270(4.26)			
		N(C ₂ H ₅) ₂ N(CH ₃) ₂ 3,4-(OCH ₃) ₂ 3,4,5-(OCH ₃) ₃ OC ₂ H ₅ COCH ₃ NHCOCH ₃	Acid	202(4.46)		279(3.49)		
				203(4.47)	~225	278(3.39)		
206(4.65)	~238			280(3.93)				
210(4.70)	~230			277(3.51)				
202(4.54)	227(4.30)			277(3.61)				
203(4.52)	~220			278(3.62)				
203(4.57)	247(4.33)			~278				
N(C ₂ H ₅) ₂ N(CH ₃) ₂ 3,4-(OCH ₃) ₂ 3,4,5-(OCH ₃) ₃ OC ₂ H ₅ COCH ₃ NHCOCH ₃	Base				246(4.24)	~262	~292	
					247(4.31)	~260	~292	
			243(4.31)		295(3.82)			
			244(4.32)		293(3.87)			
			243(4.37)		294(3.79)			
			239(4.14)		~290	338(4.45)		
			244(4.13)	271(4.26)				

Table III

U.v. spectral data on pyridine derivatives measured in different media

X	Solvent	nm and log ϵ				
2-NH ₂ -py 2-NH ₂ -3-CH ₃ -py 2-NH ₂ -4-CH ₃ -py 2-NH ₂ -5-CH ₃ -py 2-NH ₂ -6-CH ₃ -py	MeOH	201(4.32)	~226	246(4.12)	280(3.33)	308(3.34)
		202(4.44)	~227	245(4.15)	281(3.49)	305(3.44)
		204(4.48)	226(3.99)	249(4.21)	282(3.51)	306(3.42)
		202(4.48)	~226	248(4.32)	279(3.47)	314(3.59)
		202(4.37)	227(3.89)	248(4.07)	281(3.35)	310(3.41)
		2-NH ₂ -py 2-NH ₂ -3-CH ₃ -py 2-NH ₂ -4-CH ₃ -py 2-NH ₂ -5-CH ₃ -py 2-NH ₂ -6-CH ₃ -py	Acid	202(4.38)	~225	241(4.16)
203(4.48)	~225			240(4.17)	281(3.78)	308(3.94)
207(4.54)				243(4.17)	284(3.81)	308(3.90)
202(4.50)				244(4.35)	281(3.73)	320(3.98)
202(4.36)	~227			242(4.08)	282(3.48)	320(3.88)
2-NH ₂ -py 2-NH ₂ -3-CH ₃ -py 2-NH ₂ -4-CH ₃ -py 2-NH ₂ -5-CH ₃ -py 2-NH ₂ -6-CH ₃ -py	Base				244(4.30)	296(3.76)
			244(4.37)	298(3.95)		
			247(4.39)	298(3.90)		
			246(4.49)	300(3.90)		~318
			244(4.29)	303(3.85)		

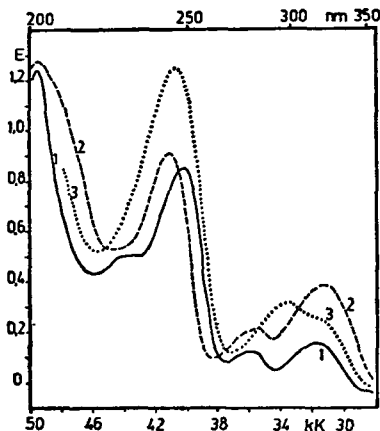


Fig. 1. Spectra of the 2-NH₂-5-CH₃ derivative in 1: methanol; 2: in 0.1 mol/dm³ H₂SO₄/CH₃OH; 3: in 0.1 mol/dm³ NaOH/CH₃OH. $c = 4.06 \cdot 10^{-4}$ mol/dm³; $d = 0.1$ cm; $T = 298$ K

Visible spectra of copper(II) complexes

The complexes have the general formula Cu(amine)(acetate). The dark-green crystalline compounds are soluble in common organic solvents. Their visible spectra contain only one medium-intensity band ($\log \epsilon \sim 1.7$ – 2.7) in the range 640–700 nm (Table IV). On analogy with literature suppositions, these compounds have a binuclear structure [5, 7]. The abovementioned band is assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$

Table IV

Visible spectral and kinetic data on copper(II) complexes

X	nm and log ϵ			$k \cdot 10^4$ (sec)
	in MeOH	in g.a.a.	in pyridine	
N(C ₂ H ₅) ₂	585(2.64)	683(1.97)	*	
N(CH ₃) ₂	~ 600	679(2.15)	*	
OCH ₃	670(1.98)	694(2.29)	668(2.33)	8.25
OC ₂ H ₅	666(2.05)	691(2.30)	679(2.27)	6.55
OC ₄ H ₉	666(2.03)	694(2.30)	683(2.29)	6.70
CH ₃	680(2.00)	694(2.29)	687(2.20)	5.75
C ₂ H ₅	682(1.98)	698(2.30)	687(2.21)	6.67
H	686(1.83)	691(2.29)	687(2.15)	4.98
Cl	692(1.74)	694(2.29)	687(2.09)	5.67
Br	700(1.60)	691(2.30)	676(2.13)	3.95
I	~ 705	691(2.29)	687(2.08)	*

* Very low soluble.

transition; the intensity corresponds to that of the $d-d$ band characteristic of a d^9 system in a strong ligand field with low symmetry.

The complex structure in the range 350–400 nm is assumed to be closely related to the weak copper-copper interaction [8, 9].

The data in Table IV reveal that the band positions change similarly as the HAMMETT σ_p constants.

In glacial acetic acid the bands shift only slightly to the red, but the intensity increases considerably. The structures of the spectra of the complexes in pyridine and in methanolic solutions are similar. The single band appears in the vicinity of 650–670 nm (Table IV).

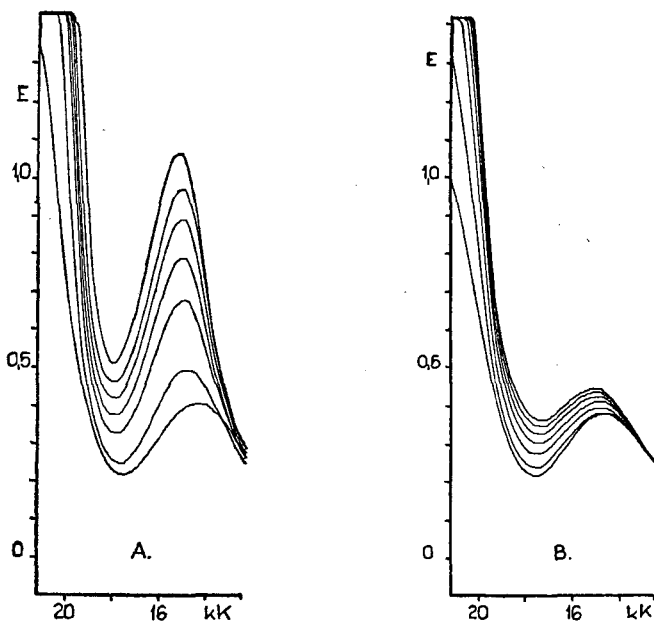
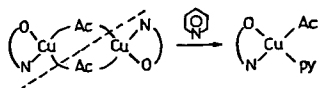


Fig. 2. Spectral changes of complexes with $X = A: \text{OCH}_3$; $B: \text{H}$ in pyridine. $t = 2, 10, 20, 30, 40, 50, 60$ min. $T = 298$ K; $d = 1.0$ cm; $c = 2.5 \cdot 10^{-3}$ mol/dm³

In pyridine solution the band appears at 650–690 nm, and its absorbance increases with time. The spectral changes of two complexes ($X = \text{OCH}_3, \text{H}$) are presented in Fig. 2. From the change in the absorbance it is possible to calculate the first-order rate constants (Table IV). The changes in k and the HAMMETT constants σ_p show the same tendency. The rate constants k decrease with decrease in the electron-releasing effects and with increase in the electron-withdrawing effects of the p - X substituents.

We presume that the charge density on the copper atom increases in the dimer molecules as a result of the electron-releasing effect of X , one of the copper-O(acetate) bonds splits, and one pyridine molecule is bound in the coordination sphere.



In this way a species of low microsymmetry is formed; the increase in absorbancy may be interpreted in terms of this change.

This assumption was supported by the fact that no change can be observed in the presence of 2-picoline or 2,6-lutidine; the steric effect of the CH_3 groups prevents bond formation between the copper atom and the basic nitrogen. Investigations of these problems are in progress.

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СПЕКТРОСКОПИЧЕСКОЕ ИЗУЧЕНИЕ ВТОРИЧНЫХ АМИНОВ И ИХ КОМПЛЕКСОВ С МЕДЬЮ(II)

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Изучены УФ-спектры и комплексообразующие свойства вторичных аминов, полученных при восстановлении оснований Шиффа. Изменения, наблюдаемые в спектрах комплексов меди(II) в пиридиновых растворах, могут быть объяснены переходом $[\text{Cu}(\text{амин})(\text{ацетат})_2] \rightarrow [\text{Cu}(\text{амин})(\text{ацетат})(\text{пиридин})]$.