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Chiroptical Properties of Some Unidentate Copper(II) Imidate–Amine Complexes in Nonaqueous Media

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Optically active amines Am induce relatively strong Cotton effects within the d → d bands in their unidentate neutral complexes of the type [CuIm$_2$-Am$_2^*$] (CuIm$_2$ = Copper(II) imidate as* e.g. *CuSu$_2$, Su = succinimidate). The stability constant K_I for the first dissociation step [CuSu$_2$Bu$_2^*$] $\rightleftharpoons$ [CuSu$_2$Bu*] + Bu* was determined from circular dichroism measurements in methylene chloride solution to be K_I = 2.15 × 10^2 mol^{-1} l. Rotational isomerism around the Cu–N bond of the imidate moieties is suggested as the reason for the different absorption properties of the complexes in crystalline state and in solution.*

Introduction

Tetracoordinated copper(II) imidate complexes with sterically not hindered amines of general formula [CuIm$_2$Am$_2$] (Im = imidate anion, like succinimidate, phthalimidate, camphorimidate; Am = amine) are known since many years [1], ahd have been investigated recently by several authors [2, 3]. They can be easily prepared from a suspension of metallic copper in the ethanolic solution of the corresponding imide and amine by the aid of molecular oxygen [1]. Most of these pink coloured complexes are readily soluble in organic solvents like chloroform, methylene chloride or benzene, forming deep blue solutions. This considerable change in the absorption spectra was ascribed to a structural "distortion" by Miki and Yamada [4] which was, however, not specified.

Since Pfeiffer's first publication [5], several authors have tried [6] to correlate the sign of a Cotton effect within the d → d region with the absolute configuration of complexes containing bi- or polydentate ligands. The favourable structural and physico-chemical properties of such [CuIm$_2$Am$_2$] complexes prompted us to investigate their chiroptical properties in the visible region, in order to correlate the observed Cotton effects with the absolute configuration of the chiral unidentate ligand. This would furthermore help in deciding whether indeed chelation is necessary to induce a Cotton effect in the visible region by a chiral ligand, as has been stated earlier [7a], or whether unidentation alone is sufficient to produce such an effect [7b].

Experimental

Some of the complexes have been prepared and purified according to the original procedure [1], their properties are fully described in refs. [4, 8].

They have the general formula: [CuSu$_2$Am$_2^*$] (Su: succinimidate; Am*: optically active amine like Bu*: (+)-sec-butylamine. Pe*: (–)-α-phenylethylamine; Da*: (–)-dehydroabietylamine) or [CuCm$_2^*$Am$_2$] (Cm*: (+)-camphoric imidate; Am: achiral amine like Et, ethylamine or Py, pyridine).

Commercially available chemicals were used except for (+)-sec-butylamine which was resolved according to lit. [9]. Circular dichroism spectra were recorded with the Dichrograph Mark III (Jobin–Yvon) from 800 to appr. 230 nm, at room temperature, in cells of path length of 0.05 to 2.00 cm. The usual concentration range was from 10^{-4} to 10^{-2} mol/liter. The solvents were dried and carefully purified (methylene chloride over molecular sieve 4Å, chloroform over CaCl$_2$ and alumina, benzene by distillation from sodium metal). The actual concentrations of copper in the solutions were used for all calculations of the $\Delta\epsilon$ values.

For the determination of the sign of the induced Cotton effects it is not necessary to isolate the complex of the corresponding optically active amine, for an in situ preparation is sufficient. This is performed by simply admixing the active amine(Am*) to a solution of an achiral complex like [CuSu$_2$Py$_2$] or [CuSu$_2$Pr$_2$] (Pr: iso-propylamine) in methylene chloride. Example: To a solution of 16 mg of *D*-valine methyl ester in 0.5 ml CH$_2$Cl$_2$ 4.5 ml of 5 × 10^{-3} mol/l [CuSu$_2$Pr$_2$] in CH$_2$Cl$_2$ was added. From the $\Delta A = 86 \times 10^{-5}$ measured (at λ = 610 nm) in a

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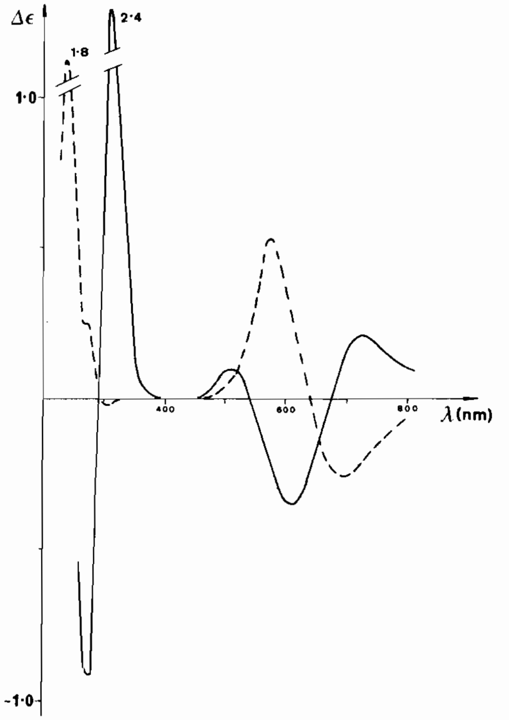


Figure 1. The CD spectra of [CuSu$_2$Bu$^*_2$] (------) and [CuSu$_2$Pe$^*_2$] (———) in presence of ~10 molar excess of Bu* or Pe* in CH$_2$Cl$_2$ ([Cu] = 5 × 10^{-3} mol/l).

cell with d = 0.5 cm, a $\Delta\epsilon$ = +0.383 results which refers to the copper concentration of the solution ([Cu] = 4.5 × 10^{-3} mol/l).

Results and Discussion

Dissolution of the crystalline pink complexes leads immediately to deeply blue coloured solutions with absorption maxima at $\lambda \cong 590$ nm, with log $\epsilon \cong 2$ (see also ref. [2, 4, 8]).

In the CD spectra of these complexes two (in a few cases three) distinct Cotton effects are observable in the visible region. Their position does not coincide exactly with the isotropic absorption maximum, which appears in between both, and close to the one at shorter wavelength. In order of decreasing wavelength, CD-Band I is found between 730–680 nm, CD-Band II in the range of 620–570 nm, and CD-Band III at 520–510 nm (*cf.* Fig. 1).

These CD bands appear instantaneously after the dissolution of the solid complex or the preparation *in situ,* and their magnitude remains constant for a long time (even several weeks if water was carefully removed).

As the signs of the CD bands I and II are independent of the conditions of measurement (solvent, concentration, proportions of excess ligand Am* to Copper *etc.*) a new and very useful method for determination of absolute configuration could be developed [10].

Further Cotton effects appear in the UV region too, namely: CD-Band IV at appr. 320 nm and CD-Band V at approx. 250 nm (see Table I). They are, however, not so suitable for stereochemical correlations, because their signs depend also upon external conditions and not only upon the chirality. They may origin in the chiral perturbation of the imidate chromophore (n → π* transition), and/or of the central atom (CT band). Furthermore, in the case of absorbing chiral ligands like (–)-α-phenylethylamine their own CD bands are superimposed on them. The relative strong absorption of the complexes as well as of the solvent causes other difficulties for investigations in this wavelength region.

The CD spectrum for Am* = (+)-α-phenylethylamine is the perfect mirror image of that recorded for

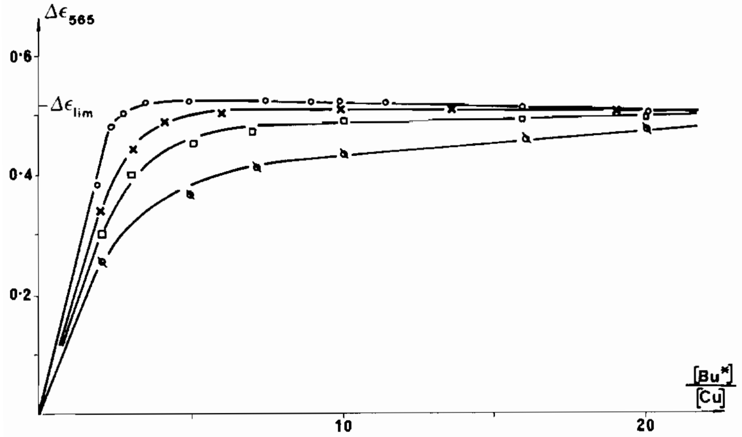


Figure 2. Molar ratio diagrams of [CuSu$_2$Bu$^*_2$] solutions in CH$_2$Cl$_2$ of various concentrations, in the presence of increasing amounts of Bu* in excess. (–o–o– [Cu] = 0.010 mol/l –x–x– [Cu] = 0.005 mol/l –□–□– [Cu] = 0.003 mol/l –ϕ–ϕ– [Cu] = 0.001 mol/l).

TABLE I. The Cotton Effect of Various $[CuSu_2Am_2^*]$ Complexes.

Am*	solvent	[Cu]	[Am*]	CD-Band									
		mol/l x 10^3	mol/l x 10^3	I		II		III		IV		V	
				λ (nm)	Δε	λ (nm)	Δε	λ (nm)	Δε	λ (nm)	Δε	λ (nm)	Δε
(+)-sec-butylamine	CH_2Cl_2	5.0	40.0	690	−0.250	565	+0.520					248	+1.80
	benzene	5.0	50.0	690	−0.290	565	+0.620			330	−0.155	a	
(−)-α-phenyl ethylamine	CH_2Cl_2	4.0	16.0	725	+0.20	620	−0.400	510	+0.09	320	+2.4	260	−2.00
(−)-S-dehydroabiethyl-amine	CH_2Cl_2	2.0	10.0	700	+0.05	590	−0.12	480	+0.03	<330	>0	b	
L-leucinmethylester[c]	CH_2Cl_2	0.5	20.0	705	+0.400	605	−0.610			300	−0.600	<280	>0
16β-amino-17β-estradiol-3-methyl-ether[c] [16]	CH_2Cl_2	5.0	5.3	710	+0.410	605	−0.540			350	−0.950	b	

[a] Not measurable due to solvent absorption. [b] Superimposed with own CD band of the ligand. [c] Complex prepared *in situ*.

the (–)-α-phenylethylamine complex. This "normal" behaviour of enantiomers was also proved in case of the (+)- and (–)-sec-butylamine complexes.

To establish the structure and stability of these complexes the CD spectra were also recorded after addition of increasing amounts of optically active amine. As shown in Fig. 2 the $\Delta\epsilon$ values increase and approach an upper limit. The same value is reached independently upon the used complex concentration. The molar ratio of excess amine to copper ([Am*] : [Cu]) necessary to reach this $\Delta\epsilon_{lim}$ value, is inversely proportional to the copper concentration. The shape of the molar ratio diagram corresponding to [Cu] = 0.01 mol/l in methylene chloride (Fig. 2) shows that a weak complex with an approximate ratio 2:1 ([Am*] : [Cu]), is formed [11].

The strong increase of the $\Delta\epsilon$ values as well as the approach to the same limiting values cannot be explained merely by an unspecific "solvent effect" by the optically active amine. The observed effects must be due to some changes within the inner coordination sphere, *i.e.* by a decrease or increase of the number of chiral amine molecules in it.

In a similar manner as $\Delta\epsilon$, the isotropic absorption ϵ also varies with concentration and/or amine excess (*e.g.* $\epsilon = 80$ for $c = 5 \times 10^{-4}$ mol/l $[CuSu_2Bu_2]$; $\epsilon = 138$ for $c = 10^{-2}$ mol/l, and $\epsilon = 166$ for the same concentration, in the presence of excess sec-butylamine). The dependence on the concentration of the $\Delta\epsilon$ values measured for the pure complex solutions (without Am* excess) indicates that a considerable dissociation (eq. 1) must take place:

$$[CuSu_2Am^*_2] \underset{+Am^*}{\overset{-Am^*}{\rightleftarrows}} [CuSu_2Am^*] \underset{+Am^*}{\overset{-Am^*}{\rightleftarrows}} [CuSu_2] \rightleftarrows [CuSu]^+ + Su^- \qquad (1)$$

In the non-aqueous media used for our investigations the dissociation of the charged imidate ligand from the copper must be some orders of magnitude smaller than the dissociation of the non-charged amine molecules. On the other hand, the contribution of the $[CuIm_2Am^*]$ (dissociated) species to the overall optical activity measured for the solution of these complexes cannot be neglected and the observed Cotton effect is described by

$$\frac{\Delta A}{d} = c_1\Delta\epsilon_1 + c_2\Delta\epsilon_2 \qquad (2)$$

(ΔA is the differential absorbance, d the cell thickness, c_1 and c_2 are the molar concentrations of $[CuIm_2Am^*]$ and $[CuIm_2Am^*_2]$, resp., and $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are the $\Delta\epsilon$ values for these pure species).

For the $\Delta\epsilon_2$ values of the "non-dissociated" complexes the $\Delta\epsilon_{lim}$ values determined from the "molar ratio" diagrams (see Fig. 2) can be substituted. The question arises then, whether $\Delta\epsilon_1$ can be taken as $0.5\Delta\epsilon_2$ which would be intuitively expected, or not.

In general the CD of a complex like $[CuSu_2Am^*(1)Am^*(2)]$ will depend on the chirality of both amine ligands Am* (1) and Am* (2). For chelate complexes with chiral ligands (like aminoacids) it has been proposed [12] that the influence of individual chirality elements is additive. Such approximation can hold only if the chirality elements of the ligands are not very close to each other, otherwise their relative interaction (vicinal effect in the general sense) will give rise to deviations from pure additivity. Experience with other chromophores [17] supports this proposal [12]. From the point of view of chiroptical properties the molecule has to be divided into "chirality spheres" (as to differentiate from coordination spheres), and that chiral sphere which is nearest to the chromophore determines the Cotton effects [17]. Assuming local D_{2h} symmetry for the complexes (see later) the first "chirality" sphere (*i.e.* the Cu with its bonds, delocalized into the imidate π-system) is achiral as well as the second one (= the torsion angles around the Cu–N bonds). In order to test the validity of any sector rule (third-sphere contributions) the "chirality order o" for such complexes with achiral D_{2h} skeleton has to be determined [18]. There are N = 8 points (*e.g.* substituents in the amine moiety which are not lying in a nodal plane) in the transitivity area [18], up to seven of which can be identical in a chiral molecule. The chirality order is thus o = 7, so the difference (N – o) = 1, which is the algebraic condition for the validity of a sector rule for such complexes [18]. According to Schellman's treatment [19] the simplest sector rule is then an octant rule, and according to such a sector rule Am* molecule (1) and Am* molecule (2) must contribute independently and additively to the CD.

To test the additivity of the individual ligand contributions to the overall induced CD the following indirect way was used. To a solution of equimolar amounts of $[CuSu_2Bu^*_2]$ (concentration = C_2) and $[CuSu_2Pr_2]$ (concentration = C'_2) in CH_2Cl_2 a 10 molar excess of each of the amines was added. Preventing thus the dissociation the solution contains only the bisamine species. Because of the mentioned high kinetic lability the mixed complex $[CuSu_2PrBu^*]$ (concentration = C_m) must also be present. Under the plausible assumption of not very different stability for these complexes containing such similar ligands on statistical grounds a ratio of $C'_2 : C_m : C_2$ = 1:2:1 must result. As the complex $[CuSu_2Pr_2]$ is achiral, the measured CD, expressed as $\Delta A/d$, is

$$\frac{\Delta A}{d} = C_m\Delta\epsilon_m + C_2\Delta\epsilon_2 \qquad (2')$$

Using $\Delta\epsilon_2 = +0.52$ as mentioned above we determined $\Delta\epsilon_m$ for various total copper complex concentrations in the range of $(1.25 \text{ to } 5.00) \times 10^{-3}$ mol/l from (2′) and obtained $\Delta\epsilon_m = +0.20 \pm 0.02$.

This value is somewhat smaller than 0.26 calculated under the assumption of additivity. A similar result is obtained for the CD-Band I of the same solutions. As on the basis of Ruch's theory [18] for third chirality sphere contributions strict additivity should hold, this result can be interpreted as an indication that by presence of a chiral amine moiety the Cu–N torsion angle slightly deviates from 90°. By this a small contribution to the Cotton effect from the second chirality sphere is produced. Anyway $\Delta\epsilon_m$ is only a crude approximation for $\Delta\epsilon_1$ as in this latter dissociated complex only three N atoms are ligated with the Cu, thus reducing "skeleton" symmetry further. Using this value $\Delta\epsilon = +0.20$ as an approximation for $\Delta\epsilon_1$ of eq. (2), it becomes possible to evaluate the stability constants of such complexes for the first dissociation step (K_I), obtaining:

$$K_I = \frac{[CuSu_2Bu_2^*]}{[CuSu_2Bu^*]\,[Bu^*]} = 2.15\ (\pm 0.15) \times 10^2\ mol^{-1}\ l$$

K_I determined in this way for various concentrations and various ratios of sec-butylamine to copper was indeed approximately constant (as long as the copper concentration was $\geqslant 10^{-4}$ mol/l) proving thus that $\Delta\epsilon_m$ is a good substitute for $\Delta\epsilon_1$. The order of magnitude found for K_I is in agreement with the known low stability of unidentate copper–amine complexes [13]. Using isotropic absorption measurements of $[CuSu_2Bu_2]$ in CH_2Cl_2, combined with a statistical computer analysis, a value of $K_I = 0.38 \times 10^2\ mol^{-1}\ l$ resulted [20]. This latter value is more accurate because it takes into account also the fact that the absorption maximum of the monodissociated species does not coincide with that of the bisamine species.

The low kinetic stability provides a new and very simple way to investigate the CD induced by a chiral amine in copper d → d transitions by merely admixing the active amine to a solution of such an achiral complex which is easily available, as *e.g.* $[CuSu_2Pr_2]$ or $[CuSu_2Py_2]$, in methylene chloride or benzene. It is worth to note that independently of the nature of the achiral complex a sufficient excess of (+)-Bu* leads always to the same limit value of $\Delta\epsilon_{lim}$ as obtained for the nondissociated complex $[CuSu_2Bu_2^*]$ (Fig. 2). To shift the equilibrium for aliphatic and alicyclic amines toward the desired direction it is thus recommended to use the $[CuSu_2Py_2]$ complex.

A very good information about the composition of this complex mixture is obtained with the aid of the method of continuous variations (Job's method) [14]. Fig. 3 shows the plots ΔA/d *vs.* the molar fraction of copper ($\gamma_{Cu} = [Cu]/([Cu] + [Am^*])$ for the three mixtures $[CuSu_2Py_2]$ + Bu* (curve a), $[CuSu_2Pr_2]$ + Bu* (curve b), and $[CuSu_2Bu_2]$ + Bu* (curve c), resp.. The sharpest maximum is observed for curve (a) which is obvious, as the binding affinities of pyridine and butylamine are quite different. The position of the maximum of ΔA/d at $\gamma_{Cu} = 0.33$ corresponds to a ratio [Bu*] : [Cu] of 2:1. By the same reasoning we can explain why the other two maxima are less sharp. Their positions correspond to a ratio [Bu*] : [Cu] of about 1.7:1 indicating thus the simultaneous presence of mono- and bis-amine species. Table II summarizes the molar ratios γ_{Cu} for several $[CuIm_2Am_2]$ + Am* systems, determined for the CD-bands in the visible region. In general molar ratios [Am*] : [Cu] between 2:1 and 1:1 are obtained. The only exception was observed for the complex with (–)-α-phenylethylamine (Pe*) within CD-band III, for which a ratio of appr. ⩾3:1 was found, though the Job curves for CD-bands I and II clearly indicated a ratio smaller than 2:1. We cannot exclude that in case of apparent disappearance of band III (especially for higher concentrations of free amine) a corresponding weak Cotton effect is hidden under the merged CD-Bands II + III [15].

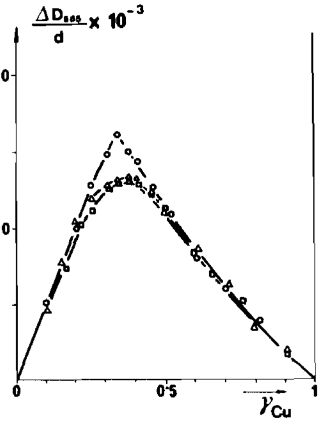


Figure 3. Job curves of a) $[CuSu_2Py_2]$ (–○–○–); b) $[CuSu_2Pr_2]$ (–□–□–); c) $[CuSu_2Bu_2]$ (–△–△–), resp., and (+)-sec-butylamine mixtures in CH_2Cl_2 with $C_{total} = [Cu] + [Bu^*] = 0.01$ mol/l for the CD band at λ = 565 nm.

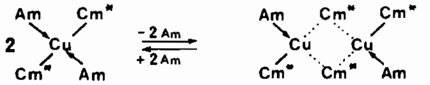
The presence of other substituents in the amine which normally also could ligate with the copper atom does in general not prevent the chiroptical investigation of the *in situ* prepared complexes. No or only extremely small Cotton effects could be recorded for mixtures of $[CuSu_2Am_2]$ with optically active alcohols like borneol, isoborneol, menthol, esters like menthyl acetate or diethyl tartrate, or ketones like camphor or menthone (Δε values below 0.005). Obviously copper bis-imidate shows a great selectivity towards amines as ligands, which is another main advantage of these complexes in studies of the stereochemistry of amines. For a few optically active amines (*e.g.* brucine, ajmaline, 5-aminosteroids) we were not able to detect Cotton effects within the range of the d → d absorption bands, which may be due to severe steric hindrance to complex formation and/or local symmetry within the third sphere around the N atom.

TABLE II. The γ_{Cu} Values of Various $[CuSu_2Am_2]$ + Am* Mixtures Corresponding to Maxima of the $\Delta A/d$ Values.

$[CuIm_2Am_2]$	Am*	λ_{max} (nm)	γ_{Cu}
$[CuSu_2Pr_2]$	(+)-sec-butylamine	685	0.37
		565	0.40
$[CuSu_2Py_2]$	- " -	685	0.33
		565	0.33
$[CuSu_2Bu_2]$	- " -	685	0.38
		565	0.40
$[CuPht_2Pr_2]$[a]	- " -	685	0.40
		565	0.38
$[CuSu_2Et_2]$	(–)-α-phenylethylamine	710	0.45
		605	0.50
		510	0.25
$[CuSu_2Pr_2]$	- " -	705	0.45
		605	0.50
		500	0.25
$[CuSu_2Bu_2]$	- " -	720	0.50
		610	0.40
		515	0.20
$[CuSu_2Pr_2]$	L-alanine methylester	705	0.40
		610	0.40
$[CuSu_2Py_2]$	L-phenylalanine methyl ester	620	0.38
		720	0.35
$[CuSu_2Py_2]$	L-proline methyl ester	620	0.40
		710	0.40

[a] Pht: phthalimidate.

For the complexes discussed hitherto the chirality is due to chiral amine ligands. We have also investigated the Cotton effects induced within d → d bands for complexes containing achiral amine but chiral imide ligands. Two such compounds have been prepared in crystalline state [8] and according to analysis they have the composition $[CuCm_2^*Et_2]\cdot H_2O$ and $[CuCm_2^*Py]$, resp.. These pink crystals dissolve in methylene chloride with green colour and show only very tiny Cotton effects ($[CuCm_2^*Et_2]$: $\Delta\epsilon_{720}$ = +0.014, $\Delta\epsilon_{600}$ = –0.010; $[CuCm_2^*Py]$: $\Delta\epsilon_{710}$ = +0.004). Addition of excess amine like Et or Pr leads to a tenfold increase of these Cotton effects as well as concomitant change of the colour of the solutions into blue (λ_{max} shifts from 652 to 602 nm). These facts must be due to another structure of the complexes and can be explained by assuming the presence of species shown in equation (3), which is confirmed by ESR measurements [8].



(3)

Excess of an amine shifts this equilibrium to the left and addition of *e.g.* Pr to a solution of $[CuCm_2^*Et_2]$ allows the measurements of the CD of $[CuCm_2^*Pr_2]$ ($\Delta\epsilon_{605}$ = +0.05). As in both complexes the ratio of chiral ligand (Cm*) to copper is the same (*viz.* 2:1) this strong relative increase of the rotational strength must be caused for these complexes by the different electronic structures of the species $[Cu_2Cm_4^*Am_2]$ and $[CuCm_2^*Am_2]$. The absolute magnitude of the CD of these complexes is, however, in general one to two orders of magnitude smaller than for the complexes discussed earlier, which contain the chiral amine ligand.

Structure of the Complexes $[CuSu_2Am_2]$

In general these complexes show quite different absorption spectra in the crystalline state and in solution (benzene, chloroform, *etc.* [4]). By comparison with absorption spectra of the Cu(II)–biuret complex, which is appr. square planar [21] and does not change its spectrum by dissolution [21] as well as from single crystal measurements Yamada and Miki [4] concluded that in the crystal $[CuSu_2Am_2]$ is also present as such a square-planar complex. The change of the absorption spectrum on dissolving the complex was ascribed to a "distortion", which was, however, not specified more [4]. The Japanese authors could rule out tetrahedral arrangement and cite arguments against a further solvation by the apolar solvent as the reason for the relatively strong bathochromic shift. In the crystal two bands at 479 and appr. 450 nm are most probably (x, y)-polarized and a band at 508 nm is z-polarized [4], whereas in solution only a very broad band with a maximum

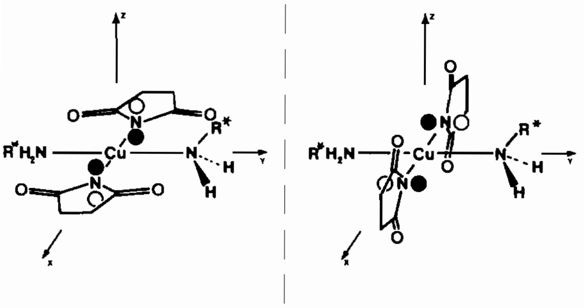


Figure 4. Most probable conformations of succinimidate moieties in [CuSu$_2$Am$_2^*$] in the crystalline state (right) and in solution (left). Only the p-orbital of the HOMO on N of the imidate is indicated. R* in the "left" Am* ligand may point up or down.

around 610 nm was recorded, in agreement with our own results. In a recent publication [22] the simplest complex of this type, [CuSu$_2$(NH$_3$)$_2$], was investigated by X-ray diffraction method. In this copper-red crystals the four N atoms around the Cu are arranged nearly coplanar, the succinimide moieties are inclined to this plane by appr. 72°. There is strong bridging between the three hydrogens of the NH$_3$ ligands and the oxygen atoms of the succinimidate moiety. The X-ray picture also proves the *trans*-configuration for this complex as hitherto already assumed tacitly.

The rather strong change in band positions for these complexes can be rationalized in the following way. It can be assumed that dissolution changes the interactions between the Cu orbitals and the orbitals within the π-system of the imidate moiety, so these units may adopt different conformations in the crystal and in solution. Two such low-energy conformations seem probable – one, in which the succinimidate moiety is coplanar with the general CN$_4$ plane (Fig. 4, left), and a second with perpendicular position (Fig. 4, right). Such a rotation is not possible in bidentate complexes of the biuret or [Cu(acac)$_2$] type, therefore nearly no change of absorption takes place for them on dissolution in apolar solvents. The similarity [8] of the absorption and ESR properties of [Cu(acac)$_2$] and [CuSu$_2$Pr$_2$] in chloroform solution pleads for the similarity of their structures in the dissolved state. This in accord with the mentioned X-ray result [22] we explain the change of absorption by assuming that in the crystal the "perpendicular" conformation is present, whereas in solution we have the "coplanar" one.

No matter which conformation is present, in these complexes the rests R* of the chiral amine ligands must stick out more or less perpendicular from the CuN$_4$ plane, as judged from molecular models, and they may then be on the same or on opposite sides of this plane. Both these conformations must, however, lead to identical Cotton effects as we have shown above that an octant rule can be expected, and a 180° rotation around the Cu–N bond will bring identical atoms into an octant of the same sign. Such a "coplanar" conformation (Fig. 4, left) explains also nicely why the most preferred conformation of the amine moiety is that with a torsion angle of 90°; only with such a conformation can all Cotton effects be rationalized in a general way [16].

In conclusion it can thus be stated that the relative magnitudes of the Cotton effects of complexes [CuIm$_2$Am$_2$] strongly depend on several factors, such as electronic structure of the complex, steric hindrance to coordination of the amine, concentration, type of solvent, *etc.*. The signs of these Cotton effects are, however, independent of these factors and the absolute configuration of amines can thus be safely determined from measurements of the CD of the corresponding complexes. Details on the application in organic stereochemistry (aminoacids, aminosteroids, *etc.*) are given in other papers [10, 16].

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