

Synthesis and Spectral Studies on Heteroleptic Chelated Copper (II) Complexes of Diamine and Acetylacetonate

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Abstract: The infrared and electronic absorption spectra of a series of new heteroleptic chelated copper (II) complexes $[\text{Cu}(\text{diamine})(\text{acac})]\text{X}$ that encompass *N,N'*-1,6-bis(2-bromophenyl)-2,5-diazahexane (diamine), acetylacetonate (acac) and ClO_4^- , BPh_4^- , PF_6^- and BF_4^- (X) were studied. The IR, electronic absorption spectra and the molar conductivity of the newly prepared complexes were presented and discussed. The molar conductivity in dichloromethane reveals a predominance of electrostatic interactions between $[\text{Cu}(\text{diamine})(\text{acac})]^+$ entity and anions, X⁻ that counterbalance the positive charge. The resulting complexes with local symmetry of CuO_2N_2 attain a square-coplanar structure and exhibit the tendency for axial ligation, which is enhanced when an electron-attracting substituent is attached to the phenyl ring of diamine moiety. The tendency for axial ligation is particularly fulfilled when suitable nucleophiles (solvents) with different 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.

Key words: Acetylacetonate; Copper(II) complexes; Diamine chelate; Heteroleptic chelate ; *N*-ligand; Solvatochromism

INTRODUCTION

Heteroleptic chelated complexes of copper (II) having the general formula $[\text{Cu}(\text{NN})(\text{OO})]^+$ are reported to have potentially useful solvatochromism properties [1-3]. In the above formula, (NN) stands for a diamine ligand and its derivatives, (OO) represents for acetylacetonate anion. The phenomenon of solvatochromism which refers to changes in electronic absorption spectra with solvent is one of the important topics in solution chemistry. The origin of solvatochromism occurrence in metal complexes are classified into two general types [4, 5]; in the first type, metal complexes in solution are interacted by solvent molecules in a direct fashion due to direct attachment of the solvent molecules onto metal center and in the second type, by indirect interactions between solvent molecules and ligands. Among the former whose color changes are due to those of d-d transitions, copper(II) complexes with a strong John-Teller effect can be anticipated to show simple and regular changes in their

electronic spectra according to the strength of interactions with solvent molecules at the axial sites. This behavior in the heteroleptic chelated copper (II) complexes has received more interest because they may be used as a Lewis acid-base color indicator [2, 6] and also utilize to develop optical sensor materials to monitor pollutant levels in the environment [7, 8]. In this regard extensive studies have been concentrated on the heteroleptic chelated complexes of copper (II) with acac and diamine derivatives (acac, stands for acetylacetonate ion) [9-15].

Recently, we prepared a series of heteroleptic chelate copper (II) complexes that are soluble almost in a large number of solvents and show solvatochromic property. Our study demonstrated that the ClO_4^- counter-ion is bound weakly above and below of the chelate plane in solution, the perchlorate ions are driven out by solvent molecules leading to their solvatochromism. In continuation of our study we wish to report the syntheses and the solvatochromic behavior of some of

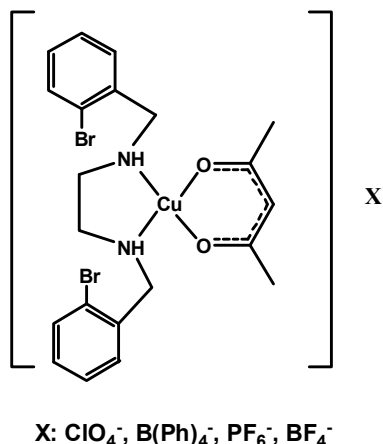


Fig. 1: The complexes under study

the heteroleptic chelated copper(II) complexes, that are shown in Fig. 1, with different counter ions ClO_4^- , BPh_4^- , PF_6^- and BF_4^- in order to explore the role of the counter ions on solvatochromism behavior and also to determine relative donor power of these anions in the complexes.

MATERIALS AND METHODS

The diamine compound and their heteroleptic chelate copper(II) complex with counter ion of perchlorate was prepared according to published procedure [16, 17]. 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. Infrared spectra (potassium bromide disk) were recorded using a Bruker FT-IR instrument. The electronic absorption spectra were measured using a Braic 2100 model UV-Vis spectrophotometer. 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.

General Procedure for Preparation of Copper Complexes
Tetraphenylborate Complex, II: The perchlorate heteroleptic chelated copper complex (0.660 g, 1 mmol) were dissolved in methanol (10 ml) and heated until dissolution occurred. A saturated aqueous solution of sodium tetraphenylborate (1.368 g, 4 mmol) in water was

then added. The crystal precipitated out almost immediately. The reaction mixture was let to stand overnight and was then filtered and the precipitate was washed with water several times. The yield was 56% (0.49 g). Selected IR data (ν/cm^{-1} KBr disk): 3250 (m, N-H str.), 3080, 2920 (m, C-H str.), 1595 (s, C-O str.) 1525 (s, C-O str.), 1340 (s), 760 (s, BPh_4 str.), 740 (s, BPh_4 str.), 580 (w, C-Br str.). Anal. calcd for $\text{C}_{45}\text{H}_{45}\text{N}_2\text{O}_2\text{CuBBr}_2$: C, 61.42; H, 5.15; N, 3.18; Cu, 7.22; Found: C, 61.10; H, 5.36; N, 3.48; Cu, 7.56%.

Hexafluorophosphate Complex, III: This complex was prepared with the similar procedure as described for tetraphenylborate complex except that NH_4PF_6 was used instead of sodium tetraphenylborate. The yield was 40%. Selected IR data (ν/cm^{-1} KBr disk): 3250 (m, N-H str.), 2920 (m, C-H str.), 1590 (s, C-O str.) 1520 (s, C-O str.), 1440 (s, C=C str.), 780 (s, P-F str.), 740 (s, BPh_4 str.), 550 (w, C-Br str.). Anal. calcd for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_2\text{CuPF}_6\text{BBr}_2$: C, 35.20; H, 3.52; N, 3.91; Cu, 8.87; Found: C, 35.55; H, 3.58; N, 3.98; Cu, 9.16%.

Tetrafluoroborate Complex, IV: This complex was prepared with the similar procedure as tetraphenylborate complex except that NH_4BF_4 was used in place of sodium tetraphenylborate. The yield was 36%. Selected IR data (ν/cm^{-1} KBr disk): 3220 (m, N-H str.), 2850 (m, C-H str.), 1600 (s, C-O str.) 1520 (s, C-O str.), 1400 (s, C=C str.), 1100 (s, B-F str.), 760 (s, B-F bend.), 540 (w, C-Br str.). Anal. calcd for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_2\text{BBr}_2\text{F}_4\text{Cu}$: C, 38.95; H, 3.89; N, 4.33; Cu, 9.81; Found: C, 38.61; H, 4.09; N, 4.36; Cu, 9.66%.

RESULTS AND DISCUSSION

Synthesis: The reaction of copper(II) perchlorate hexahydrate, *N,N'*-1,6-bis(2-bromophenyl)-2,5-diazahexane (diamine), acetylacetonate (acacH) and sodium carbonate with molar ratios of 1:1:1:0.5 resulted in formation of heteroleptic chelated complex of $[\text{Cu}(\text{diamine})(\text{acac})]\text{ClO}_4$. The substitution of perchlorate anion with anions of BPh_4^- , PF_6^- and BF_4^- resulted in formation of the corresponding complexes. The analytical dates indicate the formation of the desired complexes.

Infrared Spectra: Several bands appear in the IR spectra of heteroleptic chelated complexes in the region that are also observed, although with minor shifts, in the spectra of the free chelated ligands. The similarity among infrared spectra of the complexes might imply that all complexes are the same and the only differences are due to presence

Table 1: Molar conductivities data (Λ_m) of the complexes ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$, at 25°C)^a in different solvents.^b

Complex	CH ₂ Cl ₂	CH ₃ CN	EtOH	Acetone	DMF
[Cu(diamine)(acac)]ClO ₄	7	166	46	139	77
[Cu(diamine)(acac)]B(Ph) ₄	12	144	42	99	60
[Cu(diamine)(acac)]PF ₆	12	131	35	115	68
[Cu(diamine)(acac)]BF ₄	4	127	44	150	87
1:1 electrolytes	10-20	120-160	35-45	100-140	65-90

^a Concentration: ca. 1×10^{-3} M.

^b data for standard values taken from Ref Error! Bookmark not defined.

of different counter ions. Two intense absorption bands in the region around 1520 cm^{-1} in the complexes could be assigned to the C=C and C=O vibrational modes [18]. A vibrational band around 560 cm^{-1} observed in all complexes is associated to C-Br stretching of the diamine chelate. The N-H stretching vibration of the diamine ligands appear in the $3220\text{-}3250 \text{ cm}^{-1}$ region. The vibrational bands around 1040 cm^{-1} are corresponded to the stretching vibration of C-N bond and the bands around 1450 cm^{-1} are associated to the scissoring vibration of $-\text{CH}_2-$ groups [19]. Dependence on substitution of ClO_4^- by B(Ph)_4^- can be verified by disappearance of perchlorate bands at around 1097 and 638 cm^{-1} and appearance of the intense absorptions bands at 770 , 740 , 1510 and 1595 cm^{-1} which are corresponded to the phenyl group of tetraphenylborate ion [20]. Although, the first two absorption bands clearly perceived, the positioning of the vibrations of the acac group does not enable us to observe the last two absorptions in complex II. The existence of PF_6^- ion is exhibited by an intense and medium bands occurring at 640 and 560 cm^{-1} respectively, confirms the formation of complex III [21]. The presence of BF_4^- group is declared by two intense bands at around 1090 cm^{-1} and 1400 cm^{-1} which are attributed to the anti-symmetric stretching and anti-symmetric bending vibration modes, respectively [19]. The former band is split with a poorly defined maximum showing deformation from T_d symmetry.

Conductometric Data: Table 1 illustrates the molar conductivity values of complexes at room temperature in different solvents. The standard values of 1:1 electrolytes in the respective solvents are illustrated in the same table [22]. The results showed that in solvent of dichloromethane the values were much lower than that for 1:1 electrolyte when X is PF_6^- , BF_4^- and ClO_4^- . However, in other solvents all of the complexes are 1:1 electrolyte which indicates almost complete dissociation into X⁻ and the cationic complexes $[\text{Cu(L)(acac)}]^+$. Thus, it seems that an ion-pair formation (or anion coordination) might exist in some extent in CH_2Cl_2 . That means these 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 previous results [17]. However, the complexes of $[\text{Cu(diamine)(acac)]B(Ph)}_4$ almost completely dissociate in poor donor solvent of CH_2Cl_2 . As a result, in contrast with other counter-anions there is not any bond between copper ion and anion of B(Ph)_4^- . In case of $[\text{Cu(diamine)(acac)]B(Ph)}_4$ the conductance values are lower than the expected values due to low mobility of bulky anion of tetraphenylborate in the solution [20].

Solvatochromism: All the complexes are easily soluble in a wide range of organic solvents. The presence of a strong John-Teller effect on the Cu(II) ions made them good solvatochromic probes. The electronic absorption spectra of the complexes are characterized by a broad structureless band in the visible region attributed to the promotion of an electron in the low energy orbitals to the hole in $d_{x^2-y^2}$ orbital of the copper (II) ion (d^9). The visible spectral changes of these complexes in the selected solvents are illustrated in Fig. 2. The positions of the λ_{max} values of the complexes along with the molar absorptivities are collected in Table 2.

The electronic absorption spectra of complexes I-V were measured in solution state in some organic solvents with different donor number (DN). The donor number expresses a measure of coordinating ability of solvent on the standard of that of dichloromethane (DCM) or dichloroethane (DCE) [23]. Values of DN of the solvents used are as follows: DCM and DCE = 0.0; MeNO_2 = 2.7; MeCN = 14.1; acetone = 17.0; MeOH = 19.0; THF = 20.0; DMF = 26.6; DMSO = 29.8; Py = 33.1.

In solution the d-d band of all complexes moves to the red with the increase of the DN of the solvent (Table 2 and Fig. 2). As the results illustrate, the energy change on the absorption spectra of compounds is as large as 86-109 nm over the solvents studied. The greatest solvatochromic effect is displayed by complex

Table 2: Electronic absorption maxima of the complexes in various solvents: $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/M^{-1}\text{ cm}^{-1}$)

Solvent	Complex I	Complex II	Complex III	Complex IV
DCM	577(99)	563(100)	572(91)	563(93)
NM	563(88)	545(171)	569(74)	553(124)
AN	590(86)	585(75)	593(88)	591(128)
Ac	591(86)	578(119)	603(67)	591(188)
THF	610(92)	597(90)	608(53)	593(105)
MeOH	597(68)	594(132)	600(61)	599(129)
DMF	622(82)	613(115)	614(82)	618(83)
DMSO	627(79)	632(87)	625(72)	625(92)
Py	659(78)	654(70)	655(40)	660(74)

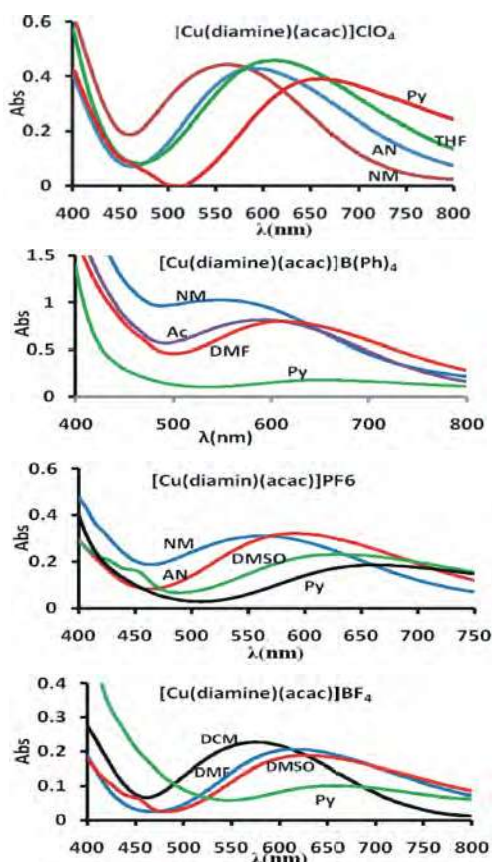


Fig. 2: Absorption spectra of the complexes in selected solvents. Absorption spectra in other solvents are omitted for clarity

[Cu(diamine)(acac)] BPh₄ (109 nm). This difference is associated with the fact that tetraphenylborate is a large and bulky anion in compared with ClO₄⁻, PF₆⁻, BF₄⁻ anions [24, 25] with lack of coordinating ability. Thus the solvent molecules can approach more easily to the axial sites of the complexes. This phenomenon causes the higher $\Delta\lambda_{\text{max}}$ values. It was also expected that the steric or electronic factors might affect the shift in the d-d band of the copper (II) heteroleptic chelated complexes [26] but as shown in Table 2 the absorption maxima of compounds

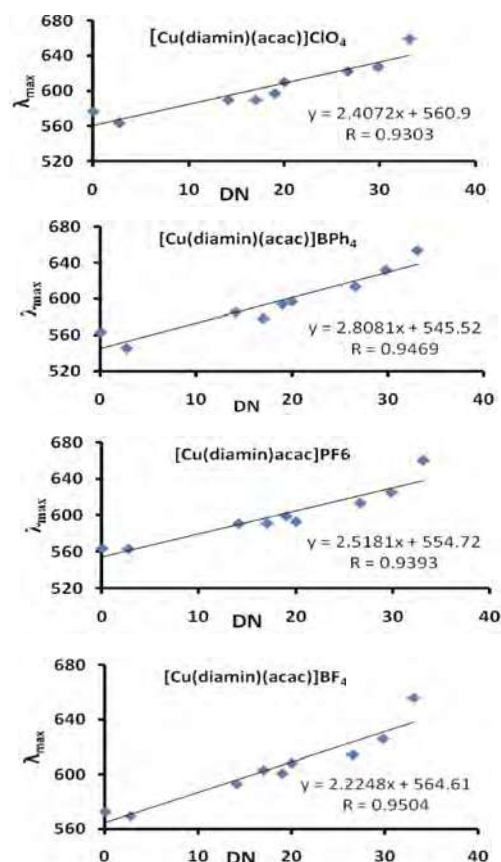


Fig. 3: Dependence of the λ_{max} values of complexes on the solvent DN values

I-IV with different substituents on the phenyl ring of diamine ligand were nearly similar to each other. This might suggest that varying the substituent attached to the phenyl ring could not influence the ligand field strength around the copper (II) center [27]. As a result, no direct correlation between the presence of electron-withdrawing groups were observed. This could be due to the far-off distance of substituent groups from the coordination center. This interpretation is confirmed with regard to X-ray crystallography reported before [18],

so that the solvatochromism behaviors of the mentioned complexes were independent to the nature of the substituent groups on the phenyl ring of the diamine ligand. The plots of the observed λ_{\max} values of the complexes versus the donor number of the solvents as shown in Fig. 3 demonstrated good correlation for all complexes.

The relative donor power of the anions can be investigated in low donor number solvents such as dichloromethane and nitromethane. As evident from Table 2 the relative donor power of anions X is in the following order.



CONCLUSION

New heteroleptic chelated copper (II) complexes with solvatochromic properties were prepared. The complexes showed a good correlation between their d-d absorption maxima in solution and the donor number of the solvent used (positive solvatochromism) due to coordination of solvent molecules with different donor power to the axial site of the copper (II) ion result in changing the geometry of the complexes from square planar to the octahedron. Among the complexes of [Cu(diamine)(acac)]X, complex 2 (X= Bph₄⁻) displayed highest $\Delta\lambda_{\max}$ value. Proving the fact that increasing the size of the counter ion X decreases the ion pair interaction between cation complex [Cu(diamine)(acac)]⁺ and X. Thus, solvent molecules facilitate the dissociation of the anion X from the cationic complex with coordinating to the axial sites of the complex.

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