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Spectroscopic studies on Solvatochromism of mixed-chelate copper(II) complexes using MLR technique

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ABSTRACT

Mixed-chelate copper(II) complexes with a general formula [Cu(acac)(diamine)]X where acac = acetylacetonate ion, diamine = N,N-dimethyl,N'-benzyl-1,2-diaminoethane and X = BPh₄⁻, PF₆⁻, ClO₄⁻ and BF₄⁻ have been prepared. The complexes were characterized on the basis of elemental analysis, molar conductance, UV-vis and IR spectroscopies. The complexes are solvatochromic and their solvatochromism were investigated by visible spectroscopy. All complexes demonstrated the positive solvatochromism and among the complexes [Cu(acac)(diamine)]BPh₄·H₂O showed the highest $\Delta \nu_{max}$ value. To explore the mechanism of interaction between solvent molecules and the complexes, different solvent parameters such as DN, AN, α and β using multiple linear regression (MLR) method were employed. The statistical results suggested that the DN parameter of the solvent plays a dominate contribution to the shift of the d–d absorption band of the complexes.

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1. Introduction

A great number of studies have been dedicated to solvatochromism of metal complexes because of their potential ability to act as a Lewis acid-base color indicator [1], molecular switch [2-5], pollutant sensor [6,7] and imaging device [8]. Solvatochromism is defined as the influence of solvent on the electronic absorption and emission spectra of molecules. Among the solvatochromic metal complexes the mixed-chelate copper(II) complexes have received great attention due to presence of a strong Jahn-Teller effect which resulted in a simple and regular changes in their electronic spectra according to the strength of interactions with solvent molecules at the axial sites[9]. There are different solvent parameters to describe the interaction between solvent and the metal complexes such as Gutmann's DN (donor number is a measure of coordinating ability of solvents on the standard of dichloromethane) [10], Mayer and Gutmann's AN (the electron acceptor property of a solvent) [11], Dimroth and Reichardt's $E_T(30)$ (a measure of the ionization power of a solvent) [12], Kosower's Z (an empirical measure of solvent polarity), Kamlet-Taft's α (hydrogen bond donation of a solvent), β (hydrogen bond acceptance of a solvent), and π^* (polarity/polarisability parameter of a solvent) [13-17]. In many cases it was found that, the shift in the electronic absorption spectra of the complexes depends on more than one solvent parameter. The correlation between the spectral shifts and solvent parameters can be examined by computational methods [18].

In this report, we prepared four mixed-chelate copper(II) complexes shown in Scheme 1. The complexes are soluble almost in a large number of solvents and show solvatochromism. The mechanism of interaction between solvents and the complexes and effect of counter ions on the solvatochromism of the complexes are investigated.

2. Experimental

2.1. Materials and methods

The preparation of the ligand N,N-dimethyl,N'-benzyl-1,2diaminoethane (diamine) was carried out as reported earlier [10]. All the chemicals used were reagent grade and solvents for spectroscopic and conductivity measurements were "spectro-grade" used without further purification. *Caution: perchlorate salts are potentially explosive and should be handled with appropriate care.*

Infrared spectra measurements were carried out using KBr disk on a Bruker FT-IR spectrometer in the range 450–4000 cm⁻¹. Conductivity measurements were performed with a Jenway 400 instrument at 25 °C. UV–vis spectra of the solutions were obtained with a Braic 2100 spectrophotometer using 1 cm quartz cells. Elemental analyses (C, H, and N) were performed using a LECO 600 elemental analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer. The following solvents were used for solvatochromic study: dichloromethane (DCM), nitromethane (NM), nitrobenzene (NB),

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Scheme 1. The structure of the complexes.

benzonitrile (BN), acetonitrile (AN), propionitrile (PN), acetone (Ac), tetrahydrofuran (THF), ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pyridine (Py) and hexamethylphosphorictriamide (HMPA).

2.2. Syntheses

2.2.1. Preparation of [Cu(acac)(diamine)]BPh₄·H₂O, 1

A solution of containing Cu(OAc)₂·H₂O (1.2 g, 6 mmol) and Na₂CO₃ anhydrous (0.3 g, 3 mmol) in absolute ethanol (45 ml) was added to the mixture of N,N-dimethyl,N'-benzyl-1,2-diaminoethane (1.0 g, 6 mmol) and acetylacetone (0.62 ml, 6 mmol). The resultant suspension was stirred for 2 h, and then was filtered to remove [Cu(acac)₂] by-product. A saturated solution of NaBPh₄ in absolute ethanol was then added to the resultant clear blue solution. After concentration of the solution at room temperature, the blue crystals were collected with filtration and dried in vacue. The yield was 58%. Selected IR data (ν/cm^{-1} KBr disk): 3525 (m, O–H str.), 3217 (m, N–H str), 1578 (s, C=O str.), 1521 (s, C=C str.), 735, 706 (s, C–H bend.). Anal. calcd. for C₄₀H₄₇N₂BO₃Cu: C, 70.84; H, 6.99; N, 4.13; Cu, 9.37; found: C, 70.80; H, 7.02; N, 4.18, Cu, 9.33%.

2.2.2. Preparation of $[Cu(acac)(diamine)]PF_6 H_2O, 2$

This complex was prepared with the same procedure as complex **1**, except that using NaPF₆ instead of NaBPh₄ (*note*: this compound is hygroscopic and should be kept in a dessicator). The yield was 32%. Selected IR data (ν/cm^{-1} KBr disk): 3649 (m, O–H str.), 3293 (m, N–H str.), 1583 (s, C=O str.), 1528 (s, C=C str.), 854 (s, P–F str.), 564 (m, P–F bend.). Anal. calcd. for C₁₆H₂₇N₂O₃PF₆ Cu: C, 38.14; H, 5.40; N, 5.56; Cu, 12.61 found: C, 38.64; H, 5.96; N, 5.02; Cu, 12.39%.

2.2.3. Preparation of [Cu(acac)(diamine)]ClO4, 3

To the solution of N,N-dimethyl,N'-benzyl-1,2-diaminoethane (1g, 6 mmol), acetylacetone (0.62 ml, 6 mmol), Na₂CO₃ (0.3 g, 3 mmol) in ethanol (20 ml) was slowly added Cu(ClO₄)₂·6H₂O (2.2 g, 6 mmol) in water (20 ml). After 15 min the by-product of [Cu(acac)₂] was separated by filtration. The midnight blue crystals were obtained from the resultant clear blue solution after concentration at room temperature. The yield was 76%. Selected IR data (ν /cm⁻¹ KBr disk): 3247 (m, N–H str.), 1587 (s, C=O str.), 1520 (s, C=C str.), 1091 (s, Cl–O str.), 625 (m, Cl–O bend.). Anal. calcd. for C₁₆H₂₅N₂O₆ClCu: C, 43.37; H, 5.72; N, 6.36; Cu, 14.43; found: C, 43.33; H, 5.48; N, 6.28; Cu, 14.38%.

2.2.4. Preparation of [Cu(acac)(diamine)]BF₄, 4

The same procedure as **1** was used for preparation of compound **4** except that using methanol as solvent and a saturated solution of NaBF₄ in water instead of NaBPh₄. The violet crystals were obtained with yield of 69%. Selected IR data (ν/cm^{-1} KBr disk): 3268 (m, N–H str), 1588 (s, C=O str.), 1520 (s, C=C str.), 1083, 1038 (s, B–F str.), 740, 710 (s, C–H bend.). Anal. calcd. for C₁₆H₂₅N₂BF₄O₂Cu: C, 44.93; H, 5.89; N, 6.55; Cu, 14.89; found: C, 44.88; H, 5.93; N, 6.57; Cu, 14.86%.

2.3. MLR analysis

All the absorption maxima reported were taken from experimental curves of the d–d transition of the complexes. Multivariate statistical methods have been used in the classification and selection of solvents. The empirical parameters of the solvent polarity were used as basic data sets. These parameters can be obtained directly from literature [19–21]. The extraction of the chemical information contained in such a data set can be carried out by statistical method of Multiple Linear Regression analysis (MLR). In this method, a dependent variable *Y* is described in terms of a series of explanatory variables X_1, \ldots, X_n , as given in Eq. (1):

$$Y = Y_0 + a_1 X_1 + a_2 X_2 + \dots + a_n X_n \tag{1}$$

It is assumed that all the explanatory variables are independent of each other and truly additive as well as relevant to the problem under study [22,23]. Y is the value of a solvent dependent physicochemical property (ν_{max} in this study) in a given solvent and Y_0 is the statistical quantity corresponding to the value of this property in the gas phase or in an inert solvent. X_1, X_2, \ldots X_n represent independent but complementary solvent parameters, which account for the different solute/solvent interaction mechanisms. a_1, a_2, \ldots, a_n are the regression coefficients describing the sensitivity of the property Y to the different solute/solvent interaction mechanisms. The postulate is that the solvent effect on a solute property Y can be represented as a linear function of some independent but complementary parameters describing the Lewis acidity and basicity of a given solvent. The AN and α , values are chosen as a measure of Lewis acidity. In addition, Gutmann's donor number DN and β were selected as a measure of solvent basicity [24–28]. In this approach, the Backward and Enter procedure were used for selection of the most relevant variables. A final set of selected equations was examined for stability and validity through a variety of statistical methods. The choice of a suitable equation for further consideration was made by using four criteria, namely, multiple correlation coefficient (R), standard error (S.E.), F-statistic and the number of variables (n) in the model. The best multiple linear regression model is one that has high R and F-values, low standard error, the least number of variables and high prediction ability [29]. In Parameter selection, variables with small variance t (not significant at the 5% level) were then removed. "t" value is the solvent-independent coefficients divided by S.E. To determine the relative significance of the solvent parameters, the regression coefficients are described in terms of percentage contribution value. Eq. (2) could be statistically qualified into percentage contribution factor $P(X_i)$. To attain this, the regression coefficients, which emerge from multiple regression equations are normalized to numerical range 0–1 [14]. Hence, the percentage contribution $P(X_i)$ of a solvent parameter in multiple regression is calculated [30].

$$P(X_i) = \frac{100|a_i|}{\sum_{i=1}^n |a_i|}$$
(2)

A comparison of the relative importance of the solvent property can easily be defined using $P(X_i)$, which show a good agreement between various system under study.

Table 1	1
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Molar conductivity data (Λ_m) of the complexes (Ω^{-1} cm² mol⁻¹, at 25 °C) in different solvents.

Complexes	DCM	NM	NB	AN	Ac	MeOH
1	7.48	51.45	16.31	93.02	83.99	53.54
2	5.6	83.13	25	133.19	133	84.1
3	4.42	87.26	21.71	142.65	133	80
4	4.79	80.14	20.2	134.5	120.18	86.7
1:1 electrolytes	10-20	75–95	20-30	120-160	100-140	80-115

Table 2

Electronic spectra of the complexes in various solvents: $\nu_{max}/10^3 \text{ cm}^{-1} (\epsilon/M^{-1} \text{ cm}^{-1})$ and their solvent parameter values.

Solvent	DN	AN	β	α	Complex 1	Complex 2	Complex 3	Complex 4
DCM	0.0	20.40	0.10	0.13	18.71(107)	18.35(91)	17.83(101)	18.08(116)
NM	2.7	20.50	0.06	0.22	18.26(107)	17.83(101)	18.15(110)	17.33(106)
NB	4.4	14.80	0.30	0.00	17.82(103)	17.42(92)	17.95(106)	18.21(123)
BN	11.9	15.50	0.37	0.00	17.36(105)	16.81(108)	17.39(100)	17.33(103)
AN	14.1	18.90	0.40	0.19	17.17(119)	16.67(105)	17.27(115)	17.15(119)
PN	16.1	16.00	0.39	0.00	17.30(120)	16.84(106)	17.04(121)	17.09(115)
Ac	17.0	12.50	0.43	0.08	17.31(103)	16.75(102)	17.15(108)	16.98(113)
THF	20.0	8.00	0.55	0.00	17.19(110)	17.21(99)	17.33(111)	17.27(109)
EtOH	22.9	37.10	0.75	0.86	16.99(106)	16.37(116)	16.58(111)	16.64(118)
MeOH	23.3	41.30	0.66	0.98	16.80(112)	16.36(109)	16.86(113)	16.81(122)
DMF	26.6	16.00	0.69	0.00	16.45(105)	16.00(108)	16.26(103)	16.42(110)
DMSO	29.8	19.30	0.76	0.00	16.09(115)	15.90(111)	16.26(124)	16.16(118)
Ру	33.1	14.20	0.64	0.00	15.57(110)	15.46(115)	15.50(106)	15.48(119)
HMPA	38.8	10.86	1.05	0.00	15.38(117)	15.36(124)	15.31(119)	15.50(120)

The solvent effect on the absorption spectra of four copper(II) complexes were recorded in the range of 12,000–25,000 cm⁻¹ using visible spectroscopy. Thus four equations were obtained for the copper(II) complexes **1–4** by applying multiple linear regression (MLR) method using SPSS software [31]. The role of the solvatochromic parameters, such as α , β , DN and AN in the above equations have been studied to investigate the mechanism of the interactions between complexes and solvents [18,32,33].

3. Results and Discussion

The complexes **1**, **2** and **4** were prepared by mixing of $Cu(OAc)_2 \cdot H_2O$, diamine, acetylacetone and Na_2CO_3 with molar ratio of 1:1:1:0.5, respectively in absolute ethanol or methanol and then addition of a saturated solution of appropriate counter ion salt. However, complex **3** was synthesized with direct use of $Cu(ClO_4) \cdot 6H_2O$ instead of $Cu(OAc)_2 \cdot H_2O$ in an ethanol–water mixture. The undesired by-product of $[Cu(acac)_2]$ was formed during the preparation of the complexes which was isolated and then separated simply by filtration. Analytical data of the obtained complexes indicated the formation of the desired mixed-chelate copper(II) complexes. The establishment of the purity of compound **2** to an acceptable level was hindered by hygroscopic nature of compound.

3.1. IR spectra

Formation of the mixed-chelate copper(II) complexes can be concluded from IR spectroscopy. The observed bands can be categorized into those corresponded to the ligands, counter ions and also the bonds formed between copper(II) and coordinating sites of the ligands [1]. The similarity among the infrared spectra of the complexes might imply that the structures of all complexes are

Table 3	
Selected models of backward MLR method and related values of F. R. S.E. and	Δv_{max}

the same and the only differences are due to presence of different counter ions. Two intense absorption bands in the region around 1520–1585 cm^{-1} in the complexes could be assigned to the C=C and C=O vibrational modes [34–37]. The N-H stretching vibration of the diamine ligand appears in the 3200 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 -CH₂- groups [38]. The strong bands around 1380 cm⁻¹ are associated to the bending vibrations of CH_3 groups. The two strong bands at 735 and 706 cm⁻¹ in complex 1 are corresponded to the phenyl group of the tetraphenylborate ion [39]. These two bands also appear in other complexes with low intensity due to the presence of phenyl group in the diamine ligand. The vibrational bands at 854 and 564 cm⁻¹ which are characteristic of PF₆⁻ anion confirms the formation of complex **2** [35]. Complexes **1** and **2** also show sharp bands around 3550 cm⁻¹ region that are associated to the presence of water molecule in the complexes [40]. The presence of ClO_4^- ions in complex **3** is confirmed by two intense bands at 1091 and 625 cm⁻¹ which are related to the antisymmetric stretching and anti-symmetric bending vibration modes of this group [38]. A strong broad band in the 1083–1038 cm⁻¹ region in complex **4** approves the presence of BF_4^- anion in the complex [35].

3.2. Conductometric data

Table 1 shows the molar conductivity values of complexes **1–4** and the standard values for 1:1 electrolytes in different solvents [41]. The results exhibited that the complexes are 1:1 electrolyte in all solvents except in solvent of dichloromethane. However, the results reveal that in solvent of dichloromethane the conductance values for all complexes are much lower than those expected for

Complexes	Equations	F	R	S.E.	$\Delta v_{\rm max}$
1	$v_{\rm max}/10^3 = -0.079 {\rm DN}_{\rm solv} + 18.502$	231.17	0.97	0.21	3326
2	$v_{\rm max}/10^3 = -0.071 \rm{DN}_{\rm solv} + 17.979$	115.77	0.95	0.27	2988
3	$v_{\rm max}/10^3 = -0.071 \rm{DN}_{\rm solv} + 18.251$	141.57	0.97	0.25	2835
4	$v_{\rm max}/10^3 = -0.066 {\rm DN}_{\rm solv} + 18.123$	89.55	0.94	0.29	2736

Table 4	
$P(X_i)$ values of complexes 1	-4.

	Complexes				
	1	2	3	4	
P(DN)	73.12%	69.72%	66.14%	59.83%	
P(AN)	12.2%	19.89%	16.50%	6.50%	
$P(\beta)$	9.06%	10.33%	13.09%	31.66%	
$P(\alpha)$	5.60%	0.045%	2.45%	1.98%	

1:1 electrolytes. Thus, it seems that an ion-pair formation (or anion coordination) might exist in some extent in dichloromethane. Additionally, the conductivity values in complex **1** are less than standard value for 1:1 electrolytes due to the low ionic mobility of BPh₄⁻ anion [41]. These results demonstrate the existence of weak interactions between the copper centers and counter ions that are driven out by high polar solvent molecules, which leads to 1:1 electrolytes [42,43] as well as solvatochromism.

3.3. Solvatochromism

The complexes **1–4** are soluble in a wide range of organic solvents and demonstrate solvatochromic properties. The electronic absorption spectra of the mixed-chelate complexes are characterized by a broad structureless band in the visible region attributed to the d–d transition of the copper(II) ions. As the electron configuration of copper(II) ion is d⁹, the broad structureless absorption band is associated to the transition of the electron from the lower energy orbitals to the hole in $d_{x^2-y^2}$ orbital. The visible spectral changes of these complexes in some selected solvents are illustrated in Fig. 1.

All of the complexes show the solvatochromic behavior and the shifts induced in certain solvents depends upon the nature of the counter ions. The position of the v_{max} of the complexes along with the molar absorptivity and their respective solvent parameter values are collected in Table 2.

To explore the solvent effects on the absorption spectra of the complexes, the absorption frequencies (ν_{max}) were correlated with the solvatochromic Eq. (1). Hence, The frequencies of the d–d absorption transition band (ν_{max}) of each complexes in various solvents with their own solvent parameters shown in Table 2 were offered in Eq. (3) one by one to the statistical computer program, being accepted, rejected, or exchanged until certain statistical criteria are met. The solvent parameters used include Gutmann's donor DN and acceptor numbers AN, electron pair donating ability β and hydrogen bonding ability α .

$$v_{\max} = v_{\max}^{\circ} + a DN + b AN + c \beta + d \alpha$$
(3)

The results obtained from the correlation of the absorption frequencies with the solvent parameters are illustrated in Table 3. The data in Table 3 show that dominate solvent effect in all complexes is DN and contribution of the other solvent parameters were rejected based on the statistical criteria explained in the experimental section.

To determine the relative contribution percentage of DN and other parameters on the shift of the ν_{max} values an Enter MLR method was also applied. Thus, the DN and AN parameters were normalized first using Marcus method [14]. The resulting normalized parameters values along with α and β parameter were then offered in Eq. (2) [30,33]. The calculated results are presented in Table 4.

The results again confirm the dominate contribution of DN parameter in the solvatochromism of the complexes. It is valuable to note that although the percentage of β parameter in Table 4 is 9–32% its contribution in solvatochromism is discarded as a result of its high Sig. value (0.026–0.768, this value should be less than 0.005 to be accepted [44]).





A cross-validation methodology was also carried out for choosing prediction power of the proposed model for all complexes. The cross-validation methodology is essential since a model with good statistics values necessarily do not have a good prediction potential. Three cross-validation parameters, calculated for the proposed model [45], are presented in Table 5. The parameters in Table 5 are defined as: PRESS, as the predictive residual error sum of squares, PRESS = $\sum (Y_{pred} - Y_{exp})^2$; SSY as the total sum of squares of deviation of the experimental values from their means, SSY = $\sum (Y_{exp} - Y_{mean})^2$ and Q^2 as the cross validation squared coefficient, $Q^2 = 1 - PRESS/SSY$, where Y_{pred} is the predicted, Y_{exp} is the experimental, and Y_{mean} is the mean values of the target properties (ν_{max}).

Table 5

The quality of the obtained models by means of Q^2 , PRESS and PRESS/SSY and predictive correlation coefficient (R_{nre}).

Compound	Q ²	PRESS	PRESS/SSY
1	0.950 $ u_{\rm max}$ experiment	0.56 al = $1.004\nu_{max}$ predicted $R_{pre} = 0.975$	0.049 0.077
2	0.91 $ u_{\rm max}$ experiment	0.89 al = 0.993 $\nu_{\rm max}$ predicted $R_{\rm pre}$ = 0.952	0.093 +0.136
3	0.92 $v_{\rm max}$ experiment	0.75 al = 1.009 v_{max} predicted $R_{pre} = 0.961$	0.078 0.164
4	0.88 $v_{\rm max}$ experiment	1.01 al = 1.004 ν_{max} predicted $R_{pre} = 0.939$	0.117 0.068

As the results showed in Table 5, good cross-validation Q^2 values were obtained ($Q^2 > 0.75$; $Q^2 = 0.88 - 0.95$). PRESS is an important cross-validation parameter accounting for a good estimate of the real predictive error of the model. Its value less than SSY indicate that the model predicts better than chance and can be considered statistically significant. To have a reasonable model, PRESS/SSY should be less than 0.4. In our case, PRESS/SSY ranges between 0.117 and 0.094, indicating that the DN model for complexes is significant. To confirm our finding, ν_{max} values predicted by Eq. (1) are compared with the obtained ν_{max} values. Within the experimental error, the values agree well with donor number of solvents. The plots obtained from ν_{max} (experimental) against ν_{max} (predicted) values are shown in Fig. 2.

According to the results obtained, the DN parameter of the solvent has a dominate contribution in Eq. (3) for compounds 1-4 and governs in the shift of the d-d absorption band of the complexes. The negative sign of the coefficient a indicates a red shift as the donor number of solvents increases. The red shift observed in the d-d visible absorption band originates in variation of Lewis acid-base interaction between the chelates around the copper ions and the respective solvents molecules. Since approaching of the polar solvent molecules to the axial position of the complexes causes a strong repulsion between electron in the dz² orbital of the copper(II) ions and the electron pair of the solvents and hence decreasing the required energy for transferring the electrons to $d_{x^2-y^2}$ orbital. Accordingly, the position of this band decreases nearly linearly with the increasing of the donor numbers of the solvents. The plots of the observed v_{max} values of the complexes versus the donor number of the solvents as shown in Fig. 3 demonstrated good correlation for all complexes.

There is an identical trend in the visible absorption spectra of the investigated complexes. The nature of counter ion X in all investigated complexes is generally ineffective to the v_{max} value in solvents with high donor power. However in low DN solvents differences in v_{max} is larger among the complexes. It seems that as the approach of the solvent molecules with different donor power to the axial vacant sites of the complexes causes a change in the geometry of the copper center from square planar to octahedron. This conclusion is in agreement with our pervious results [10,46]. However, It was found that the Δv_{max} (= (v_{max})_{DCM} – (v_{max})_{HMPA}) values depend on the counter ion, X used in the complex and are in order of $BPh_4^- > PF_6^- > ClO_4^- > BF_4^-$. The best results were obtained for complex 1 indicating this fact that the size of counter ions are effective in the solvatochromism phenomenon. The bulkier counter ions have looser binding to the Cu(II) center and can be driven out more easily by solvent molecules cause the higher Δv_{max} value.



Fig. 2. The plots of the observed ν_{max} values against the calculated ν_{max} values for complexes 1–4.



Fig. 3. Dependence of the v_{max} values of complexes 1–4 on the solvent DN values.

4. Conclusion

Four new mixed-chelate copper(II) complexes with solvatochromic properties were prepared. Their solvatochromism were examined with different solvent parameters models using MLR computational method. The statistical evaluation of the data (R, S.E., *F*-test, *Q*² and PRESS/SSY) indicated that DN model of the solvent plays the most important role in the solvatochromic behavior of the complexes. All complexes demonstrated 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 octahedron. Among the complexes of [Cu(acac)(diamine)]X, complex 1 $(X = BPh_4^{-})$ displayed highest Δv_{max} value. As the size of the counter ion X increase the ion pair interaction between cation complex [Cu(acac)(diamine)]⁺ and X decreases. Thus, solvent molecules facilitates the dissociation of the anion X from cationic complex with coordinating to the axial sites of the complex.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2011.08.042.

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