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Synthesis, Characterization, and Photochemical Studies of Some Copper Complexes of Schiff Bases Derived from 3-Hydrazino-6-methyl[1,2,4]triazin-5(4*H*)one

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ABSTRACT

Cu(II) complexes of new bidentate and tridentate Schiff bases derived from the condensation of 3-hydrazino-6-methyl[1,2,4]triazin-5(4*H*)one and aromatic aldehyde derivatives were synthesized and characterized. The structure of the complexes proposed according to elemental analyses, molar conductance, IR UV-Visible absorption spectra is square-planar. The thermodecomposition kinetics of the complexes were investigated under non-isothermal condition. TG and DTG curves indicated that the complexes decompose in three to six steps. The photochemical behavior

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of the complexes depends on the substituted group on the aromatic aldehyde. A mechanism has been suggested to account for the recorded results.

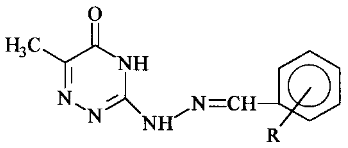
Key Words: Schiff bases; Copper(II) complexes; 3-Hydrazino-6-methyl[1,2,4]triazin-5(4*H*)one; Photochemical and thermal behavior.

INTRODUCTION

Schiff bases continue to occupy an important position as ligands in coordination chemistry even after almost a century since their discovery. This is manifested by the huge number of publications ranging from the purely synthetic[1,2] to modern physical and biochemical relevant studies of Schiff base complexes.[3–6] To the best of our knowledge, no work has been done on the metal complexes of Schiff bases derived from 3-hydrazino-6-methyl [1,2,4]triazin-5(4*H*) one, and as a continuation of our previous studies on photochemical and thermal behavior of transition metal complexes,[7,8] the present investigation reports synthesis, photolysis, and thermogravimetrical studies on some new copper(II) complexes of the above-mentioned Schiff bases; their structures are given in Fig. 1.

EXPERIMENTAL

All chemicals used in the present work are of analytical grade. 3-Hydrazino-6-methyl[1,2,4]triazin-5(4*H*)one was prepared according to published procedures.[9]



R	Notation
H	HBe
p-$N(CH_3)_2$	HDBe
p-OCH_3	HMBe
o-NO_2	HNBe
o-OH	H_2Sal

Figure 1. Structures of Schiff base ligands.

Synthesis of Schiff Base Ligands

A mixture of 10 mL of an ethanolic solution of 3-hyrazino-6-methyl [1,2,4]triazin-5(4*H*)one (10 mL, 1.41 g) and 10 mL of an ethanolic solution of the appropriate aromatic aldehyde (10 mmol of benzaldehyde, 1.06 g; *p*-dimethylaminobenzaldehyde 1.21 g; *p*-methoxybenzaldehyde, 1.36 g; *o*-nitrobenzaldehyde, 1.51 g or *o*-hydroxybenzaldehyde, 1.22 g) was refluxed for 4 hr. The reaction mixture was cooled to 5 °C, and yellow products precipitated immediately. The precipitates were filtered, washed with ethanol, diethyl ether, and finally dried *in vacuo*. The ^{1}H NMR solution spectra of the ligands in DMSO-d_6 were recorded on a Jeol LA 400 spectrometer with TMS as reference and are given in Table 1.

Synthesis of Cu(II) Schiff Base Complexes

The complexes were prepared by adding a DMF solution (20 mL) of Cu(II) acetate (1 mmol, 0.19 g) to a DMF solution (20 mL) of the Schiff base (2 mmol for the ligands HBe, HDBe, HMBe, and HNBe, or 1 mmol for H_2Sal). The mixture was heated on a water bath at 80 °C for 1 hr. On cooling, a green to brown precipitate was separated immediately for HBe. HDBe, and HMBe. For HNBe or H_2Sal, the green product was precipitated after addition of a 1 : 1 acetone/diethyl ether mixture (30 mL). The solid complexes were filtered, washed with acetone and diethyl ether, and finally dried *in vacuo*. The carbon, hydrogen, and nitrogen contents of the ligands and their Cu(II) complexes were determined by an Elementar-Analysensystem GmbH Vario El analyzer.

Physical Measurements

The infrared spectra were recorded as KBr pellets on a 470 Shimadzu infrared spectrophotometer. The electronic spectra were measured in DMF solution on a Perkin Elmer, Lambda, 35 UV/Vis spectrophotometer. Electrical conductivities of 10^{-4} M DMF solutions of the complexes were measured at 25 °C by a Jenway 4330 conductivity-pH meter. The thermal studies were carried out on a TGA V5 1A Dupont 2000 thermal analyzer at a heating rate 10 °C/min. The photolyses were achieved using an Osram HBO 200 w/2 lamp as a light source. Monochromatic light was obtained using the Scholt IL interference filter 298 nm. Irradiations were carried out in solutions of DMF in 1-cm spectrophotometer cells at room temperature. Progress of the photolysis was monitored by the above-mentioned spectrophotometer.

Table 1. ^{1}H NMR data (in ppm) of Schiff bases ligands in DMSO-d_6.

Ligand	$-CH_3$	$-N(CH_3)_2$	$-OCH_3$	Aromatic protons	$-N{=}CH$	$-OH$	$>NH$	$-\overset{\overset{O}{\|}}{C}-NH$
HBe	2.06 (3H, s)	—	—	7.39–7.89 (5H, m)	8.06 (1H, s)	—	11.64 (1H, s)	12.67 (1H, s)
HDBe	2.07 (3H, s)	2.95 (6H, s)	—	6.68–7.67 (4H, m)	7.94 (1H, s)	—	11.34 (1H, s)	12.49 (1H, s)
HMBe	2.08 (3H, s)	—	3.78 (3H, s)	6.95–7.84 (4H, m)	8.05 (1H, s)	—	11.50 (1H, s)	12.59 (1H, s)
HNBe	2.09 (3H, s)	—	—	7.59–8.60 (4H, m)	8.48 (1H, s)	—	11.91 (1H, s)	12.80 (1H, s)
H_2Sal	2.19 (3H, s)	—	—	6.80–8.09 (4H, m)	8.38 (1H, s)	10.13 (1H, s)	11.52 (1H, s)	12.63 (1H, s)

Note: s, singlet; m, multiplet.

RESULTS AND DISCUSSION

The reactions of the Schiff base ligands (HL or H_2L) with Cu(II) acetate can be represented by Eq. (1) for 1 : 2 (M : HL ratio) and Eq. (2) for 1 : 1 (M : H_2L) ratio. The ligands HBe, HDBe, HMBe, and HNBe form 1 : 2 complexes, while H_2Sal forms 1 : 1 complex.

$$Cu(CH_3COO)_2 + 2HL \longrightarrow [CuL_2] + 2CH_3COOH \qquad (1)$$

$$Cu(CH_3COO)_2 + H_2L \xrightarrow{H_2O} [CuL(H_2O)] + 2CH_3COOH \qquad (2)$$

For 1 : 2 complexes, the chelation is brought about by proton displacement from the –CO–NH group in each ligand. On the other hand, the 1 : 1 complex may be formed through two protons displacement from the phenolic OH and –CO–NH groups to satisfy the divalency of the metal ions. A survey of the published results shows that *N*-salicylidenes react with Cu(II) acetate yielding *bis*(*N*-salicylidenaniline)Cu(II) complexes by deprotonation of the OH group, the liberated protons are continuously removed from the reaction medium via the formation of weakly ionized acetic acid and the decrease in acetate concentration.[10]

The Cu(II) complexes are fairly soluble in DMF and DMSO and are not suitable in alcohol, acetone, chloroform, and diethyl ether. All complexes under investigation are amorphous solids. The colors, yields, analytical data, and decomposition points of the free Schiff bases and their Cu(II) complexes are collected in Table 2.

Conductance Measurements

The molar conductance of the Cu(II) complexes measured in 10^{-4} M dimethyl formamide are in the range 1.5–3.6 $ohm^{-1} cm^2 mol^{-1}$ thereby indicating their non-electrolytic nature.[11]

Infrared Spectra

The important IR bands of the free ligands and their Cu(II) complexes together with their assignments are listed in Table 3. Relevant IR bands provide structural evidence for the mode of attachment of the ligands to the metal ion. All spectra of the free ligands exhibit a strong band at 1580–1615 cm^{-1}, which is characteristic of the azomethine (–HC=N) group. It is to be expected that coordination of the nitrogen to metal atom would reduce the electron density in the azomethine link and thus lower the –HC=N absorption. In the IR spectra

Table 2. Color, elemental analysis, and decomposition temperature of Schiff bases and their Cu(II) complexes.

Compound	Formula	Formula weight	Color	Yield (%)	Element analysis, found (calcd) (%)			Decomposition points (°C)
					C	H	N	
HBe	$C_{11}H_{11}N_5O$	229.25	Yellow	70	57.23 (57.62)	5.00 (4.83)	30.31 (30.55)	310
$[Cu(Be)_2] \cdot 3H_2O$	$C_{22}H_{26}CuN_{10}O_5$	574.06	Green	65	45.46 (46.03)	4.05 (4.53)	23.90 (24.41)	360
HDBe	$C_{13}H_{16}N_6O$	272.31	Yellow	70	56.99 (57.33)	6.01 (5.92)	30.25 (30.86)	320
$[Cu(DBe)_2]$	$C_{26}H_{30}CuN_{12}O_2$	606.16	Brown	65	51.11 (51.51)	4.80 (4.98)	28.01 (27.73)	320
HMBe	$C_{12}H_{13}N_5O_2$	259.27	Yellow	71	55.19 (55.58)	5.26 (5.05)	26.76 (27.01)	309
$[Cu(MBe)_2]$	$C_{24}H_{24}CuN_{10}O_4$	580.07	Green	64	49.21 (49.69)	3.87 (4.17)	23.84 (24.15)	320
HNBe	$C_{11}H_{16}N_6O_3$	274.25	Yellow	69	48.38 (48.17)	4.00 (3.67)	30.35 (30.65)	305
$[Cu(NBe)_2]$	$C_{22}H_{18}CuN_{12}O_6$	610.02	Green	63	42.99 (43.31)	2.89 (2.97)	27.20 (27.55)	310
H_2Sal	$C_{11}H_{11}N_5O_2$	245.24	Yellow	70	53.57 (53.86)	4.89 (4.52)	28.06 (28.56)	330
$[Cu(Sal)H_2O)]$	$C_{11}H_{12}CuN_5O_3$	325.79	Green	63	40.28 (40.55)	3.61 (3.71)	21.35 (21.50)	340

Table 3. IR spectral bands of the Schiff base ligands and their Cu(II) complexes (cm^{-1}).

Compound	ν(C=N)	ν(CONH)	ν(M–N)
HBe	1,615 s	1,640 s	—
$[Cu(Be)_2] \cdot 3H_2O$	1,590 s	1,680 s	565 w
HDBe	1,590 s	1,670 m	—
$[Cu(DBe)_2]$	1,580 s	1,690 m	560 w
HMBe	1,600 s	1,620 sh	—
$[Cu(MBe)_2]$	1,545 s	1,640 sh	570 w
HNBe	1,590 s	1,670 m	—
$[Cu(NBe)_2]$	1,560 s	1,690 m	580 w
H_2Sal	1,580 s	1,660 m	—
$[Cu(Sal)(H_2O)]$	1,540 s	1,680 m	540 w

Note: s, strong; m, medium; w, weak; sh, shoulder.

of the complexes, this band is shifted to the 1540–1580 cm^{-1} region, indicating coordination of the Schiff base through the azomethine nitrogen.[12,13] Due to the presence of more than one-N–H group in the complexes, the deprotonation of this group could not be confirmed. However, bands at 1620–1970 cm^{-1} assigned to the amido group (–CONH) in the Schiff base were shifted to lower frequencies by 20–40 cm^{-1} in the complexes, indicating coordination of the amido nitrogen to the metal. This is also supported by the appearance of a new band around 540–580 cm^{-1} attributable to the M–N bond.[14]

For the $[Cu(Sal)(H_2O)]$ complex, the strong OH stretching band at 3329 cm^{-1} of the free ligand is absent in the spectra of the complexes,which suggests that the phenolic oxygen atom is coordinated to the metal atom in the ionized form. The coordination of the phenolic oxygen is further supported by the fact that the strong band observed at 1260 cm^{-1} in the spectrum of the ligand, which was attributed to the phenolic C–O stretching vibration, undergoes a shift to a higher wave number at 1280 cm^{-1} in the spectrum of the complex. In addition, a new band was observed at 470 cm^{-1}, which is assigned to the M–O bond.[15]

Electronic Spectra

The electronic spectra of the complexes are recorded in DMF and the relevant data are presented in Table 4. The spectra are characterized by a broad band at 16,583 cm^{-1}, which is assigned to the transition $^2B_{1g} \rightarrow {}^2A_{1g}$. Besides to the d–d transition, two bands are observed in the regions 25,542–

Table 4. Electronic spectra and thermal data of the complexes.

	UV-spectra			Thermal data			
Complex	ν_{max} ($cm^{-}1$)	ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)	Assignment	Step	T_i	T_m	T_f
$[Cu(Be)_2]\cdot 3H_2O$	16,583	60	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1st	55	148	200
	29,112	8,122	IL-charge transfer	2nd	250	293	329
	32,786	10,038	$\pi-\pi^*$ transition	3rd	330	333	336
				4th	337	340	390
$[Cu(DBe)_2]$	16,583	60	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1st	275	292	325
	263,157	6,756	IL-charge transfer	2nd	350	381	383
	31,746	9,133	$\pi-\pi^*$ transition	3rd	385	400	402
				4th	403	404	460
$[Cu(MBe)_2]$	16,583	65	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1st	275	309	320
	28,288	7,804	IL-charge transfer	2nd	320	347	395
	31,545	8,785	$\pi-\pi^*$ transition	3rd	397	430	475
$[Cu(NBe)_2]$	16,583	60	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1st	50	75	100
	32,711	9,494	IL-charge transfer	2nd	240	260	292
	37,105	10,322	$\pi-\pi^*$ transition	3rd	293	313	325
				4th	326	347	358
				5th	359	381	408
				6th	409	450	525
$[Cu(Sal)(H_2O)]$	16,583	63	$^2B_{1g} \longrightarrow {}^2A_{1g}$	1st	211	238	260
	25,542	9,718	IL-charge transfer	2nd	262	307	325
	30,581	9,738	$\pi-\pi^*$ transition	3rd	327	351	355
				4th	356	367	403

Note: T_i, initial temperature; T_m, peak temperature; and T_f, final temperature.

32,711 and 30,581–37,105 cm^{-1}, respectively, which are attributed to intraligand charge transfer π–π^* transitions. The nature of the electronic spectra of all complexes indicates a square-planar geometry around the Cu(II).[16]

Thermal Behavior

The TG thermograms for example were carried out within the temperature range from room temperature up to 700 °C. The observed mass losses are based on the TG results, and the calculated mass losses are based on the molecular weight of the proposed formulas. The initial, maximum, and final temperature of the different decomposition step are listed in Table 4. Non-isothermal kinetic analysis of the decomposition of Cu(II) complexes was carried out by the application of two different procedures: the Coats–Redfern[17] and Horowitz–Metzger[18] methods. Table 5 includes the following kinetic parameters: reaction order (*n*), activation energy (*E*), pre-exponential factor (*Z*), together with the correlation coefficient (*r*). These parameters were evaluated only for clear-cut and non-overlapping steps. Kinetic studies were not attempted for decomposition stages which occur within a very narrow temperature range. In general, the calculated activation energies of the complexes are relatively low indicating the autocatalytic effect of copper on the thermal decomposition of the complexes. The catalytic activity of many catalysts containing Cu(II) has been reported.[19] The following are the detailed thermal decomposition of the complexes. The TG curve of $[Cu(Be)_2]\cdot 3H_2O$ shows four steps of decomposition within the temperature range 55–340 °C (Fig. 2). The first step at 55–200 °C corresponds to the loss of three water molecules of hydration (calcd 9.30%, found 9.45%) with an activation energy of 42.60 kcal mol^{-1}. The small value of the activation energy indicates a rather fast dehydration of crystal water molecules which are loosely bonded.[20] The anhydrous complex decomposes in a major stage consisting of three overlapping steps.

The $[Cu(DBe)_2]$ complex was found to decompose in four steps within the temperature range 275–460 °C. The first step occurs in the temperature range 275–325 °C with a mass loss of 11.48% and an activation energy of 228.22 kcal mol^{-1}. This step cannot be correlated with any proper decomposition product. The major step of decomposition consists of three overlapping steps in the range 350–460 °C. The TG curve of $[Cu(MBe)_2]$ exhibits three stages starting at 275 °C with an activation energy of 69.31 kcal mol^{-1}. The latter two complexes did not show any loss of mass up to their decomposition indicating their anhydrous nature. The pyrolysis of $[Cu(NBe)_2]$ shows a stepwise decomposition in six stages, which are well discernible in the TG curve. The first stage (50–100 °C) is commensurate with the release of some moisture in the complex (2.24%). The complex then decomposes in a major step

Table 5. Kinetic parameters of the thermal decomposition of the Cu(II) complexes.

		Coats–Redfern equation				Horowitz–Metzger equation			
Complex	Step	n	r	E (kJ mol^{-1})	Z	n	r	E (kJ mol^{-1})	Z
$[Cu(Be)_2] \cdot 3H_2O$	1st	0.33	0.996	42.60	1.71×10^{4}	0.33	0.9998	48.70	1.06×10^{6}
$[Cu(DBe)_2]$	1st	1.0	0.994	228.22	4.59×10^{19}	1.0	0.9991	238.53	9.71×10^{20}
[Cu(MBe)2]	3rd	2.0	0.9914	69.31	7.74×10^{7}	2.0	0.9868	65.31	5.76×10^{5}
$[Cu(NBe)_2]$	1st	2.0	0.9986	57.62	2.31×10^{6}	2.0	0.9959	64.14	9.18×10^{10}
$[Cu(Sal)H_2O)$	2nd	1.0	0.9999	165.43	3.33×10^{14}	1.0	0.9989	175.11	9.87×10^{15}
	3rd	2.0	0.9991	247.29	4.97×10^{21}	2.0	0.992	255.71	9.73×10^{23}

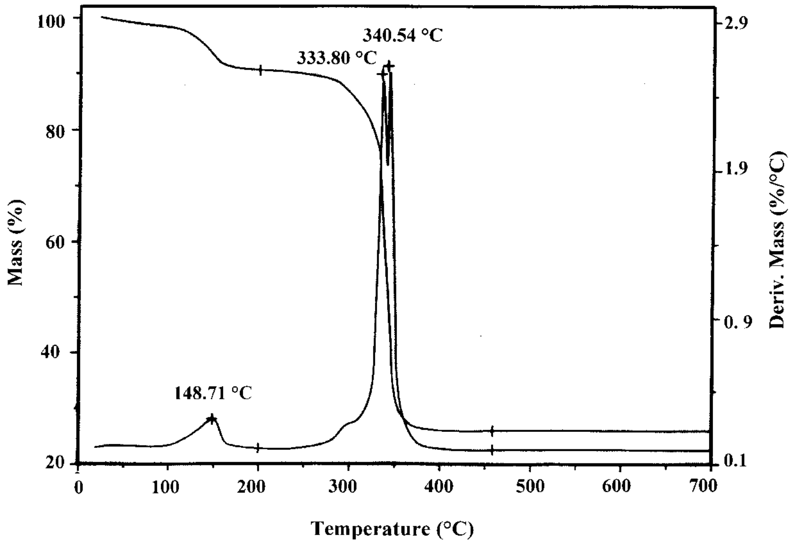


Figure 2. TG and DTG thermograms of $[Cu(Be)_2] \cdot 3H_2O$.

consisting of five overlapping steps in the temperature range 240–525 °C. In its TG curve, $[Cu(Sal)H_2O)]$ shows a mass loss within the temperature range 211–260 °C, corresponding to evolution of one coordinated water molecule (found 5.64%, calcd 5.5%) with an activation energy of 165.43 kcal mol^{-1}. Another three overlapping steps occurring in the temperature range 262–430 °C are also observed as a major stage.

The decomposition of all complexes ended with oxide formation. An almost horizontal thermal curve is observed above 525 °C. The percentage weight of the residue in this horizontal region agrees well with CuO formation (calcd 24.88%, found 24.83% for the $[Cu(Sal)(H_2O)]$ complex as an example).

Based on the above studies, the suggested structures of the two types of Cu(II) complexes are represented in Fig. 3. For the 1 : 2 complexes, structures (a) and (b) are proposed, but structure (a) is more favorable through hydrogen bond formation. Structure (c) is suggested for the 1 : 1 complex.

Photochemical Behavior

All studied Cu(II) Schiff base complexes, as mentioned above, exhibit, in addition to d–d transition, two bands which have been assigned to

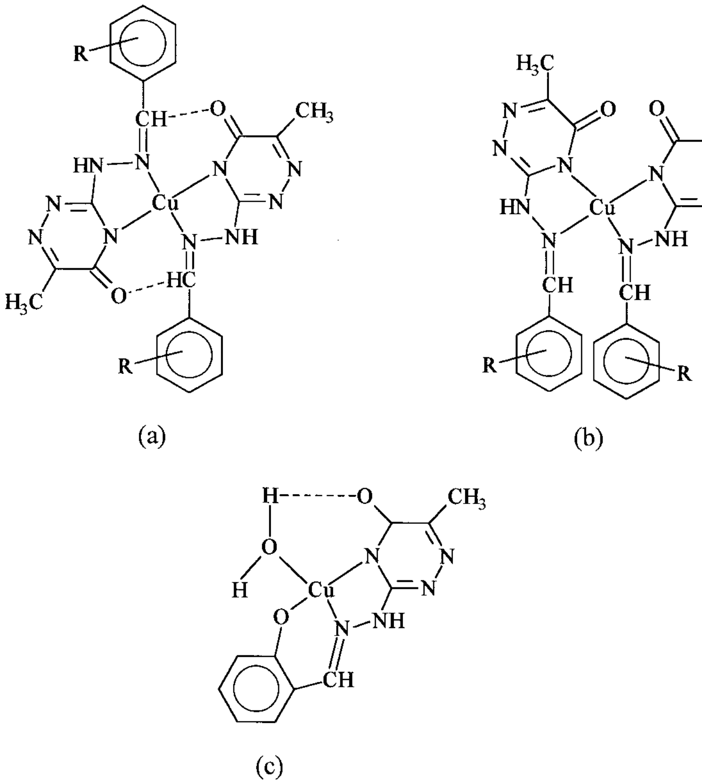


Figure 3. Proposed structures of Cu(II) Schiff base complexes; (a) and (b) are two isomers of the 1 : 2 complexes and (c) is the 1 : 1 complex; R = H, *p*-$N(CH_3)_2$, *p*-OCH_3 or *o*-NO_2.

intraligand and $\pi-\pi^*$ transitions (Table 4). Upon irradiating a DMF solution of the complexes with monochromatic light of $\lambda = 298$ nm and recording the spectral changes at different time intervals, the complexes behave differently. For $[Cu(Be)_2]$, $[Cu(MBe)_2]$, and $[Cu(NBe)_2]$, within the first 2 min of irradiation, the absorbance of the intraligand band increases, while the absorption of the $\pi-\pi^*$ band decreases, followed by a general decrease in the intensity (Fig. 4). For $[Cu(DBe)_2]$ and $[Cu(Sal)H_2O]$, the most prominent features in the absorption spectra is a decrease in intensity upon irradiation. To explain these different behaviors, one assumes that the photochemical reactions, which are rather clean as indicated by the observed isosbestic points, occur in two steps for the $[Cu(Be)_2]$, $[Cu(MBe)_2]$, and $[Cu(NBe)_2]$ complexes. In the first step, absorption of light leads to a weakening of

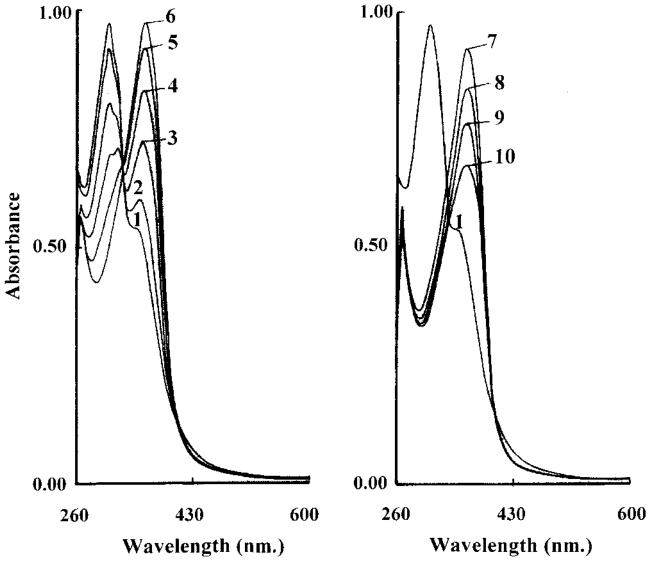


Figure 4. Spectral changes during the photolysis of $[Cu(Be)_2]\cdot 3H_2O$ in DMF at various irradiation times: **1** = 0 sec, **2** = 5 sec, **3** = 15 sec, **4** = 30 sec, **5** = 45 sec, **6** = 120 sec and **7** = 15 min, **8** = 30 min, **9** = 45 min, **10** = 60 min ($\lambda_{ex} = 298$ nm; 1 cm cell).

Cu–N ionic bond in the complexes which facilitates the charge transfer from the N-atom to the rest of the organic molecule. This is indicated by the increase of the IL-charge transfer band. It is well known that light absorption leads to charge separation which attracts much interest owing to its important applications such as artificial photosynthesis and non-linear optical properties.[21] This assumption is confirmed by the observation that this first step is only recorded for Schiff base complexes containing a powerfull electron withdrawing group such as the NO_2 group in $[Cu(NBe)_2]$ or H in $[Cu(Be)_2]$ or a weakly electron donating group such as OCH_3 in $[Cu(MBe)_2]$. However, in case of strongly electron donating groups such as $N(CH_3)_2$ in $[Cu(DBe)_2]$ or OH in $[Cu(Sal)H_2O]$, the first step was not detected. As a result of the weakening of the Cu–N bond, the complexes decompose in the second step as indicated by the general decrease of the absorption.

For the $[Cu(Sal)H_2O]$ and $[Cu(DBe)_2]$ complexes, the photodecomposition occurs directly upon irradiation as indicated by their spectral changes during photolysis (Fig. 5 as an example). From the above discussion, a reaction scheme given by Eqs. 3–5 is suggested to account for our results.

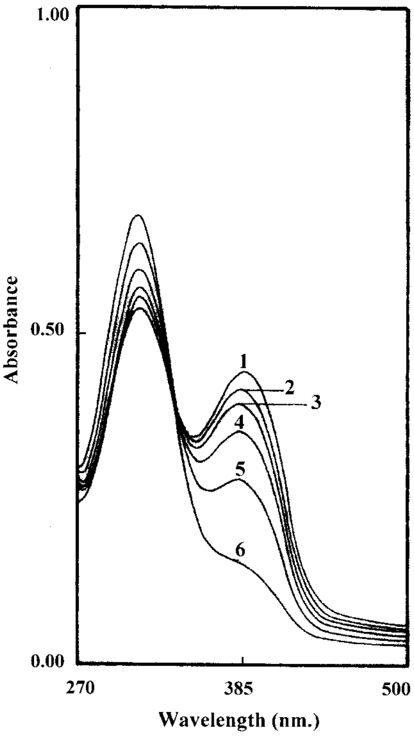
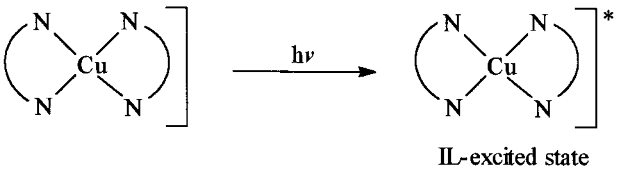


Figure 5. Spectral changes during the photolysis of [Cu(Be)$_2$] in DMF at various irradiation times: **1** = 0 min, **2** = 1 min, **3** = 2 min, **4** = 4 min, **5** = 8 min, **6** = 16 min (λ_{ex} = 298 nm; 1-cm cell).



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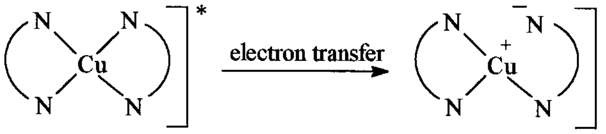

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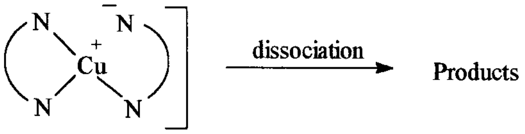

(5)

(where  represents a bidentate Schiff base ligand). The IL-excited state generated by light absorption [Eq. (3)] transfers an electron to the N-atom [Eq. (4)]. This step has been detected by the increase of the absorption intensity of the IL-ligand band of [Cu(Be)$_2$], [Cu(MBe)$_2$], and [Cu(NBe)$_2$]. The resulting complex seems to be unstable and decomposes to unidentified products in a secondary thermal reaction [Eq. (5)]. A similar mechanism has been proposed for the photolysis of the (acetylacetonato)*bis*(benzohydroxomato)iron(III) complex.[22]

As an alternative to the above suggested assumption, one may attribute the observed spectral changes of [Cu(Be)$_2$], [Cu(MBe)$_2$], and [Cu(NBe)$_2$] within the first step to a photoisomerization reaction. As a result of an electron-transfer reaction represented by Eq. (4), another isomer may be formed due to rotation of one ligand with respect to the another. The structure of this isomer may be represented by Fig. 3(b). This isomer seems to be unstable and decomposes to unidentified products. This assumption is based on the following considerations: (i) only the [Cu(Be)$_2$], [Cu(MeBe)$_2$], and [Cu(NBe)$_2$] complexes show this photorearrangement, *i.e.*, those having bidentate ligands. (ii) For [Cu(Sal)H$_2$O] which contains a tridentate ligand, such isomerization is impossible. (iii) In addition, the rotation in [Cu(DBe)], which have a bulky group, such as N(CH$_3$)$_2$, is unfavorable, *i.e.*, for [Cu(Sal)H$_2$O] and [Cu(DBe)$_2$], such isomerization does not occur and the complexes decompose directly.

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