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Synthesis, Characterization and Solvatochromism Investigation of Mixed Ligand Chelate Copper(II) Complexes with Acetyleacetonate and Three Diamine Ligands

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The syntheses of three mixed ligand chelate copper(II) complexes of the type [Cu(L)(acac)(H_2O)]BPh_4 where acac＝acetyleacetonate; L＝*N*,*N*-dimethyl,*N'*-benzylethane-1,2-diamine (**L**^{1}), *N*,*N*-dimethyl, *N'*-2-methylbenzylethane-1,2-diamine (**L**^{2}) or *N*,*N*-dimethyl,*N'*-2-chlorobenzylethane-1,2-diamine (**L**^{3}) are reported and characterized by elemental analyses, spectroscopic and molar conductance measurements. The X-ray structure of complex **1** shows that the central copper atom is placed in a distorted square pyramidal geometry made by acac and diamine chelate in the base and a H_2O molecule on the apex. The prepared complexes are fairly soluble in a large number of organic solvents and show positive solvatochromism. Calculations of SMLR (stepwise multiple linear regression) method was utilized to find the best model explaining the observed solvatochromic behavior and showed that among different solvent parameters, donor number (DN) is a dominant factor responsible for the shift in the d-d absorption band of the complexes to the lower wavenumber with increasing its values. The importance of substituent effect in diamine ligand on the spectral and SMLR measurements is also discussed.

Keywords mixed-chelate, solvatochromism, X-ray crystal structure, SMLR method, diamine, copper(II), tetraphenylborate

Introduction

Synthesis of copper(II) mixed ligand chelate complexes and investigating their solvatochromic behavior have greatly helped for understanding the behavior of solute in various solvents and solute-solvent interactions.[1,2] Copper(II) complexes with a strong Jahn-Teller effect show simple changes in electronic spectra causing different colors that originate from the strength of the interaction between solvent molecules which approach to the axial sites of the complexes. This property leads to using them as solvent polarity indicators[3-5] and many other practical applications such as imaging,[6,7] photo switching[8,9] and sensor materials.[10] In this regard, extensive studies have been focused for different kinds of mixed ligand chelate copper(II) complexes with general formula of [Cu(dike)(diam)]X[11-18] which are easily soluble in a large number of organic solvents and show solvatochromic behavior. In such complexes different diketonate ions (dike), ethylenediamine derivatives (diam) and various equivalent anions (X) were used. We have also reported the synthesis and electronic spectral studies of several copper(II) mixed ligand chelate complexes.[19-23] Previous studies showed that among different counter ions used, copper(II) complexes containing BPh_4^- exhibited better solvatochromism behavior (larger $\Delta\nu_{max}$)[23,24] because of its non-coordinating property and disinclination in ion-pair formation which led to less competition between solvent molecules and the anion for coordination to metal center. On the other hand, it was found that the nature of substituent group in the diamine ligand could also affect the spectra of these types of complexes.[22] With use of this background, in the present work we study the synthesis and solvatochromic behavior of three tetraphenylborate mixed ligand chelate copper(II) complexes of the type [Cu(L)(acac)(H_2O)]BPh_4, as shown in Scheme 1, where acac is acetylacetonate ion and L is ethylenediamine derivatives. It was interesting to investigate how the steric or electronic factors of the substituent groups might affect the solvatochromic behavior of these types of complexes. The solvatochromism studies of the complexes were developed by application of the stepwise multiple linear regression (SMLR) method. In this

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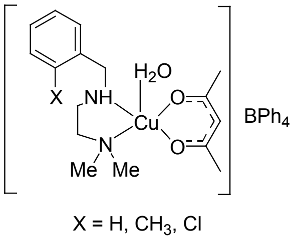
method six solvatochromism-related parameters such as DN, AN, ET(30), α, β and $\pi^{*[1,25\text{-}27]}$ were employed to derive the best model to explain the positive solvatochromic behavior of these complexes.

Scheme 1 The complexes under study



Experimental

Materials and methods

The ligand **L**^{1}, *N*,*N*-dimethyl,*N'*-benzylethane-1,2-diamine and complex **1** were prepared according to published procedures,[20,24] respectively. All solvents were spectro-grade and used without further purification. All the samples were dried to constant weight under a high vacuum prior to analysis. Conductivity measurements were made at 25 ℃ with a Jenway 400 conductance meter on 1.00×10^{-3} mol/L samples in selected solvents. Infrared spectra were recorded in KBr disks by a Bruker FT-IR instrument. The electronic absorption spectra were measured with a Braic2100 model UV-Vis spectrophotometer using 1 cm quartz cells. ^{1}H NMR and ^{13}C NMR spectra for ligands were recorded on a Bruker 400 MHz Ultrashield avance III Spectrometer. Elemental analyses were performed on a LECO 600 CHN elemental analyzer. The solvents used for the solvatochromic study are dichloromethane (DCM), nitromethane (NM), nitrobenzene (NB), benzonitrile (BN), acetonitrile (AN), propionitrile (PN), acetone (Ac), tetrahydrofuran (THF), ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO), pyridine (Py) and hexamethylphosphorictriamide (HMPA).

Synthesis

***N*,*N*-Dimethyl,*N'*-2-methylbenzylethane-1,2-diamine (L^2)** A mixture of 2-methyl benzaldehyde (30 mmol), *N*,*N*-dimethylethylenediamine (30 mmol) and a few drops of acetic acid in ethanol (15 mL) was prepared and refluxed for 10 min. The solvent was then evaporated under reduced pressure. $NaBH_4$ (45 mmol) was added gradually to the resultant yellow oil that was dissolved in ethanol (30 mL). The resulting mixture was allowed to stand overnight. After heating the solution near the boiling point, HCl (10 mL, 17 mol/L) was added to it while placing the solution in an ice bath and was heated again to the boiling temperature. The mixture was then made alkaline by NaOH (4 mol/L). The sodium borate precipitate was removed by filtration. The evaporation of the solvent from the filtrate resulted in a yellow oil which was subsequently extracted with dichloromethane (15 mL×3). The combined CH_2Cl_2 fractions were dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure resulted in desired product as yellow oil. The yield was 45%. Selected IR (KBr) v: 3297 (m, NH str.), 2817 (s, CH str. aliphatic), 1459 (s, C=C str. aromatic), 1043 (s, NCH_3 str. aliphatic) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.24 (s, 6H, $C\mathbf{H}_3NC\mathbf{H}_3$), 2.36 (s, 3H, $C\mathbf{H}_3Ph$), 2.51 (t, J=12.4 Hz, 2H, $CH_2C\mathbf{H}_2N(CH_3)_2$), 2.79 (t, J=12.4 Hz, 2H, $NHC\mathbf{H}_2CH_2$), 3.82 (s, 2H, $PhC\mathbf{H}_2NH$), 7.17—7.21 (m, 4H, aryl**H**); ^{13}C NMR (126.77 MHz in $CDCl_3$) δ: 45.4 ($CH_3N\mathbf{C}H_3$), 58.6 [$CH_2\mathbf{C}H_2N(CH_3)_2$] 46.5 ($NH\mathbf{C}H_2CH_2$), 19 ($\mathbf{C}H_3Ph$), 51.3 ($Ph\mathbf{C}H_2NH$), 126.0, 127.1, 128.6, 130.3, 136.3 (aryl**C**).

***N*,*N*-Dimethyl,*N'*-2-chlorobenzylethane-1,2-diamine (L^3)** The same procedure as **L**^{2} was used for the preparation of ligand **L**^{3}, except that using 2-chlorobenzaldehyde instead of 2-methyl benzaldehyde. The yield was 55%. Selected IR (KBr) v: 3309 (m, NH str.), 2817 (s, CH str. aliphatic), 1448 (s, C=C str. aromatic), 1043 (s, NCH_3 str. aliphatic). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.17 (s, 6H, $CH_3NC\mathbf{H}_3$), 2.41 [t, J=12.0 Hz, 2H, $CH_2C\mathbf{H}_2N(CH_3)_2$], 2.67 (t, J=12.0 Hz, 2H, $NHC\mathbf{H}_2CH_2$), 3.87 (s, 2H, $PhC\mathbf{H}_2NH$), 7.13—7.38 (m, 4H, aryl**H**); ^{13}C NMR (126.77 MHz in $CDCl_3$) δ: 45.4 ($\mathbf{C}H_3N\mathbf{C}H_3$), 59.0 [$CH_2\mathbf{C}H_2N(CH_3)_2$], 46.5 ($NH\mathbf{C}H_2CH_2$), 51.3 ($Ph\mathbf{C}H_2NH$), 126.7, 128.2, 129.4, 130.1, 133.7, 137.6 (aryl**C**).

[Cu(L^2)(acac)(H$_2$O)]BPh$_4$ (2) A mixture of *N*,*N*-dimethyl,*N'*-2-methylbenzylethane-1,2-diamine, **L**^{2} (1.2 g, 6 mmol), acetylacetone (0.7 mL, 6 mmol) and anhydrous Na_2CO_3 (0.3 g, 3 mmol) in ethanol (30 mL), was added to an aqueous solution of $Cu(OAc)_2{\bullet}H_2O$ (1.2 g, 6 mmol). After removing the by-product of [$Cu(acac)_2$], a saturated solution of $NaBPh_4$ in ethanol was added to the resultant clear blue solution. The dark blue precipitate was gradually formed which was separated by filtration. The blue solid was recrystallized from acetonitrile. The yield was 48%. Selected IR (KBr) v: 3527 (m, OH str.), 3288 (m, NH str), 1585 (s, C=O str.), 1519 (s, C=C str.), 738, 705 (s, CH bend.). Anal. calcd for $C_{41}H_{49}BCuN_2O_3$: C 71.14, H 7.14, N 4.05; found C 71.60, H 6.83, N 3.88.

Preparation of [Cu(L^3)(acac)(H$_2$O)]BPh$_4$ (3) This compound was prepared according to the procedure used for **2** except that *N*,*N*-dimethyl,*N'*-2-chlorobenzylethane-1,2-diamine was used instead of *N*,*N*-dimethyl,*N'*-benzylethane-1,2-diamine as diamine ligand. A dark blue precipitation was obtained, recrystallized from acetonitrile and dried at room temperature under high vacuum. The yield was 40%. Selected IR (KBr) v: 3588 (m, OH str.), 3274 (m, NH str), 1585 (s, C=O str.), 1519 (s, C=C str.), 738, 705 (s, CH bend.). Anal. calcd for $C_{40}H_{46}BClCuN_2O_3$: C 67.42, H 6.51, N 3.93; found C 67.81, H 6.12, N 4.14.

X-ray structure determination

Data were collected at room temperature with a Bruker APEX II CCD area-detector diffractometer using

MoKα radiation ($\lambda = 0.71073$ Å). Data collection, cell refinement, data reduction and absorption correction were performed using multiscan methods with Bruker software.[28-30] The structures were solved by direct methods using SIR2004.[31]

The non-hydrogen atoms were refined anisotropically by the full matrix least squares method on F^2 using SHELXL.[32] All the hydrogen (H) atoms were placed at the calculated positions and constrained to ride on their parent atoms. Details concerning collection and analysis are reported in Table 1.

Table 1 Crystal data and structure refinement of complex **1**

Empirical formula	$C_{40}H_{47}BCuN_2O_3$
Formula weight	678.15
Color	Blue
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size/mm	0.86×0.45×0.23
Unit cell dimensions	
a/Å	9.678
b/Å	31.586
c/Å	12.755
α	90°
β	103.349(4)°
γ	90°
Volume/Å^3	3794.1
Z	4
Calculated density/(Mg•m^{-3})	1.184
Absorption coefficient/mm^{-1}	0.613
F(000)	1436
θ range for data collection/(°)	2.09—30.10
Index ranges	$-13 \leqslant h \leqslant 13$
	$-44 \leqslant k \leqslant 44$
	$-17 \leqslant l \leqslant 17$
μ/mm^{-1}	1.187
Reflections collected/unique	159628/11101 [R(int)$=0.0567$]
Completeness to $\theta = 30.10$	99.5%
Absorption correction	Multi-scan
Refinement method^a	Full-matrix least-square on F^2
Data/restraints/parameters	11101/0/451
Final R indices^a [$I > 2\sigma(I)$]^b	$R_1 = 0.0711$, $wR_2 = 0.1600$
Goodness-of-fit on $F^{2\,c}$	1.112
R indices (all data)	$R_1 = 0.1256$, $wR_2 = 0.1813$
Largest diff. peak and hole/(e•Å^{-3})	0.504 and −0.381

[a] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR = [\Sigma(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$; [c] $S = \Sigma[w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$.

SMLR analysis

In this report a multiple linear regression (MLR) analysis was performed by SPSS/PC software (SPSS ver. 16, SPSS Inc.) by using stepwise method for model building.[33] Stepwise-MLR is a popular technique that has been used to select the most appropriate parameters in solvent-solute interaction.[34] After passing three main steps of SMLR method, identifying an initial model, changing the model of previous step by adding or removing a parameter and obtaining the best model at the final step, the goodness of model can be analyzed by considering closeness of the R (multiple correlation coefficients) value to one and high F-statistic values, low standard errors (S.E), the least number of parameters and high ability for prediction.[35]

Results and Discussion

To prepare the mixed ligand chelate complexes, $Cu(OAc)_2$•H_2O, acac, the diamines and $NaCO_3$ with molar ratios of 1∶1∶1∶0.5, respectively were mixed in the solvent of ethanol. After removing the by-product of $[Cu(acac)_2]$ from the dark mixture and addition of an ethanolic saturated solution of $NaBPh_4$ to the clear resultant solution, the desired complexes were obtained as dark blue crystals with typical yield of 40%—60%. Analytical data, molar conductivity, IR spectra and X-ray crystallography indicated formation of the desired mixed ligand chelate copper(II) complexes.

X-ray structure

An ORTEP view of the cationic part of complex **1** is depicted in Figure 1 together with the numbering scheme. Selected bond distances and angles are presented in Table 2.

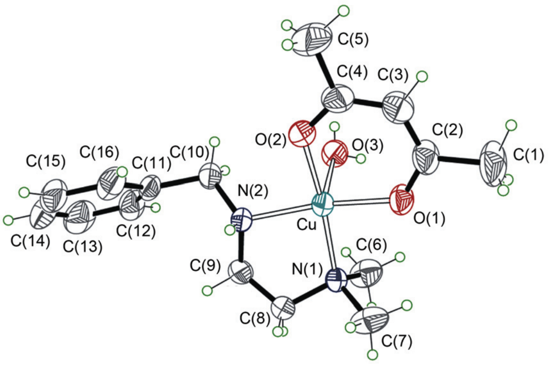


Figure 1 ORTEP view of $[Cu(acac)(L^1)(H_2O)]^+$ (**1**). Non H-atoms represented as displacement ellipsoids are plotted at the 30% probability level, while H atoms are shown as small spheres of arbitrary radius.

The compound crystallizes in the monoclinic space group $P2_1/c$. The geometry about the copper can be regarded as a distorted square-pyramid with the N_2O_2 donor atoms of diamine and acetylacetonate chelates on the base and water oxygen at the apex. The geometric discrimination parameter τ[36] between squarepyramid

Table 2 Selected bond distances (Å) and angles (°) for complex **1**

Bond distance/Å		Bond angle/(°)	
Cu—O(1)	1.905(2)	O(1)-Cu-O(2)	93.84(12)
Cu—O(2)	1.924(3)	O(1)-Cu-N(2)	169.78(14)
Cu—N(1)	2.047(3)	O(2)-Cu-N(2)	89.57(12)
Cu—N(2)	2.011(3)	O(1)-Cu-N(1)	89.85(11)
Cu—O(3)	2.391(3)	O(2)-Cu-N(1)	172.40(11)
		N(2)-Cu-N(1)	85.71(12)

(τ=0) and trigonal-bipyramid (τ=1) is 0.04. The copper(II) ion is displaced by 0.135(4) Å from the basal least square plane toward the water oxygen atom. Such a coordination has been observed previously in a Cu(II) complex including Cl-acac as dike ligand.[23] The basal Cu—O(1) and Cu—O(2) distances are 1.905(2) Å and 1.924(3) Å, respectively with a bite angle of O(1)-Cu-O(2) 93.84(12)°. The mean Cu—N distance of the diamine ligand and the bite angle N(1)-Cu-N(2) are 2.029 Å and 85.71°, respectively and close to the related values of the analogous copper(II) complexes.[22,23] The axial Cu—O(3) (water) bond is elongated [2.391(3) Å] owing to Jahn-Teller effect for d^9 electronic configuration. As a result, the water molecule is weakly coordinated to the copper(II) center and can be easily replaced by solvent molecules in solution leading to the observed solvatochromism. The asymmetric nitrogen N(2) has a configuration of *R* in the Figure 1; the benzyl substituent on the amine nitrogen and water molecule are situated *cis* to each other and are axially oriented with respect to mean molecular plane (N_2O_2). The packing of the structure in the unit cell is shown in Figure 2. This arrangement shows that tetaphenylborate, as the counter ion, has no any interaction with copper(II) center probably due to non-coordinative ability and its large size and is located far-off from this center. However, inter molecular interactions between the ligand moieties of the cation and tetraphenylborate anions along crystallographic *c* axis stabilize the crystal packing. Also the crystal packing shows two-dimensional sheet with zigzag structures along crystallographic *b* axis as shown in Figure 2.

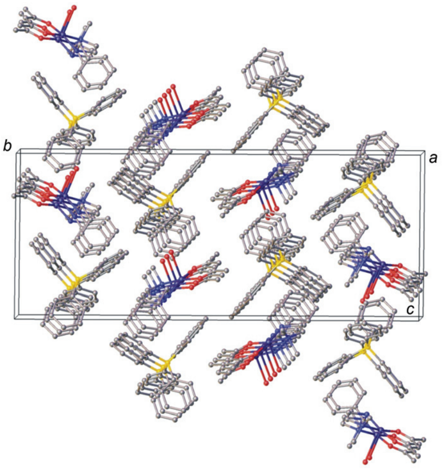


Figure 2 Crystal packing of [Cu(acac)(L^1)(H_2O)]BPh_4. For clarity, H atoms have been omitted.

IR spectra

The IR spectra of Schiff-base imines show a sharp and strong band around 1640 cm^{-1} due to C=N stretching vibration.[37,38] Disappearing of these bands in IR spectra of diamine ligands along with emergence of the N—H stretching vibrations at 3300 cm^{-1}, indicates reduction of the C=N bond and formation of the desired ligands. Other characteristic bands in the spectra of diamines, are observed at 1040 cm^{-1} and 1450 cm^{-1} that can be assigned to the vibrations of the C—N bond and CH_2 phenyl groups, respectively.[39] Upon coordination of diamine ligand to the copper(II) center and formation of the mixed ligand chelate complexes, the N—H bond of the free diamines shifts to the lower wavenumber in comparison to the free ligand. 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 ligand involves electron depopulation of the N—H bond, which culminates in a shift to lower frequencies. The presence of acetylacetonate (acac) ligand in the complexes is confirmed by two intense and sharp bands around 1520 and 1580 cm^{-1} that can be assigned to the C=C and C=O vibrational modes, respectively.[40-42] The absorption band occurring in the region 1525—1585 cm^{-1} in IR spectra of all the mixed ligand chelate complexes is associated with coordination of water molecule to the axial position of copper(II) ion which is confirmed by X-ray crystallography. The two intense absorption bands at 705 and 735 cm^{-1} observed in all complexes correspond to tetraphenylborate ion which exists as counter ion.[43] The difference in substituent of diamine ligands can be observed in spectra of **3**, in this case a moderate band that appears at around 600 cm^{-1} is probably due to the C—Cl bond stretching vibration[44] that is absent in spectra of **1** and **2**.

Conductometric data

The molar conductances of three mixed ligand chelate complexes in some organic solvents with different polarities are presented in Table 3. The standard values for 1∶1 electrolyte for solvents are given in the same table.[45] It can be observed that the values in all solvents are lower than the expected values. These results arise from the nature of counter ion in mixed ligand chelate complexes; tetraphenylborate is a bulky ion so that its ionic mobility in the solution is low.[45]

Solvatochromism

The prepared mixed ligand chelate complexes are soluble in a large number of organic solvents. The position of the ν_{max} values of the complexes with the molar absorptivities and their respective solvent parameter values are collected in Table 4. As shown in Figure 3 the

Table 3 Molar conductivities data (Λ_m) of the complexes ($\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$) at 25 ℃ in different solvents.

Complex	NM	NB	AC	ACN	MeOH
1[a]	52	17	84	93	54
2	51	16	60	88	58
3	39	15	53	85	63
1∶1 electrolytes	75—95	20—30	100—140	120—160	80—115

[a] Taken from reference 24.

absorption spectra of the complexes exhibit a broad structureless band in the range of 11000—25000 cm^{-1} that is attributed to the promotion of an electron from lower orbitals to the hole of $d_{x^2-y^2}$ orbital of copper(II) ion (d^9).

In order to ascertain presence of a trend for the observed solvatochromism behavior of the complexes, solvatochromism parameters containing DN (negative ΔH value for a 1∶1 adduct formation between $SbCl_5$ and solvent molecules in a dilute solution of 1,2-dichloroethane or dichloromethane), AN (derived from ^{31}P NMR of triethylphosphine oxide in different solvents), $E_T(30)$ (molar electronic transition energy of dissolved negatively solvatochromic pyridinium *N*-phenolate betaine dye), α [solvatochromic parameter of a solvent's HBD (hydrogen-bond donor) acidity], β [solvatochromic parameter of solvent's HBA (hydrogen-bond acceptor) basicity] and π^* (solvatochromic parameter index of a solvent's polarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect) were used to generate the best model with using SMLR method. The choice of parameters is crucial in order to set up a reasonable model.[46] To reach our aim we used these parameters along with the absorption frequencies (ν_{max}) of the complexes to the solvatochromism Eq. (1). The ν_{max} values were obtained experimentally by visible spectroscopy. The parameter values were taken directly from literature[47-49] which are collected in Table 4. These parameters are independent to each other, but relevant to the case under study.[50,51]

$$\nu_{max} = \nu^{\circ}_{max} + paDN + pbAN + cE_T(30) + d\beta + e\alpha + f\pi^* \quad (1)$$

In this equation ν_{max} is the value of the absorption energy in the solvent under study and ν°_{max} is the value of the absorption energy in an inert solvent. DN, AN, $E_T(30)$, β, α and π^* represent independent but complementary solvent parameters. The a, b, c, d, e and f values are the regression coefficients describing the sensitivity of the property ν_{max} to the different solute/solvent interaction mechanisms. The SMLR results were collected in Table 5.

According to observed results the dominant parameter responsible for solvatochromism behavior of the complexes is DN; so that the higher DN value the more shift to the lower wavenumber in the spectra of the complexes. The R values near unity and also high F-statistics values prove existence of an appropriate inter correlation between DN parameters and wavenumbers.

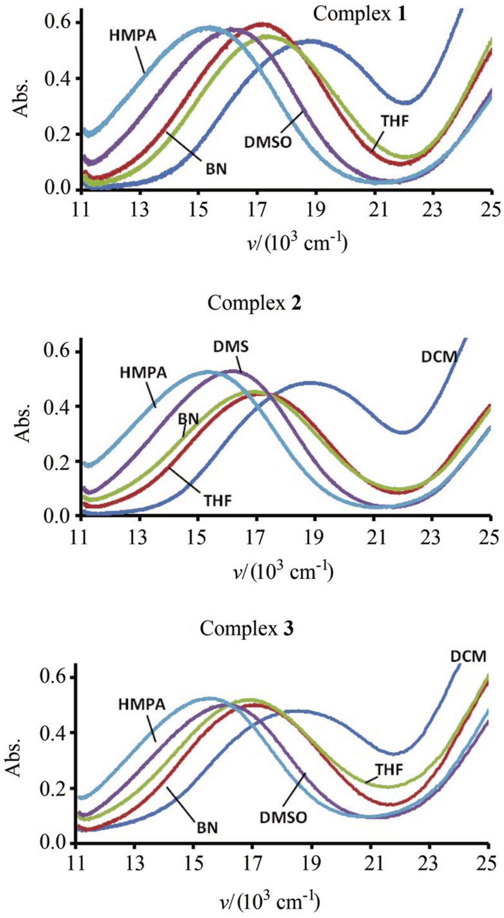


Figure 3 Absorption spectra of complexes **1**—**3** in selected solvents. Absorption spectra in other solvents are omitted for clarity.

Cross validation is a well-known technique to estimate the reliability of a statistical model.[52] In this report the cross validation technique was utilized to determine the accuracy of the proposed SMLR model. Based on this technique, the most popular cross-validation procedure LOO (leave one-out) technique was used.[53] The predictive abilities of the models were determined by the cross validation coefficient (Q^2) which is based on PRESS (predicted residual sum of squares), $PRESS = \Sigma(Y_{pred.} - Y_{exp.})^2$ and SSY (total sum of squares derivations), $SSY = \Sigma(Y_{exp.} - Y_{maen})^2$, and can be calculated by Eq. 2.

$$Q^2 = 1 - PRESS/SSY \quad (2)$$

where $Y_{pred.}$; the predicted wavenumbers of the solvents by the best SMLR model, $Y_{exp.}$; the experimental measured wavenumbers, Y_{maen}; mean values of the predicted wavenumbers. Using this model showed that the Q^2 parameters of the complexes are in an acceptable range ($Q^2 > 0.5$), and also the PRESS values are much less

Table 4 The solvent parameter values and electronic spectra of the complex in various solvents: $\nu_{max}/(10^3\ cm^{-1})$ [$\varepsilon/(L\bullet mol^{-1}\bullet cm^{-1})$]

Solvent	DN	AN	$E_T(30)$	β	α	π^*	Complex **1**^{b}	Complex **2**	Complex **3**
DCM	0.0	20.4	40.7	0.10	0.13	0.82	18.71 (107)	18.76 (95)	18.52 (95)
NM	2.7	20.5	46.3	0.06	0.22	0.85	18.26 (107)	17.83 (90)	18.05 (122)
NB	4.4	14.8	41.5	0.30	0.00	1.01	17.82 (103)	18.08 (136)	18.02 (102)
BN	11.9	15.5	41.5	0.37	0.00	0.90	17.36 (105)	17.33 (88)	17.06 (100)
AN	14.1	18.9	45.6	0.40	0.19	0.75	17.17 (119)	17.12 (92)	17.01 (110)
PN	16.1	16.0	43.6	0.39	0.00	0.71	17.30 (120)	16.98 (74)	17.18 (96)
Ac	17.0	12.5	42.2	0.43	0.08	0.71	17.31 (103)	17.15 (80)	17.01 (90)
THF	20.0	8.0	37.4	0.55	0.00	0.58	17.19 (110)	16.95 (90)	17.01 (104)
EtOH	22.9	37.1	51.9	0.75	0.86	0.54	16.99 (106)	16.72 (80)	16.69 (71)
MeOH	23.3	41.3	55.4	0.66	0.98	0.60	16.80 (112)	16.81 (94)	16.89 (106)
DMF	26.6	16.0	43.8	0.69	0.00	0.88	16.45 (105)	16.39 (100)	16.23 (102)
DMSO	29.8	19.3	45.1	0.76	0.00	1.00	16.09 (115)	16.21 (106)	16.13 (100)
Py	33.1	14.2	40.5	0.64	0.00	0.87	15.57 (110)	15.50 (98)	15.29 (96)
HMPA	38.8	10.6	40.9	1.05	0.00	0.87	15.38 (117)	15.38 (104)	15.53 (105)

^{a} Taken from reference [24]. ^{b} The spectrum taken at 0 ℃ at concentration of 1.00×10^{-3} mol/L.

Table 5 The equations resulting from the linear correlation of the ν_{max} values with the DN of the solvents^a

Complex	Equation	F	R	S.E.	$\Delta\nu_{max}/cm^{-1}$
1	$\nu_{max}/10^3=-0.079DN_{solv}+18.502$ $DN_{solv}=-11.997\nu_{max}+222.91$	231.17	0.97	0.21	3326
2	$\nu_{max}/10^3=-0.078DN_{solv}+18.395$ $DN_{solv}=-10.967\nu_{max}+205.21$	231.314	0.975	0.21	3380
3	$\nu_{max}/10^3=-0.077DN_{solv}+18.333$ $DN_{solv}=-12.166\nu_{max}+224.24$	173.490	0.967	0.24	3230

^{a} The number of variables, $n=14$.

than SSY, indicating the models predict better than chance and are considered statistically important. In this case, PRESS/SSY ranges between 0.049 and 0.089, indicating the DN parameter plays the most important role in solvatochromism behavior of the complexes. The obtained ν_{max} values versus the predicted ν_{max} values were plotted by using Eq. 1 to confirm our findings. The results are shown in Table 6.

These results revealed that in all complexes the slopes are near unity (Table 6) with good correlation coefficient. Considering the DN parameter of different solvents the complexes show a color change from violet via blue to green as the polarity of solvent increases from DCM (DN=0) to HMPA (DN=38.8). This observation demonstrates the donor-acceptor interactions between Cu(II) ion and solvent molecules are responsible in solvatochromic behavior of the complexes. This is as a result of the weak axial bond of H_2O molecule to the copper(II) center that can be easily replaced by solvent molecules and also occupation of another vacant axial site by solvent molecule which results in change in the energy gap between d_{z^2} and $d_{x^2-y^2}$ orbitals. As shown in Figure 4 the ν_{max} values decrease nearly linear with the increasing DN of solvents. Increasing Lewis basicity of solvents causes more interaction between solvent molecules and the copper center. As a result, the energy levels of these orbitals become closer to each other and therefore, the required energy for electron transition is lowered and a red shift is observed. The results demonstrate that all complexes are solvatochromic and show larger $\Delta\nu_{max}=(\nu_{max})_{DCM}-(\nu_{max})_{HMPA}$ values in comparison with the analogous perchlorate complexes.[24] This difference is associated with the fact that tetraphenylborate is a large, bulky anion in comparison with ClO_4^-, PF_6^- and BF_4^- anions[23,24] with lack of coor-

Table 6 The quality of the obtained models by means of Q^2, PRESS and PRESS/SSY and predictive correlation coefficient $(R_{pre})^a$

Complex	Q^2	PRESS	PRESS/SSY
1	0.95	0.56	0.049
	$\nu_{max\ experimental}=1.004\nu_{max\ predicted}-0.077$ $R_{pre}=0.975$		
2	0.94	0.65	0.058
	$\nu_{max\ experimental}=1.0203\nu_{max\ predicted}-0.337$ $R_{pre}=0.9698$		
3	0.91	0.98	0.089
	$\nu_{max\ experimental}=0.9865\nu_{max\ predicted}-0.2282$ $R_{pre}=0.9544$		

^{a} The number of variables, $n=14$.

dinating ability. Thus the solvent molecules can approach more easily to the axial sites of the complexes. This phenomenon causes the higher $\Delta\nu_{\max}$ values. It was also expected that the steric or electronic factors might affect the shift in the d-d band of the copper(II) mixed-chelate complexes,[19,22] but as shown in Figure 4 the spectra of compounds **1**—**3** 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 copper(II) center so no direct correlation between the presence of electron-withdrawing or electron-releasing groups was 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, so that the solvatochronism behaviors of the mentioned complexes were independent to the nature of the substituent groups on the phenyl ring of the diamine ligand.

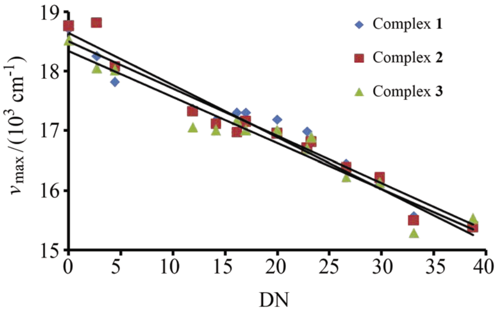


Figure 4 Dependence of the $\nu_{\max}$ values of complexes **1**—**3** on the solvent DN values.

Conclusions

Three mixed ligand chelate copper(II) complexes have been prepared and their spectral and structural studies were carried out. The X-ray structure of complex **1** confirms a five coordinate geometry around copper(II) center. The acetylacetonate and diamine chelates coordinate at the equatorial plane and water molecule at the apical position. This structure has led to the high solubility in a large number of organic solvents and solvatochromic behavior. The solvatochromism results obtained and SMLR study confirmed that among different solvent parameters, donor number (DN) plays the most important role in the observed $\nu_{\max}$ values causing red shift of complexes in various solvents. The $\Delta\nu_{\max}$ values for these complexes are higher than those analogous perchlorate complexes which represents non-coordinating property of BPh_6^- anion that facilitates coordination of solvent molecules to the axial positions of copper(II) center. It was also found that the presence of substituent groups on the phenyl ring of the diamine ligand does not show significant effect in the ligand field strength due to lack of an effective intermolecular interaction of phenyl ring moiety.

Supplementary Data

CCDC 851370 for **1** contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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