Syntheses, Characterization and Solvatochromism Study of Heteroleptic Chelated Copper(II) Complexes Containing N,N- dibezyl Substituted Ethylenediamine and Acetylacetonate Ligands

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Abstract: A series of new heteroleptic chelated copper(II) complexes that encompass *N,N*-dibezyl substituted derivative of ethylenediamine (X-diamine) and acetylacetonate (acac) were prepared. The IR and electronic absorption spectra and the molar conductivity of the complexes are presented and discussed. The molar conductivity values of the complexes in different solvents reveals a predominance of electrostatic interactions between $[Cu(X\text{-diamine})(acac)]^+$ entity and tetraphenylborate anions 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 the ethylenediamine chelate. 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: Heteroleptic chelate, Copper(II) complexes, Solvatochromism, N-ligand; Diamine chelate, Acetylacetonate

1. Introduction

Solvatochromic materials, *i.e.* the materials which change their color with variation of solvents bear the promise for applications [1-3]. They may be purely organic [4,5], inorganic [6,7], organmetallic [8,9] or metal complexes [10,11]. Several applications have been envisioned to use the solvatochromic materials as a Lewis acid-base color indicator [12] and also utilizes to develop optical sensor materials to monitor pollutant levels in the environment [13,14]. Among these materials a series of metal complexes containing heteroleptic chelated ligands have been studied by many researchers [15].

These complexes with copper(II) metal ion showed gradual color change by variation of solvent due to a

strong Jahn–Teller effect. We and the others have proposed on the basis of X-ray single crystal analysis, absorption, emission, E. P. R spectroscopies and molar conductance measurements that the regular change of color which occurs by changing solvent is due to changing of the ligand field strength resulting from approaching the solvents molecules to the axial positions of the square planar of the copper(II) complex [15,16].

In some cases that the axial positions are occupied by water molecules or anions such as perchlorate, halide or pseudo halide substitution mechanism have been proposed for color change in the same species of these types of solvatochromic complexes [16].

The heteroleptic chelated complexes of copper(II) [Cu(diamine)(acac)]$^+$, where diamine chelates are ethane-1,2-diamine, and acac are acetylacetonate, and its N and/or C-alkyl substituted derivatives are well documented [17,18].

The steric and inductive effect of alkyl groups as well as the nature of the counter-ions make the chemistry of copper(II) heteroleptic chelated complexes very interesting. However, studies with diamines where the substituted group is a part of flexible ring are scarce. Recently, we reported novel heteroleptic chelated complexes of copper(II) with substituent in the γ–position of acetylacetonate and their solvatochromic property [17].

 The above report led us to pursue such a system using substituent on the diamine chelate. In this paper we report the syntheses, characterization and solvatochromic behavior of heteroleptic chelated copper(II) complexes [Cu(X-diamine)(acac)]BPh$_4$, shown in Scheme 1.
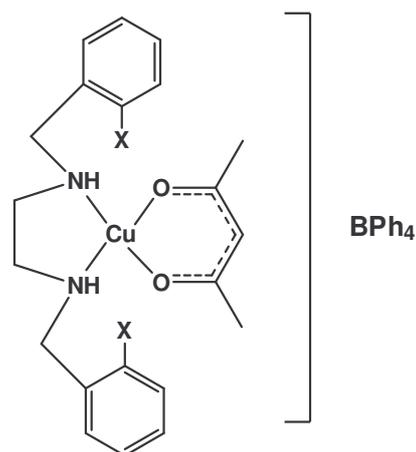
Scheme 1. The complexes under study

2. Experimental
2.1 General

The diamine compounds and their perchlorate heteroleptic chelated copper(II) complexes were prepared according to similar procedure [19,20]. 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 ^{o}C with a Jenway 400 conductance meter on 1.00 x 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 Braic2100 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.

2.1. General procedure for preparation of copper complexes

The perchlorate heteroleptic chelated copper(II) complexes (1 mmol) were dissolved in methanol (10 mL) and heated until dissolution occurred. A saturated aqueous solution of sodium tetraphenylborate (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.

[Cu(CH$_3$-diamine)(acac)]BPh$_4$.

The yield was 69% (0.52 g). Selected IR data (ν/cm^{-1} KBr disk): 3240 (m, N-H str.), 3080, (m, C-H str.), 2930, 1590 (s, C-O str.) 1525 (s, C-C str.), 1590 (s), 750 (s, BPh$_4$ str.), 720 (s, BPh$_4$ str.). Anal. calcd for C$_{47}$H$_{51}$N$_2$O$_2$CuB (MW = 750.28 g. mol^{-1}): C, 75.24; H, 6.85; N, 3.73; Cu, 8.47; Found: C, 75.60; H, 6.36; N, 3.48; Cu, 8.56 %.

[Cu(H-diamine)(acac)]BPh$_4$.

The yield was 57% (0.41 g). Selected IR data (ν/cm^{-1} KBr disk): 3240 (m, N-H str.), 3075 (m, C-H str.), 2940, 1590 (s, C-O str.) 1525 (s, C-O str.), 1390 (s), 760 (s, BPh$_4$ str.), 720 (s, BPh$_4$ str.). Anal. calcd for C$_{45}$H$_{47}$N$_2$O$_2$CuB (MW = 722.22 g. mol^{-1}): C, 74.84; H, 6.56; N, 3.88; Cu, 8.80; Found: C, 75.10; H, 6.36; N, 3.61; Cu, 8.63 %.

[Cu(Br-diamine)(acac)]BPh$_4$.

The yield was 56% (0.49 g). Selected IR data (ν/cm^{-1} KBr disk): 3250 (m, N-H str.), 3080 (m, C-H str.), 2920, 1595 (s, C-O str.) 1525 (s, C-O str.), 1340 (s), 758 (s, BPh$_4$ str.), 636 (s, BPh$_4$ str.), 580 (w, C-Br str.). Anal. calcd for C$_{45}$H$_{45}$N$_2$O$_2$CuBBr$_2$ (MW = 880.02 g. mol^{-1}): 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 %.

[Cu(Cl-diamine)(acac)]BPh$_4$.

The yield was 59% (0.47 g). Selected IR data (ν/cm^{-1} KBr disk): 3240 (m, N-H str.), 3010 (m, C-H str.), 2950, 1590 (s, C-O str.) 1520 (s, C-O str.), 1390 (s), 780 (s, BPh$_4$ str.), 740 (s, BPh$_4$ str.), 570 (w, C-Cl str.). Anal. calcd for C$_{45}$H$_{45}$N$_2$O$_2$CuBCl$_2$ (MW = 789.22 g. mol^{-1}): C, 68.32; H, 5.73; N, 3.54; Cu, 8.03; Found: C, 67.93; H, 6.01; N, 3.81; Cu, 8.23 %.

[Cu(F-diamine)(acac)]BPh$_4$.

The yield was 56% (0.42 g). Selected IR data (ν/cm^{-1} KBr disk): 3250 (m, N-H str.), 3080 (m, C-H str.), 2920, 1595 (s, C-O str.) 1525 (s, C-O str.), 1340 (s), 758 (s, BPh$_4$ str.), 680 (s, BPh$_4$ str.), 638 (w, C-F str.). Anal. calcd for C$_{45}$H$_{45}$N$_2$O$_2$CuBF$_2$ (MW = 758.20 g. mol^{-1}): C, 71.28; H, 5.98; N, 3.69; Cu, 8.38; Found: C, 70.87; H, 6.28; N, 3.89; Cu, 8.50 %.

3. Result and discussion
3.1. Synthesis

Several bands appear in the IR spectrum of heteroleptic chelated complexes in the region that are also observed, although with minor shifts, in the spectra of the free ligands.

The absorption band around 1050 cm^{-1} is probably due to the stretching vibration of carbon-nitrogen bond. [21]. The strong bands at around 1400 cm^{-1} are very likely associated with the scissoring vibration of -CH$_2$- groups [3].

The band at around 760 cm^{-1} that in the spectra of free diamine ligand appears broader and is split in

two in region of 730-790 cm^{-1} may be due to the rocking vibration of CH$_2$ groups [3]. The stretching vibrations of N-CH$_2$ groups in the free ligands, and the well-known bands in the region 2850 ± 100 cm^{-1} 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 their intensity, become shifted to the higher frequencies and combine with other C-H absorption bands. Dependence on coordination is also exhibited by the intense and narrow band occurring at 3245 ± 5 cm^{-1} which is associated with N-H vibration and is observed at around 3400 cm^{-1} 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 acetylacetone where

observed in around 1700 cm^{-1} was shifted to the lower wave number in complexes spectra indicating the coordination of acetylacetone to the copper ion.

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 [22].

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 the complexes.

3.3. 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 [23]. The results show that the conductivity values in complexes are less than standard value for 1:1 electrolytes due to the low ionic mobility of BPh$_4^-$ anion [23].

Table 1. Molar conductivities data (Λ_m) of the complexes (Ω^{-1} cm^2 mol^{-1}, at 25 ^{o}C)[a] in different solvents.[b]

Complex	CH$_2$Cl$_2$	CH$_3$CN	EtOH	Acetone	DMF
[Cu(CH$_3$-diamine)(acac)]B(Ph)$_4$	4	90	29	89	46
[Cu(H-diamine)(acac)]B(Ph)$_4$	7	101	15	79	47
[Cu(Br-diamine)(acac)]B(Ph)$_4$	8	99	22	83	59
[Cu(Cl-diamine)(acac)]B(Ph)$_4$	4	92	31	91	41
Cu(F-diamine)(acac)]B(Ph)$_4$	6	96	25	88	56
1:1 electrolytes	10-20	120-160	35-45	100-140	65-90

[a.] Concentration: *ca.*1 x 10^{-3} M.

[b.] data for standard values taken from Ref **Error! Bookmark not defined.**

3.4. 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. 1.
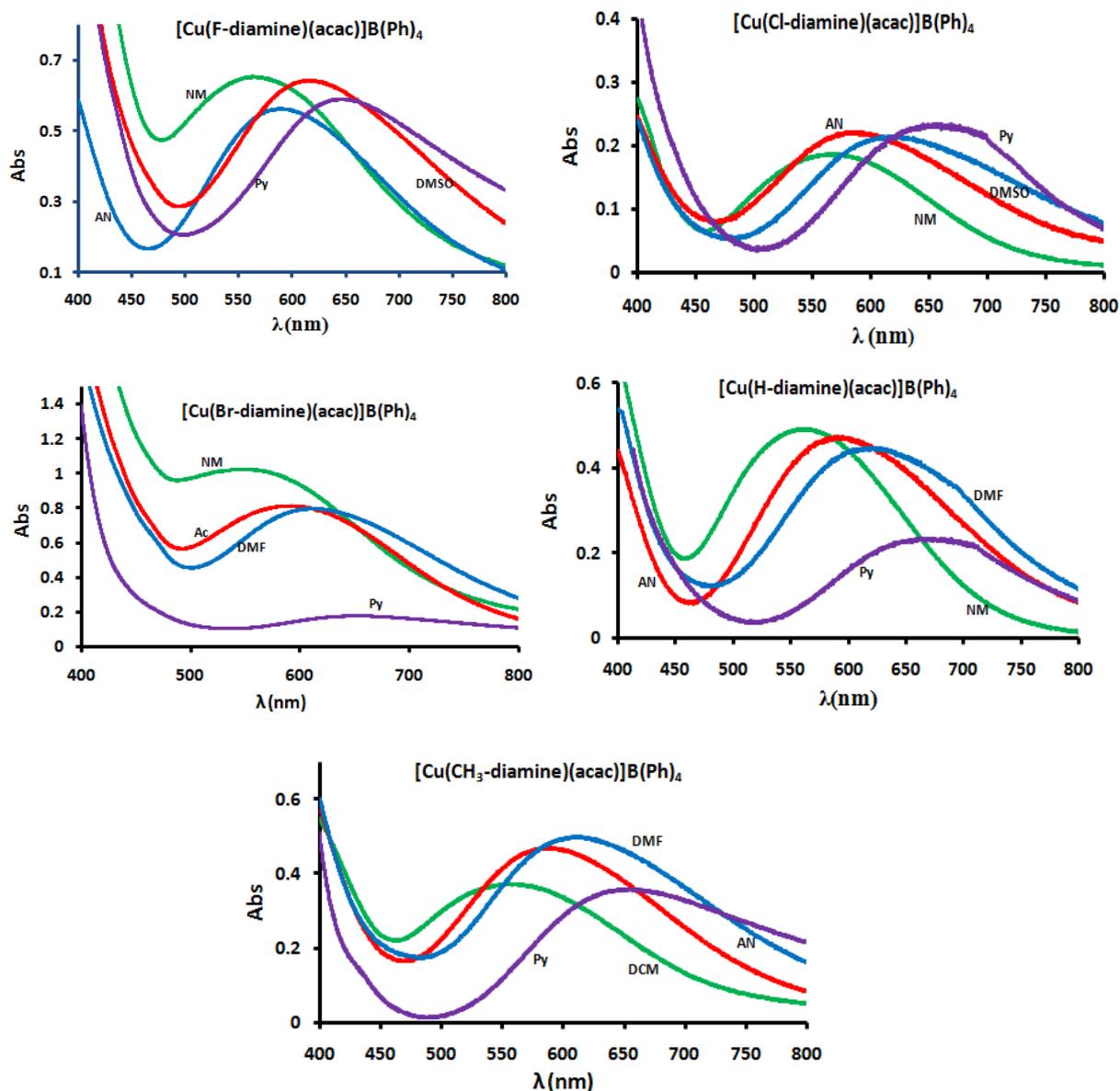
Figure 1. Absorption spectra of complexes in selected solvents. Absorption spectra in other solvents are omitted for clarity.

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 the complexes 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) [24].

Table 2. Electronic absorption maxima of the complexes, Cu(X-diamine)(acac)]B(Ph)$_4$ in various solvents: λ_{max}/nm (ε/M^{-1}cm^{-1})

Solvent	X = CH$_3$	X = H	X = Br	X = Cl	X = F
DCM	601(81)	588(58)	563(100)	553(114)	540(92)
NM	605(107)	589(101)	565(145)	554(90)	562(121)
AN	610(93)	594(109)	585(88)	589(103)	570(112)
Ac	615(80)	597(90)	588(119)	590(77)	573(83)
MeOH	620(80)	596(72)	590(132)	597(90)	577(195)
THF	618(94)	608(109)	597(90)	602(90)	581(133)
DMF	627(99)	618(179)	613(115)	609(77)	611(149)
DMSO	631(61)	623(172)	617(79)	616(101)	618(128)
Py	650(71)	657(102)	654(70)	656(108)	647(118)
$\Delta\lambda$	49	69	94	103	107

Values of DN of the solvents used are as follows: DCM and DCE = 0.0; MeNO$_2$ (NM) = 2.7; MeCN (AN) = 14.1; acetone (AC) = 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 1). In the series the shifts induced by a certain solvent depends upon the electronic properties of substituent group attached in the phenyl ring of the diamine chelate which controls the magnitude of the in-plane 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(X-diamine)(acac)]$^+$. Introducing an electron-attracting (X = F, Cl and Br) or electron-releasing (X = CH$_3$) substituent on the phenyl ring of the diamine chelate alters the Lewis acidity of CuN$_2$O$_2$ chromophore and consequently, its equatorial ligand field strength.
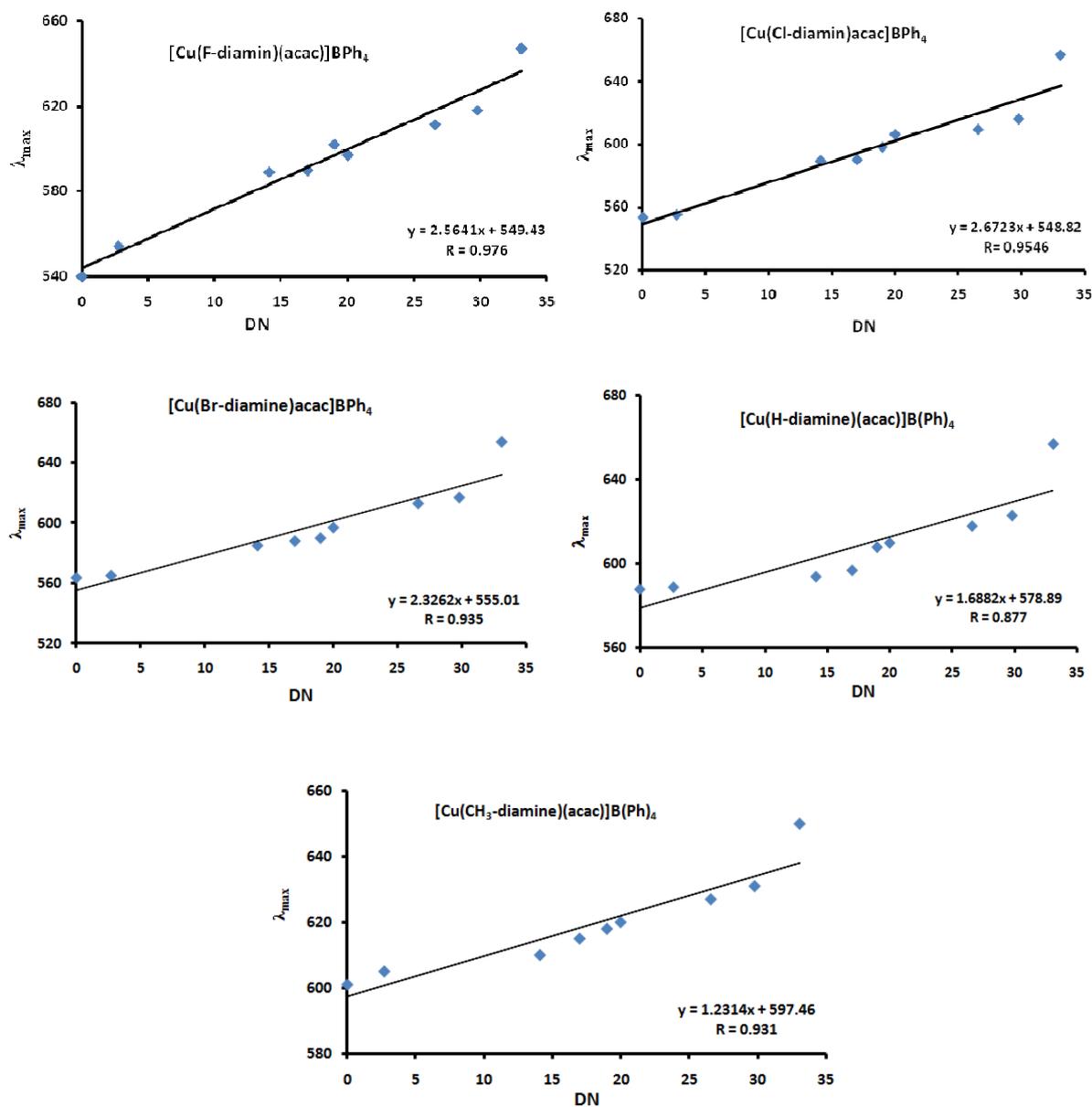
Figure 2. Dependence of the λ_{max} values of complexes on the solvent DN values.

In other words, presence of an electron withdrawing group 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. 1 and Table 2 the λ_{max} values in one particular solvent decreases in the following order of diamine chelate.

F-diamine > Cl-diamine > Br-diamine > H-diamine > CH$_3$-diamine

As the results illustrate, the energy change on the absorption spectra of compounds is as large as 49-107 nm over the solvents studied. The greatest solvatochromic effect is displayed by complex [Cu(F-diamine)(acac)]BPh$_4$ and the least belongs to [Cu(CH$_3$-diamine)(acac)]BPh$_4$.

Regression analyses of the band maxima of the complexes against the donor number of the solvents are represented in Fig. 2 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. As stated before [25], 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.

4. Conclusion

New heteroleptic chelated copper (II) complexes were prepared and characterized. The complexes are highly soluble in various organic solvents and represent solvatochromism. The complexes are almost conductive in all solvent investigated even in dichloromethane indicating predominance of ionic interaction between copper(II) center and tetraphenylborate anions, also the electronic

absorption spectra suggest the likelihood of coordination taking place along an axis perpendicular to the CuN$_2$O$_2$ plane. In high donor power solvents donor-acceptor interactions induce tetragonal distortion of the CuN$_2$O$_2$ 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 phenyl ring of the ethylenediamine 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.

5. Acknowledgements

6. References

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