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Substituent effect in the γ -position of acetylacetonate on the solvatochromic property of mixed-chelate copper(II) complexes consisting of diamine and acetylacetonate ligands

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ABSTRACT

The infrared and electronic absorption spectra of a series of new mixed-chelate copper(II) complexes that encompass *N*,*N*-dibenzylethylenediamine (diamine) and 3-substituted derivatives of acetylacetone (xacacH) were studied. The IR and electronic absorption spectra and the molar conductivity of the newly prepared complexes are presented and discussed. The molar conductivity in dichloromethane reveals a predominance of electrostatic interactions between [Cu(diamine)(x-acac)]⁺ entity and perchlorate anions that counterbalance the positive charge. The resulting complexes with local symmetry of CuO₂N₂ attains a square-coplanar structure and exhibits the tendency for axial ligation, which is enhanced when an electron-attracting substituent is attached to the γ -position of acetylacetonate moiety. The tendency for axial ligation is particularly fulfilled when suitable nucleophiles (solvents) with deferent donor abilities exist, leading to solvatochromism. The solute–solvent interactions are revealed by shifts in the ligand field absorption spectra that are enhanced as the donor power of the solvent increases. Linear dependence of the ligand field absorption maximum on solvent donor number is generally observed.

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1. Introduction

Solvatochromic behaviors of inorganic compounds have been recently reviewed by many researchers [1–3]. There are a number of empirical scales for solvent polarity such as Dimroth and Reichardt's E_T , Kosower's Z, Kamlet and Taft's α , β , π^* , dielectric constant ε and Gutman's donor DN and acceptor numbers AN [4–9]. Among these, only a few have gained widespread use, E_T mainly for organic compounds [10] and DN and AN for transition metal complexes [1]. The methods using solvatochromic behavior of transition metal complexes will serve, as visualized model of solute-solvent interactions. However, the position and intensity of d-d bands also have been correlated with some success with different solvent parameters. There exist a number of examples of solvatochromism metal complexes and origins of color changes are quite diverse. A certain class of complexes such as mixed-chelate complexes of copper(II) show gradual color change over a wide range of solvent donor number (DN). The donor number expresses a measure of coordinating ability of solvent on the standard of that of 1,2-dichloromethane (DCM) or dichloroethane (DCE) [11]. This phenomenon is not only interesting in its own right but also provides information on various factors determining coordination geometries of transition metal ions in solution and also on the

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mechanism of salvation. However, the synthesis of mixed-chelate complexes is not a trivial procedure since the formation of homo bis-chelate complexes must be suppressed [12]. It was established that combination of diamine ligand containing bulky substituents on the nitrogen atoms and a slim chelate such as acetylacetonate or its derivatives desired hetero-bis chelate complex forms with characteristic properties such as chromotropic and catalytic properties [13]. We recently reported two classes of mixed-chelate copper complexes that show reversible solvatochromism in various solvents [14,15]. It was suggested that the steric hindrance and electronic effects exert significant role in solvatochromic behavior of mixed-chelate complexes.

Fukuda and co-workers extensively studied on the effect of substituent groups on the diamine and acac chelates on the chromotropic behavior of mixed-chelate complexes [16]. Their studies mainly focused on the electronic effect of substituents in the β -position of the acac chelate.

In this paper which is a continuation of our studies on the solvatochromic behavior of the mixed-chelate copper(II) complexes we intend to study the electronic property imposed by a substituent in the γ -position of the acac chelate on the copper ion. Based on to our knowledge such investigation has not been carried out on the mixed-chelate complexes. Thus a series of mixed-chelate copper(II) complexes, that shown in Scheme 1 where x is substituent groups with different electronic properties were synthesized and their solvatochromic behavior were investigated.





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Scheme 1.

2. Experimental

2.1. Materials and methods

The complexes of $[Cu(diamine)_2](ClO_4)_2$ [14], $[Cu(x-acac)_2]$ [17] and $[Cu(diamine)(x-acac)](ClO_4)$ [14] were prepared according to published procedures. 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 1.00×10^{-3} M samples in CH₃CN and CH₂Cl₂. 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. The 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.

3. Results and discussion

The reaction of copper(II) perchlorate hexahydrate, *N*,*N*-dibezylethylenediamine (diamine), 3-substituted derivative of acetylacetone (x-acacH) and sodium carbonate with molar ratios of 1:1:1:0.5 resulted in the formation of mixed-chelate complexes. The color, typical yields and analytical date of the new mixed chelate complexes are presented in Table 1. The obtained results indicate the formation of the desired complexes.

The yield of compound **III** is much lower than compounds **I** and **II** (74%) [14]. It seems that insertion of the Cl as a electron-attracting group in the γ -position of acetylacetonate chelate alter the electron distribution around the copper(II) ion and in some extent destabilizes the formation of the mixed-chelate complex [18]. It

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Color, yields and analytical data of the new complexes obtained.

No.	Compound (color/yield)	Analysis ^a			
		C%	H%	N%	Cu%
I	[Cu(diamine)(Cl-acac)]ClO ₄	46.74	4.45	4.80	11.75
	(green/45%)	(46.98)	(4.88)	(5.22)	(11.84)
ш	[Cu(diamine)(CH ₃ -acac)]ClO ₄	51.11	5.60	5.12	11.14
	(blue/71%)	(51.16)	(5.66)	(5.42)	(11.20)

^a Calculated values are in parentheses.

Table	2			

Infrared band positions and band assignments of complex	es.
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Complex	$v_{\rm N-H}~({\rm cm}^{-1})$	$v_{C=0}, v_{C=C} (cm^{-1})$	$v ClO_{4}^{-} (cm^{-1})$
[Cu(diamine)(H-acac)](ClO ₄) ^a	3231	1583	1110, 623
[Cu(diamine)(Cl-acac)](ClO ₄)	3223	1607	1110, 627
[Cu(diamine)(CH ₃ -acac)](ClO ₄)	3235	1580	1110, 624
[Cu(H-acac) ₂]	-	1580	-
[Cu(Cl-acac) ₂]	-	1592	-
[Cu(CH ₃ -acac) ₂]	-	1585	-
[Cu(diamine) ₂](ClO ₄) ₂	3230	-	1110, 623

^a Results taken from Ref. [14].

was also observed that compound **III** in solvent of high donor power decomposes in ambient temperature over few days and its decomposition enhances in higher temperature. However, this phenomenon was not detected for compounds **I** and **II**. In conjunction with this proposal, Fukuda and co-workers reported impossibility of preparation of mixed-chelate complex of [Cu(teen)(hfa)]⁺ and [Cu(teen)(hfa)₂] was obtained instead ("teen" and "hfa" stand for *N*,*N*,*N*'-tetraethylenediamine and hexafluoroacetylacetonate, respectively) [19] (Table 2).

3.1. IR spectra

Certain vibrational bands that are characteristics of the [Cu(diamine)₂](ClO₄)₂ and [Cu(x-acac)₂] complexes are presented in the IR spectra of the mixed-chelate complexes (see Fig. 1). In the spectra the disappearance of other bands in conjunction with the merger of absorptions in specific regions of the spectra are indicative of the band formed and the entities present in the newly obtained chelate complexes (Table 3). The bands are distinguished into those emanating form the ligands and those associated with the counter ion, ClO_4^- .

Insertion of substituents in the γ -position of x-acacH culminates in a merge of the bands emanating from the perturbed double bands. Replacement of one acetylacetonate chelate ring by that of the diamine and formation of mixed-chelate complex diminishes the extent of conjunction and the repercussions of the presence of diamine on the aforementioned perturbed double bonds become evident when the wave number of the vibrational modes are compared with the corresponding ones in the [Cu(x-acac)₂]. For instance, while the absorption due to the perturbed C=O in [Cu(x-acac)₂] peaks at around 1585 cm⁻¹, upon formation of the mixed-chelate species the band is shifted to 1595 cm⁻¹.

Corroboration of the variable nature of the interactions of the bulky perchlorate group with the copper(II) complex cation, implied by the molar conductivity values, is obtained from the IR spectra. The presence of perchlorate group is confirmed by two bands around 1110 cm^{-1} and 620 cm^{-1} which correspond to the triply degenerate asymmetric stretching and asymmetric bending vibration modes of T₂ of the tetrahedral ClO₄ group, respectively [20]. The former band at 1110 cm^{-1} of compounds I–III, not withstanding other groups that also absorb in the same region, is split with a poorly defined maximum showing the deformation from T_d 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 [21]. These bands disappear in the spectrum of [Cu(x-acac)₂].

3.2. Conductometric data

The molar conductivity values of the mixed-chelate complexes **I–III** in solvents of dichloromethane and acetonitrile are illustrated in Table 3. The solutions of the mixed-chelate complexes in acetonitrile are electrically conductive with molar conductivity values indicative of 1:1 electrolytes [22]. However, significant drop in



Fig. 1. Infrared spectra of $[Cu(x-acac)_2]$, $[Cu(diamine)(x-acac)]ClO_4$ and $[Cu(diamine)_2](ClO_4)_2$, complexes.

Table 3

Molar conductivities data (\varDelta_m) of the complexes $(\Omega^{-1}\,cm^2\,mol^{-1},$ at 25 $^\circ C)^a$ in dichloromethane and acetonitrile.

Complexes	I	II ^b	III
CH ₂ Cl ₂	1.1	4.2	2.5
CH ₃ CN	161.1	155.0	113.6

^a Concentration: *ca.* 1×10^{-3} M. Standard values for a 1:1 electrolyte type in CH₂Cl₂ and CH₃CN are in the range of 10–20 and 120–160 (Ω^{-1} cm² mol⁻¹, at 25 °C), respectively, from Ref. [22].

^b Results taken from Ref. [14].

the molar conductivities are observed in solvent of dichloromethane. These results suggest that an ion-pair formation or covalent interactions of perchlorate anions might exist to some extent in CH₂Cl₂ mainly, in [Cu(diamine)(Cl-acac)]ClO₄ in which exhibits non-conductive behavior. That means ClO₄⁻ ions are bound weakly in compounds I and III and moderately in compound II in above and below of the chelate planes and can be removed by high donor power solvent molecules which leads to the solvatochromism. These results are in general agreement with the expectation from the spectral data and with our pervious results taken from X-ray analyses of type [Cu(diamine)(H-acac)]ClO₄ [23,24]. Those results demonstrated that two ClO_4^- ions lie above and below the plane of chelate rings and are weakly coordinate to the copper ion. The forces holding ClO_4^- ions in those complexes are relatively weak so that the ions will be easily ejected from the coordination sphere by solvent molecules in solution.

3.3. Solvatochromism

The electronic absorption spectra of the mixed-chelate complexes are characterized by a broad structureless band in the visible region attributed to the promotion of the electron in the low energy orbitals to the hole in $d_{x^2-y^2}$ orbital of the copper(II) ion (d⁹). The position of this band is shifted to longer wavelengths as the donor number of solvent increases (Table 4). This red shift is ascribed to the strong repulsion of the electrons in d_z^2 orbital by lone pair electrons of the solvent molecules that are axially coordinated to the copper center, decreasing the energy required to transfer the electrons to the $d_{x^2-y^2}$ orbital.

The spectral changes of the complexes in solvents with various donor numbers (DN) are illustrated in Fig. 2. Values of DN of the solvents utilized are as follows: DCM = 0.0; MeNO₂ = 2.7; MeCN = 14.1; acetone = 17.0; THF = 20.0; MeOH = 23.5; DMF = 26.6; DMSO = 29.8 pyridine = 33.1; HMPA = 38.8.

In the series the shifts induced by certain solvent depend upon the electronic properties of substituent group attached in the γ -position of the acac chelate which controls the magnitude of the inplane ligand field strength, the strength of the axial bonds formed between the central copper(II) ion and solvent molecules and finally the species (counter ion) neutralizing the charge of the [Cu(diamine)(x-acac)]⁺. Introducing an electron-attracting (x = Cl) or electron-releasing (x = CH₃) substituent on the acac chelate alters the Lewis acidity of CuN₂O₂ chromophore and consequently, its equatorial ligand field strength. In other words, presence of Cl-acac chelate makes the coordination sphere around the metal ion electron-poor, which makes it easier for solvent molecules to approach the axial center and accordingly, leading to a greater solvatochromic effect. As evident from Fig. 3 and Table 4 the λ_{max} values in one particular solvent decreases in the following order of acac chelate.

$Cl-acac > H-acac > CH_3-acac$

It is clear from Fig. 2 that the spectra in coordinating solvents such as pyridine and DMSO do not follow a single-Gaussian profile while non-coordinating solvents, at least, follow such a profile.

Table	4
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Electronic spectra of the complexes in various solvents in order of DN values.

Complexes	$ \sum_{\lambda_{\max}/nm} (\epsilon/M^{-1} cm^{-1}) $									
	DCM (0.0) ^b	MeNO ₂ (2.7)	ACN (14.1)	Acetone (17.0)	THF (20.0)	MeOH (23.5)	DMF (26.6)	DMSO (29.8)	Py (33.1)	HMPA (38.8)
I II ^a	569 (104) 572 (96)	558 (104) 554 (111)	631 (96) 584 (110)	590 (110) 585 (102)	595 (107) 594 (103)	602 (115) 594 (111)	615 (113) 610 (107)	625 (119) 616 (113)	656 (102) 646 (117)	635 (112)
 III	551 (93)	526 (101)	571 (105)	573 (94)	573 (98)	581 (101)	599 (95)	605 (104)	633 (119)	639 (90)

^a Results taken from Ref. [14].

^b Donor number of solvents.



Fig. 2. Absorption spectra of complexes in selected solvents. Absorption spectra in other solvents are omitted for clarity.

Thus, it can be reasonably assumed that an octahedral coordination geometry contributes to the solution molecular structure, making the copper(II), d⁹, complexes susceptible to the Jahn-Teller effect as manifested by splitting of the ligand-field transition.

Regression analyses of the band maxima of compounds I–III against the donor number of the solvents is represented in Fig. 4 and demonstrate good correlation and also proved the solvatochromic behavior of these complexes. The slope represents the sensitivity of the compounds and linearity of the λ_{max} values against donor number confirms the solvatochromic behavior of complexes. Deviations were also observed in this correlation indicative of the complex nature of the solute–solvent interaction. An obvious deviation is found in the solvent of pyridine and HMPA. As stated before, in strongly coordinating solvents the electronic structure becomes more similar to an octahedral instead of square planar structure. However, this deviation may be due to another factor, *i.e.* the field strength of the ligating solvents, the trend of which does not necessarily correlate with the DN trend for the different solvents.



Fig. 3. λ_{max} values of complexes **I–III** in various solvents in order of DN values. The symbols "a" to "j" represent: a = CH₂Cl₂, b = MeNO₂, c = CH₃CN, d = acetone, e = THF, f = MeOH, g = DMF, h = DMSO, I = py, j = HMPA.



Fig. 4. Dependence of the λ_{max} values of compounds I–III on the solvent donor number values.

Another deviation also observed in solvent of dichloromethane. The λ_{max} of the complexes in CH₂Cl₂ occur at longer wavelength than in nitromethane, although the donor number of CH₂Cl₂ (=0) is lower than that of nitromethane (=2.7). This anomaly is ascribed to the formation of ion pairs by mean of an axial coordination of ClO₄⁻ in CH₂Cl₂. As the relative dielectric constant of nitromethane is much higher value (28.5 for nitromethane versus 8.9 for CH₂Cl₂ in room temperature), this solvent facilitates the dissociation of cationic chelate [25].

4. Conclusion

In conclusion, the mixed-chelate copper(II) complexes are highly soluble in various organic solvents and represent solvatochromism. The complexes are almost non-conductive in dichloromethane indicating predominance of covalent interaction between copper(II) center and perchlorate anions, while the electronic absorption spectra suggest the likelihood of coordination taking place along an axis perpendicular to the CuN₂O₂ plane. In high donor power solvents donor-acceptor interactions induce tetragonal distortion of the CuN₂O₂ chromophore and the ligand field band maxima correlate linearly with DN of the solvents employed (positive solvatochromism). Solvatochromism studies of these complexes showed that presence of an electron-withdrawing group on the γ -position of the acetylacetonate chelate makes the copper ion electron-poor and favors the approach of solvent molecules along the z axis. In contrast, an electron-releasing group proceeds in reverse trend.

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