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## Chromotropism of a new mixed-chelate copper(II) complex

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### 1. Introduction

During the past decade, particular interest has been directed towards the investigation of chromotropism phenomenon due to its application in thermosensitive [1], imaging [2-5], photo-switching [6-8], and sensor materials [9]. Chromotropism defines as a reversible variation of the spectral properties of compound under differing physical or chemical conditions such as temperature (thermochromism) and solvent (solvatochromism). Whereas there are a large number of solvatochromic compounds and complexes [10-12], the mixed-chelate complexes, especially those containing copper(II) exhibited the most attention due to existence of simple and regular changes in their electronic spectra according to the strength of interaction with solvent molecules at the axial sites and consequently, their potential use as molecular switch [13-16], and pollutant sensor [17,18] and Lewis-acid-base color indicator [19]. Among ligands examined in mixed-chelate complexes β-diketonato and ethylenediamine derivatives find to illustrate the most effective combination to form stable complexes and demonstrate a pronounce solvatochromism [20,21]. However, the syntheses of mixed-chelate complexes are cumbersome since the formation of homogenous bis-chelate complexes must be suppressed [22]. It was establish that diamine ligand containing bulky substituents on the nitrogen atoms prevents the stabilization of bis-diamine complexes if another ligand is slim such as acetylacetonate or its derivatives [23]. On the other hand, electronic and structural properties of the both chelates perform important

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### ABSTRACT

A new mixed-chelate copper(II) complex with the general formula [Cu(Cl-acac)(diamine)]ClO<sub>4</sub>, where Clacac is 3-chloroacetylacetonate ion and diamine is *N*,*N*-dimethyl,*N*'-benzyl-1,2-diaminoethane, was prepared and characterized on the basis of elemental analysis, spectroscopic and conductance measurements. The mixed-chelate complex is soluble in various solvents and presents an interesting combination of solvato- and thermochromism. Its reversible chromotropism behavior is discussed in detail.

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functions in stabilization of the mixed-chelate complexes [24]. Thus fine tuning of electronic and steric hindrance in the chelates are crucial in preparation of stable solvatochromic complexes. In this paper which is in continuation of our studies on the solvato-chromic behavior of mixed-chelate copper(II) complexes [25,26] we prepared a new mixed-chelate complex abbreviated as  $[Cu(Cl-acac)(diamine)]ClO_4$  shown in Scheme 1 and its solvato-chromism and thermochromism behaviors was studied.

### 2. Experimental

### 2.1. Materials and methods

[Cu(Cl-acac)<sub>2</sub>] [27] were prepared according to published procedure. All solvents were spectral-grade and all other reagents were used as received. All the samples were dried to constant weight under a high vacuum prior to analysis. *Caution: perchlorate salts are potentially explosive and should be handled with appropriate care.* 

Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on  $1.00 \times 10^{-3}$  M samples in CH<sub>3</sub>CN and CHCl<sub>3</sub>. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument. The electronic absorption spectra were measured using a Braic2100 model UV–Vis spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker 500 DRX Spectrometer. Mass spectra were obtained on a VG 70E spectrometer. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer.





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#### 2.2. Syntheses

#### 2.2.1. Preparation of N,N-dimethyl,N'-benzyl-1,2-diaminoethane

A typical procedure is as follow: a mixture of benzaldehyde (30 mmol) and N,N-dimethyl-1,2-diaminoethane (30 mmol) in ethanol (60 mL) was stirred for 24 h. Then the solvent was evaporated under reduced pressure. The resultant yellow oil was then dissolved in *n*-hexane (40 mL), washed with a minimal volume of water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Concentration under reduced pressure gave diimine product as yellow oil. To the stirred solution of yellow oil (3.5 g) in methanol (60 mL) at room temperature was gradually added NaBH<sub>4</sub> (30 mmol) over 0.5 h. The resulting mixture was allowed to stand overnight, and then was added acetic acid (10 mL). The mixture was made alkaline by NaOH (4 M) and was extracted with dichloromethane (5  $\times$  10 mL). The combined CH<sub>2</sub>Cl<sub>2</sub> fractions were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure resulted in desired product as orange oil. The typical yields were 45-55%. Selected IR data ( $v/cm^{-1}$  using KBr): 3370 (m, N–H str.), 2810 (s, C-H str. aliphatic), 1475 (s, Ph-O str.), 680 (m, C-CH<sub>3</sub> + ring def. + Cu–O). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ: 2.19 (s, 6H, CH<sub>3</sub>); 2.42  $(t, J = 6.0 \text{ Hz}, 2\text{H}, \text{CH}_2)$ ; 2.69  $(t, J = 6.0 \text{ Hz}, \text{H}, \text{CH}_2)$ ; 3.80  $(s, 2\text{H}, \text{CH}_2)$ ; 3.8 CH<sub>2</sub>-Ph); 7.23-7.32 (m, 5H, Ar-H). Mass spectra for C<sub>11</sub>H<sub>18</sub>N<sub>2</sub> (electron impact, 70 eV): *m/z* 58 (MW – C<sub>8</sub>H<sub>11</sub> N), *m/z* 91 (MW –  $C_4H_{11}N_2$ ), *m/z* 120 (MW -  $C_3H_8$  N).

# 2.2.2. Preparation of mixed-chelate complexes [Cu(Cl-acac)(diamine)] (ClO<sub>4</sub>)

To the solution of *N*,*N*-dimethyl,*N'*-benzyl-1,2-diaminoethane (6 mmol, 1 g), 3-chloroacetylacetone (6 mmol, 0.7 mL), Na<sub>2</sub>CO<sub>3</sub> (3 mmol, 0.3 g) in ethanol (30 mL) were slowly added Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (6 mmol, 2.2 g) in water (15 mL). After few minutes homo bis-chelate of [Cu(Cl-acac)<sub>2</sub>] precipitated as green solid which was separated off by filtration. The resultant clear blue solution was allowed to stand overnight at room temperature. After concentration at room temperature, blue solid precipitated that was collected with filtration and washed with water and diethylether. The yield was 40%. Selected IR data ( $\nu/cm^{-1}$  KBr disk): 3320 (m, N–H str.), 1580 (s, C=O str.), 1405 (s, -CH<sub>2</sub>- bend.), 1090 (s, Cl–O str.), 620 (m, Cl–O bend.). Anal. Calcd. for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>Cl<sub>2</sub>O<sub>6</sub>Cu: C, 40.47; H, 5.09; N, 5.90; Cu, 13.38; Found: C, 40.68; H, 4.78; N, 5.88; Cu, 13.44%. Molar conductance ( $\Delta_m/\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>): 115.0 in ACN; 0.0 in chloroform.

### 2.2.3. Preparation bis-chelate complexes $[Cu_2(diamine)_2(OH)_2](ClO_4)_2$

To the solution of desired diamine (10 mmol) in ethanol (30 mL) were slowly added Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (5 mmol) in ethanol (10 mL). The resultant mixture was stirred for 2 h at room temperature. The desired compound precipitated from the reaction mixture as violet solid. The typical yields were 80%. Selected IR data ( $\nu$ /cm<sup>-1</sup>



KBr disk): 3470 (m, O–H str.), 3261 (m, N–H str.), 1456 (m, CH<sub>2</sub>– Ph str.), 1089 (s, Cl–O str.), 695 (w, CH<sub>2</sub> rock.), 612 (m, Cl–O bend.). Anal. Calcd. for C<sub>22</sub>H<sub>38</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>10</sub>Cu<sub>2</sub>: C, 36.88; H, 5.35; N, 7.82; Cu, 17.74; Found: C, 37.04; H, 5.36; N, 7.78; Cu, 17.66%.

### 3. Results and discussion

The diamine ligand was prepared by condensation of an equimolar of *N*,*N*-dimethyl-1,2-diaminoethane and benzaldehyde and further reduction of diimine by sodium borohydride. The mixedchelate complexes of copper(II) was synthesized with mixing of Cu(ClO<sub>4</sub>)·6H<sub>2</sub>O, 3-chloroacetylacetone, Na<sub>2</sub>CO<sub>3</sub> anhydrous and *N*,*N*-dimethyl,*N*'-benzyl-1,2-diaminoethane with molar ratios of 1:1:0.5:1, respectively, in ethanol–water mixture. The homo bischelate copper(II) complexes were also prepared for comparison proposes.

### 3.1. IR spectra

Several bands appear in the IR spectrum of mixed-chelate complex in the region that is also observed, although with minor shifts, in the spectra of the free ligands. The absorption band around 1040 cm<sup>-1</sup> is probably due to the stretching vibration of carbonnitrogen bond [28]. The strong bands at 1405 cm<sup>-1</sup> are very likely associated with the scissoring vibration of -CH<sub>2</sub>- groups [28]. The band at around 760 cm<sup>-1</sup> that in the spectra of free diamine ligand appears broader and is split in two in region of 730–790 cm<sup>-1</sup> may be due to the rocking vibration of CH<sub>2</sub> groups [28]. The stretching vibrations of N-CH<sub>2</sub> groups in the free ligands, and the well-known bands in the region 2850 ± 100 cm<sup>-1</sup> that are associated with it, are more important since they serve as an indication of coordination of diamine ligand. Upon covalent bond formation, these absorption bands apparently lose intensity, become shifted to the higher frequencies and mix with other C-H absorption bands. Dependence on coordination is also exhibited by the intense and narrow band occurring at  $3240 \pm 30 \text{ cm}^{-1}$  which is associated with N–H vibration and is observed at around 3370 cm<sup>-1</sup> and broader in the free diamine ligands. As the lone pair of electrons of the donor nitrogen atoms become involved in the metal-ligand bond, the transfer of electron density to the metal and the subsequent polarization of the ligands involves electron depopulation of the N-H bond, which culminates in a shift to lower frequencies. Coordination of acetylacetonate chelate can be concluded from IR spectroscopy so that the C=O stretching vibration of the free 3-chloroacetylacetone where observed in the 1700 cm<sup>-1</sup> was shifted to the lower wave number in complex spectrum indicating the coordination of 3chloroacetylacetone to the copper ion. The presence of  $ClO_4^-$  group is confirmed by two intense bands at around 1110 and 610 cmwhich are attributed to the anti-symmetric stretching and antisymmetric bending vibration modes, respectively [28]. Poorly splitting of the former band is resulted from coordination of  $ClO_4^$ to the copper ion and distortion from T<sub>d</sub> symmetry. It is well known that the degree of splitting of this band serves as a measure of the degree and mode of the coordination of perchlorate ions to the copper ion [29]. Infrared spectra of the bis-chelates of [Cu<sub>2</sub>(diamine)<sub>2</sub>(OH)<sub>2</sub>]<sup>2+</sup> and [Cu(Cl-acac)<sub>2</sub>] complexes as well as the mixedchelate complex are illustrated in Fig. 1 for comparison. These spectra clearly indicated formation of desired mixed-chelate complex.

### 3.2. Conductometric data

The molar conductivity values of the mixed-chelate complex in solvents of chloroform and acetonitrile have been studied. The results show that the complex is 1:1 electrolyte in acetonitrile. However, in solvent of chloroform the value is fairly lower than that for







1:1 electrolyte [30]. Thus, it seems that an ion-pair formation (or anion coordination) might exist in some extent in chloroform. That means  $ClO_4^-$  ions are bound weakly above and below of the chelate planes and can be driven out by high donor power solvent molecules which leading to their solvatochromism. These results are in general agreement with the expectation from the spectral data and with our pervious results [31,32].

### 3.3. Solvatochromism

The electronic absorption spectra of the mixed-chelate complex were measured in solution in some organic solvents with different

Table 1Electronic spectra of the complex in various solvents:  $\lambda_{max}/nm \ (\epsilon/M^{-1} \ cm^{-1}).$ 



Fig. 2. Absorption spectra of the mixed-chelate complex  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  in selected solvents. Absorption spectra in other solvents are omitted for clarity.

donor numbers (DN). Table 1 shows  $\nu_{max}$  and  $\epsilon$  values for the mixed-chelate complex in some solvents.

The donor number expresses a measure of coordinating ability of solvent on the standard of that of dichloromethane (DCM) [33]. The mixed-chelate complex is strongly solvatochromic. The absorption spectra of the compound shows a broad structureless band (envelop) attributed to the promotions of the electrons in the lower energy orbitals to the hole in  $d_{x^2-y^2}$  orbital of the copper(II) ion (d<sup>9</sup>). Since the  $d_{z^2}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals of the Cu(II) ion in a mixed-chelate will all be lifted up by its interaction with polar solvent molecules approaching from above and below the chelate plane, the broad d-d transition band will be shifted to the lower energy and demonstrates a positive solvatochromic. That means the  $v_{max}$  value of this band gradually shifts to the red as the DN of the solvent increases. An obvious exception from this general trend is found in the  $v_{max}$  value in acetonitrile. The donor number of this solvent (14.1) is logically lower than that of acetone (17.0), so that the  $v_{max}$  in this solvent should be higher than that in acetone. In fact, this might possibly be due to the linear shape of MeCN molecule, and its head-on mode of coordination with Cu-N-C angle of 180° which facilitates the approach of MeCN to the copper ion with high steric hindrance. As a result, this makes MeCN an apparently more basic species than acetone in certain case. However, it may be due to another effect, i.e. the fact that the copper ion and MeCN are rather soft and MeCN can operate as a  $\pi$ -acceptor ligand as shown in Scheme 2. Even small contribution from this type of bonding makes the  $\sigma$ -bond synergetically stronger, and the ligand field strength of MeCN remarkably higher [18].

The spectral changes of the mixed-chelate complex in some solvents are illustrated in Fig. 2 as an example of its solvatochromism. The range of  $\lambda_{max}$  variation for the mixed-chelate complex in different solvents is about  $3.36 \times 10^3$  cm<sup>-1</sup> and this wide range might be

Solvent	DCM	MeNO <sub>2</sub>	ACN	Acetone	THF	MeOH	DMF	DMSO	Ру	HMPA
DN	0.0	2.7	14.1	17.0	20.0	23.5	26.6	29.8	33.1	38.8
$v_{\rm max}/10^3 {\rm cm}^{-1}$	17.65	18.35	17.03	17.18	17.00	16.78	16.45	16.07	14.99	15.43
( $\epsilon/{ m M}^{-1} { m cm}^{-1}$ )	(117)	(116)	(132)	(151)	(115)	(121)	(122)	(116)	(116)	(110)



**Fig. 3.** Dependence of the  $v_{\text{max}}$  values of mixed-chelate complex on the solvent donor number value;  $R^2 = 0.97$ ,  $y = 18.464 - 778 \times 10^3$ .



**Fig. 4.** Spectral changes of mixed-chelate complex  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  in solvent of nitromethane at 80 °C after (a) 0 min, (b) 5 min, (c) 15 min, and (d) 35 min.

due to presence of a large steric hindrance in complex. It is known that the increase of steric hindrance of the axial coordination of incoming solvent molecules tends to make the complex more solvatochromic, bringing about a large structural change with progressive solvation of the complex caused by the increase of DN.

Deviations were also observed in the solvents of dichloromethane and pyridine. This anomaly was ascribed to the formation of ion pairs by mean of an axial coordination of  $ClO_4^-$  in  $CH_2Cl_2$ . As the relative dielectric constant of nitromethane takes a much higher value (28.5 for nitromethane versus 8.9 for  $CH_2Cl_2$  in room temperature), this solvent facilitates the dissociation of cationic chelate. Thus reducing the axial interactions of the  $ClO_4^-$  and eliminating the tetragonal distortion [34]. In solvent of pyridine the absorption maximum occur at lower energy than HMPA although the donor number of former is lower than latter. This inconsistency in the absorption maxima may be due to planar shape of pyridine molecule which facilitates its approach to the copper ion with high steric impediment [35].

Regression analysis of band maxima of the mixed-chelate complex against donor number of solvents is shown in Fig. 3 and indicates good correlation and also confirms the solvatochromic behavior of the complex. A linear correlation of the  $v_{max}$  values



**Fig. 5.** Spectral changes of mixed-chelate complex  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  in solvent of pyridine at 80 °C after (a) 0 min, (b) 5 min, (c) 15 min, and (d) after several days and cooling down to the room temperature. The inset is the charge transfer region of the complex  $(2.0 \times 10^{-4} \text{ mol dm}^{-3})$  in the same time scale.

with the solvent donor number (DN) yields the following expression. Thus the solvatochromic behavior the complex can be studied quantitatively.

$$\begin{split} \nu_{\text{max,Solv}} &= 18.46 - 778 \times 10^3 \text{DN}_{\text{solvent}} \quad (r^2 = 0.97) \\ \text{DN}_{\text{solvent}} &= 237.33 - 12.853 \nu_{\text{max,Solv}} \end{split}$$

The mixed-chelate complex exhibits strongly pronounced thermochromism. The nitromethane solution of the complex gradually changes color from violet to the green upon heating (Fig. 4). In the course of these spectral changes, no distinct isosbestic point was observed. Thus, it suggests that this phenomenon is not due to the simple salvation equilibrium of type (A) presented in Scheme 3. Although the exact mechanism of this thermochromism is still unknown, it seems the origin of this behavior lies in the reversible endothermic reaction (B) given in Scheme 3.

Increasing the temperature in solvent of nitromethane the shift in d-d band indicates change in the coordination geometry around the copper ion. It also indicates that the solvent molecules coordinate to the copper ion replacing the diamine chelate and thus the ligand field around the metal ion alters that resulted in the shift of absorption maximum. However, this process is reversible and after cooling the solution to the room temperature the diamine chelate presence in the solution recoordinates to the copper ion and causes the reappearance of original violet color. The reverse process is fairly slower than the forward reaction and takes several weeks for full development of the original color. The drop in the rate of the reverse process could be due to the presence of a large amount of solvent molecules in the solution which hinders the recoordination of the diamine. It is interesting to note that when a large excess of the diamine chelate (ca. an equimolar of solvent) is added to the green solution of  $[Cu(x-acac)(solv)_4]^+$  the maximum absorption changes faster so that it takes several days for reappearance of its original color.

Interestingly the complex is also thermochromic in solvents of pyridine, dimethyl sulfoxide and acetonitrile. In solvent of pyridine, the original green color turns orange–yellow after heating for few minutes (Fig. 5). Upon heating the d–d band of the complex loses its intensity and the CT band located in the

 $[Cu(Cl-acac)(diamine)]ClO_4 + 2(solvent) \longrightarrow [Cu(Cl-acac)(diamine)(solvent)_2]ClO_4 (A)$  $[Cu(Cl-acac)(diamine)]^+ + 4(solvent) \longrightarrow [Cu(Cl-acac)(solvent)_4]^+ + diamine (B)$ 

region  $29-32 \times 10^3$  show bathochromic shift with an increase in extinction coefficient as a result of ease in  $\pi$ -back donation of the pyridine molecules in compare with that of the diamine chelate.

### 4. Conclusion

The prepared mixed-chelate complex demonstrated high solubility in a variety of organic solvents and illustrates noticeable chromotropism. Additionally, it shows good correlation between the d–d absorption maxima in the solution and donor strength of the solvent used when DN lies between 3 and 30. However, inconsistencies appear in very weak or very strong donor solvents. As it can be envisioned from Table 1 the  $\lambda_{max}$  value of the complex declines with the increase of DN in going from nitromethane to pyridine, but when the basicity turns into smaller it decreases remarkably again. Such behavior also observed in the solvents with high basicity, as the DN of the solvent increases the  $v_{max}$  value increases. The visualized reversible thermochromic property of the complex seems to be on account of substitution of solvent molecules with the coordinated diamine chelate and vice versa.

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