

Solvatochromic Properties of Heteroleptic Copper(II) Complexes Containing *N,N,N',N'*-Tetramethylethylenediamine and 2-Acetylcyclopentanone Ligands

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Three new heteroleptic copper(II) complexes, [(tmen)Cu(dike)H₂O]X where tmen = *N,N,N',N'*-tetramethylethylenediamine, dike = 2-acetylcyclopentanone anion and X = ClO₄⁻ (1), Cl⁻ (2) and Br⁻ (3) are prepared and characterized by elemental analyses, molar conductance measurements and IR and UV-Vis spectroscopy techniques. The complex 1 is fairly soluble in various organic solvents and demonstrates distinctive solvatochromism. However, the solubility of complexes 2 and 3 is less than 1 and their color changes are limited to polar solvents. The influence of the solvent polarity and counter ions on the wave length maxima, λ_{max} values of the d-d bands of the complexes have been investigated by visible spectroscopy. A multi-parametric equation has been utilized to explain the solvent effect on the d-d transition of [(tmen)Cu(dike H₂O)]ClO₄ using SPSS/PC software. The stepwise multiple linear regression (SMLR) method demonstrated that the donor power of the solvent plays the most important role in the observed negative solvatochromism of the compound.

Keywords: Heteroleptic, Diketonate, Ethylenediamine, Copper(II), Solvatochromism

INTRODUCTION

Solvatochromism properties of inorganic compounds have been studied during the past four decades [1-4]. The phenomenon of solvatochromism which refers to changes in electronic absorption spectra with solvent is one of the significant subjects in solution chemistry and helped in understanding the role of solute in different solvents and solute-solvent interactions [5,6]. There exist a number of examples of solvatochromic metal complexes and origins of the color changes are quite diverse. Among the metal complexes whose color changes are due to those of d-d transitions, the copper(II) complexes with strong Jahn-Teller effect demonstrate simple changes in the electronic spectra producing different colors that originate from the strength of the interaction between solvent molecules, which approach to the axial sites of the complexes. This property lead to using them as solvent polarity indicators [2,7,8] and many other practical applications such as imaging [9,10],

photo switching [11,12] and sensor materials [13]. In this regard, extensive studies have focused on the heteroleptic chelate complexes of copper(II). Heteroleptic chelated complexes of copper(II) with the general formula [Cu(N∩N)(O∩O)]⁺ were reported to have potentially useful solvatochromism properties [1,2,7]. In this formula, (N∩N) signifies a diamine ligand or its derivatives; (O∩O) stands for diketonate anion. Recently, we prepared a series of heteroleptic chelate copper(II) complexes that are soluble in a large number of solvents and show solvatochromic properties [14-25]. Our study demonstrated that the ClO₄⁻ as a counter-ion is weakly bound above and below the chelate plane in solution, which is driven out by solvent molecules leading to their solvatochromism. In continuation of our study, we report the synthesis and the solvatochromic behavior of some of the heteroleptic chelated copper(II) complexes, shown in Fig. 1, with different counter ions ClO₄⁻, Cl⁻ and Br⁻ in order to explore the function of the counter ions on the solvatochromism properties in the complexes.

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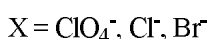
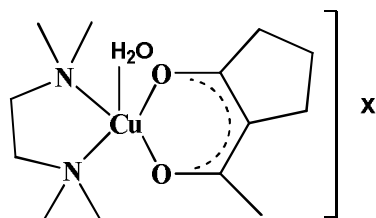


Fig. 1. The complexes under study.

Several empirical scales for solvent polarity, mainly based on effects of the solvation process, have been proposed to describe the interaction between the solvent and the metal complexes such as Gutmann's donor number, DN (donor number is a measure of coordinating ability of solvents on the standard of dichloromethane) [26], Mayer and Gutmann's acceptor number, AN (the electron acceptor property of a solvent) [27], Dimroth and Reichardt's $E_T(30)$ (a measure of the ionization power of a solvent) [38], Kosower's Z (an empirical measure of solvent polarity), Kamlet- Taft's α (hydrogen bond donation of the solvent), β (hydrogen bond acceptance of solvent) [5], and π^* (polarity/polarisability parameter of solvent) [29]. In many cases, it was established that the shift in the electronic absorption spectra of the complexes affected by more than one solvent parameter. Hence, several computational methods for correlation of the experimentally observed quantities to the solvent properties have been developed to study the solvatochromic effect [30]. One of the statistical methods is stepwise multiple linear regression (SMLR). As a result, this statistical analysis was utilized to derive the best model to explain the solvatochromic behavior of these complexes.

EXPERIMENTAL

Reagents and Apparatus

The ligands *N,N,N',N'*-tetramethylethylenediamine, 2-acetylcyclopentane and solvents used were of "spectrograde" Merck and Aldrich Chemical Co. without further purification. 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 concentrations of 1.00×10^{-3} , 6.00×10^{-4} , 4.00×10^{-4} and 2.00×10^{-4} M of samples in selected solvents. Then for each solvent, a curve was plotted by drawing the molar conductance versus concentration of sample. The curve was then extrapolated to an infinitely dilute solution to obtain the molar conductance value. Infrared spectra were recorded using KBr disks and a Bruker FT-IR instrument. The electronic absorption spectra were measured with a Braic2100 model UV-Vis spectrophotometer using 1 cm quartz cells. 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. 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 hexamethylphosphorotriamide (HMPA).

Synthesis

[(tmen)Cu(dike)H₂O]ClO₄, 1. Copper(II) perchlorate hexahydrate (6 mmol, 2.2 g) was dissolved in ethanol (30 ml), and an ethanolic solution (5 ml) containing *N,N,N',N'*-tetramethylethylenediamine (tmen) (6 mmol, 0.9 ml) and 2-acetylcyclopentanone (dike) (6 mmol, 0.7 ml) was added with stirring. Then, an aqueous solution of sodium carbonate (3 mmol, 0.3 g in 15 ml of water) was added to the solution and stirred for 24 h. After partial concentration of the solution at room temperature, blue crystals precipitated that were collected by filtration (1.45 g, 78%). Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{N}_2\text{O}_7\text{CuCl}$ (MW = 422.36 g M^{-1}): C, 36.97; H, 6.44, N, 6.63; Cu, 15.05. Found: C, 35.18; H, 6.24; N, 6.28; Cu, 15.22%. Selected IR data (v/cm^{-1}) 3446 (m, O-H str.), 1606 ($\text{v}(\text{C}=\text{O})$) (dike), 1085 ($\text{v}(\text{Cl}-\text{O}$ str.) (perchlorate), 627 ($\text{v}(\text{Cl}-\text{O}$ bend).

[(tmen)Cu(dike)]Cl, 2. This compound was prepared according with the procedure used for 1, except that copper(II) chloride dihydrate was used instead of copper(II) perchlorate hexahydrate. A green precipitate was obtained, recrystallized from acetonitrile and dried at room temperature under high vacuum. The yield was 72%.

Table 1. Molar Conductivities Data (Λ_m) of the Complexes ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) at 25 °C in Different Solvents

Complexes	DCM	NM	NB	Ac	EtOH	MeOH	DMF	DMSO
1	14	79	24	139	34	122	57	36
2	2	37	5	29	32	88	68	34
3	2	19	2	14	29	80	65	39
1:1	10-20	75-95	20-30	100-140	35-45	80-115	65-90	35
Electrolyte ^a								

^aTaken from reference 34.

Selected IR data (ν/cm^{-1} using KBr disk): 3422 (m, O-H str.), 1608 (s, C=O str.). Anal. Calcd. for $\text{C}_{13}\text{H}_{27}\text{ClCuN}_2\text{O}_3$ (MW = 358.63 g M^{-1}): C, 43.57; H, 7.59; N, 7.82, Cu, 17.73; found : C, 44.43; H, 6.52; N, 8.14; Cu, 17.47%.

[(tmen)Cu(dike)]Br, 3. This compound was prepared according with the procedure used for 1, except that copper(II) bromide dihydrate was used instead of copper(II) perchlorate hexahydrate. A green precipitate was obtained, recrystallized from acetonitrile and dried at room temperature under high vacuum. The yield was 60%. Selected IR data (ν/cm^{-1} using KBr disk): 3433 (m, O-H str.), 1605 (s, C=O str.). Anal. Calcd. for $\text{C}_{40}\text{H}_{46}\text{BClCuN}_2\text{O}_3$ (MW = 402.82 g M^{-1}): C, 38.76; H, 6.76; N, 6.95, Cu, 15.78; found : C, 39.14; H, 6.12; N, 7.44; Cu, 15.32%.

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 [31]. Stepwise-MLR is a popular technique that has been used to select the most appropriate parameters in solvent-solute interaction [32]. 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 quality of the model can be determined 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 [33].

RESULTS AND DISCUSSION

The heteroleptic complexes were prepared in high yield. Analytical data, molar conductivity and IR spectra indicated formation of the desired copper(II) complexes. The molar conductivity values of three complexes in some organic solvents with different polarities are presented in Table 1. The standard values for 1:1 electrolyte for solvents are given in the same table [34]. It can be observed that the values for compounds 2 and 3 in solvents with low to moderate polarities are lower than the expected values. This is due to strong bond formation between chloride and bromide ions with copper(II) complex. Therefore, these compounds have neutral identity in these solvents. However, when the polarity of the solvent increases, as with ethanol, methanol, DMF and DMSO, the coordinated halide anion is removed by solvent molecules and solvent coordinates to copper(II) ion. Thus, the solution demonstrates 1:1 electrolyte.

Formation of the heteroleptic copper(II) complexes can be established from IR spectroscopy. The observed bands in the spectra can be divided into those associated to the ligands, counter ions and also the bonds formed between copper(II) and coordinating sites of the ligands [35]. The similarity among the infrared spectra of the complexes might imply that the structures of all complexes are the same and the only differences are due to presence of different counter ions as shown in Fig. 2. Coordination of 2-acetylcyclopentanone chelate can be concluded from IR

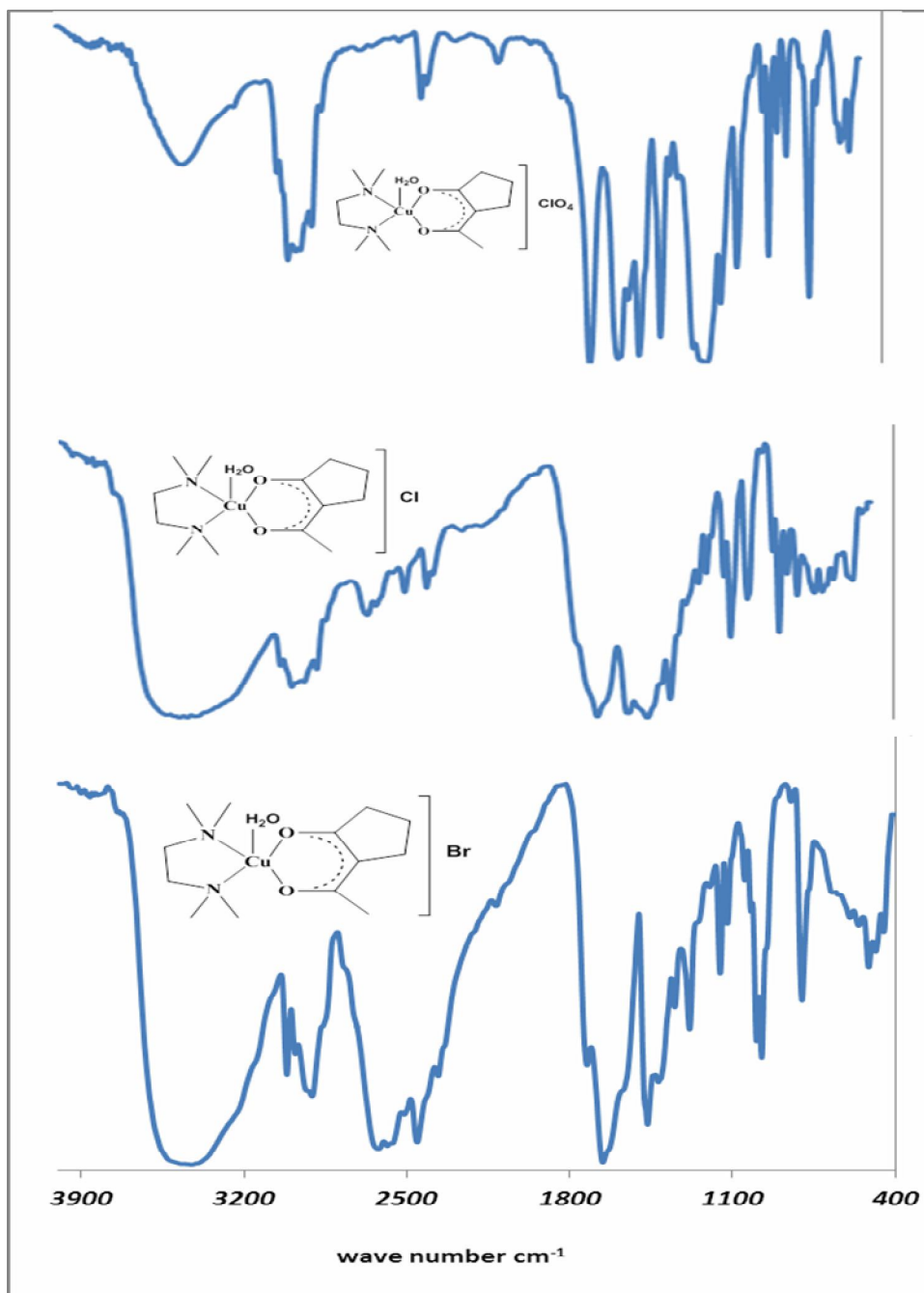


Fig. 2. The comparative IR spectra of $[(tmen)Cu(dike)H_2O]ClO_4$, $[(tmen)Cu(dike)H_2O]Cl$, and $[(tmen)Cu(dike)H_2O]Br$.

spectroscopy so that the C=O stretching vibration of the free 2-acetylcyclopentanone where observed in the 1706 cm^{-1} was shifted to the lower wave number ($1605\text{-}1610\text{ cm}^{-1}$) in

complexes spectra indicating the coordination of 2-acetylcyclopentanone to the copper ion [36]. The vibrational bands around 1040 cm^{-1} corresponded to the stretching

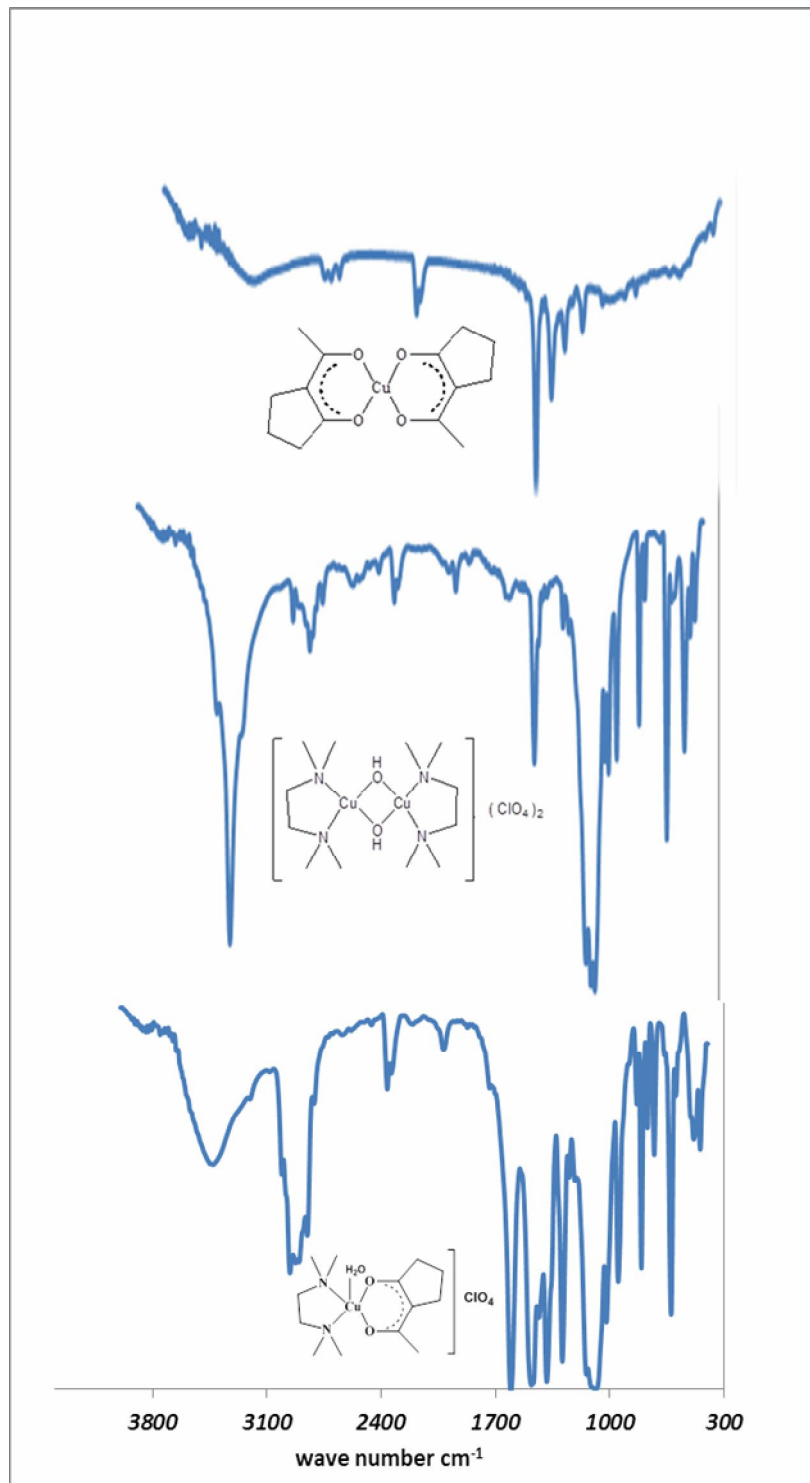


Fig. 3. Infrared spectra of $[\text{Cu}(\text{dike})]_2$, $[\text{Cu}_2(\text{tmen})_2(\mu\text{-OH})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{tmen})(\text{dike})\text{H}_2\text{O}]\text{ClO}_4$ complexes.

vibration of C-N bond and the bands around 1450 cm^{-1} are associated with the scissoring vibration of $-\text{CH}_2-$ groups [37]. The strong bands around 1380 cm^{-1} are associated with the bending vibrations of CH_3 moieties. The complexes show a broad band around 3450 cm^{-1} indicates the presence of water molecule in the complexes [38]. The presence of ClO_4^- ions in complex 1 is confirmed by two intense bands at 1085 cm^{-1} and 627 cm^{-1} which are related to the anti-symmetric stretching and anti-symmetric bending vibration modes of this group [37]. The formation of the heteroleptic complexes are supported by addition of the infrared spectra of $[\text{Cu}(\text{dike})]_2$ and $[\text{Cu}_2(\text{tmen})_2(\mu\text{-OH})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{Cl}, \text{Br}$) complexes which gives a composite spectrum with peak positions that almost match with those in the spectrum of $[\text{Cu}(\text{tmen})(\text{dike})\text{H}_2\text{O}]\text{X}$ complex. This can be seen by inspection of the relevant peak positions of the individual spectra for those complexes shown in Fig. 3 and Figs. S1-S2 in the supplementary contents.

Solvatochromism

Complex 1 is fairly soluble in various organic solvents and demonstrate distinctive solvatochromism. However, the solubility of compounds 2 and 3 are less than 1 and their color changes are limited to polar solvents. The origin of the color changes are attributed to the shift in the d-d transition of the copper(II) ions due to solvent-solute interactions. The spectra in all solvents have nearly the same pattern of octahedral complexes with low intensities. The observed λ_{max} values of the complexes in various solvents are illustrated in Table 2. The broad structureless absorption band is related to the transition of the electron from the lower energy orbitals to the hole in $d_{x^2-y^2}$ orbital of the copper(II) ion (d^9). The less solvatochromism properties of complexes 2 and 3 are due to coordination of chloride and bromide ion, respectively to the copper ion and formation of neutral compounds. The visible spectral changes of these complexes in the selected solvents are illustrated in Fig. 4.

The SMLR technique was carried out to identify the main solvent parameters that influence the solvatochromic behavior of the complex 1. In this regard, the absorption frequencies (λ_{max}) were correlated to the solvatochromic Eq. (1). Hence, the d-d absorption transition band (λ_{max}) of complex 1 in various solvents with their own solvent parameters that were obtained directly from literature [5]

and shown in Table 2 were offered in Eq. (1) one by one to the statistical computer program until certain statistical criteria are met. The solvent parameters used include Gutmann's donor DN and acceptor numbers AN, Dimroth and Reichardt's $E_{\text{T}}(30)$, Kamlet and Taft's electron pair donating ability β , hydrogen bonding ability α and polarity/polarisability π^* parameter.

$$\lambda_{\text{max}} = \lambda_{\text{max}}^0 + a\text{DN} + b\text{AN} + cE_{\text{T}}(30) + d\beta + e\alpha + f\pi^* \quad (1)$$

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 [39]. In this equation, λ_{max} is the value of the absorption maximum in the solvent under study and λ_{max}^0 is the value of the absorption maximum in an inert solvent. DN, AN, $E_{\text{T}}(30)$, β , α and π^* represent independent but complementary solvent parameters, which account for the different solute/solvent interaction mechanisms and defined in the introduction section. a , b , c , d , e and f values are the regression coefficients describing the sensitivity of the property λ_{max} to the different solute/solvent interaction mechanisms. A final set of selected equations was examined for stability and validity by stepwise method through a variety of statistical methods. The results of the correlation of the absorption frequencies with solvent parameters are illustrated in Table 3. As the data show the DN parameter has a dominate contribution on the shift of the absorption maxima of the complex. The contribution of the other solvent parameters was rejected based on the statistical criteria explained in the experimental section.

To estimate the quality of the proposed model for the complex with regard to predictive ability of the model, the cross-validation statistical technique was carried out. The cross-validation methodology is essential since a model with good statistics values necessarily do not have a good prediction potential. The simplest and the most general cross-validation procedure is the leave-one-out technique (LOO technique) [40]. This method uses cross-validated parameters: PRESS (predicted residual sum of squares), $\text{PRESS} = \sum(Y_{\text{pred}} - Y_{\text{exp}})^2$; SSY (total sum of squares deviation), $\text{SSY} = \sum(Y_{\text{exp}} - Y_{\text{mean}})^2$; Q^2 as the cross validation squared coefficient, $Q^2 = 1 - \text{PRESS}/\text{SSY}$, and R_{pre}

Table 2. The Solvent Parameter Values and Electronic Absorption Maxima of the Complexes in Solvents Studied: λ_{\max}/nm ($\epsilon/l \text{ cm}^{-1} \text{ mol}^{-1}$)

Solvent	DN	AN	β	α	π^*	$E_T(30)$	Complex 1	Complex 2	Complex 3
DCM	0.0	20.4	0.1	0.13	0.82	40.7	537(80)	683(150)	722(158)
1,2-DCE	0.0	16.2	39.4	0.1	0.1	0.48	537(102)	672(138)	- ^a
CH ₃ Cl	0.0	23.1	39.1	0.1	0.2	0.58	525(85)	668(115)	733(102)
NM	2.7	20.5	0.06	0.22	0.85	46.3	525(85)	641(126)	733(101)
NB	4.4	14.8	0.3	0.0	1.01	41.5	527(88)	- ^a	- ^a
BN	11.9	15.5	0.37	0.0	0.9	41.5	571(83)	- ^a	- ^a
An	14.1	18.9	0.4	0.19	0.75	45.6	578(88)	640(150)	703(122)
PN	16.1	16.0	0.39	0.0	0.71	43.6	576(98)	644(146)	723(105)
Ac	17.0	12.5	0.43	0.08	0.71	42.2	592(84)	696(156)	735(95)
THF	20.0	8.0	0.55	0.0	0.58	37.4	592(79)	596(156)	709(85)
EtOH	22.9	37.1	0.75	0.86	0.54	51.9	603(94)	602(109)	699(96)
MeOH	23.3	41.3	0.66	0.98	0.6	55.4	596(92)	586(108)	678(97)
DMF	26.6	16.0	0.69	0.0	0.88	43.8	612(75)	652(87)	733(90)
DMSO	29.8	19.3	0.76	0.0	1.0	45.1	621(81)	620(128)	707(64)
Py	33.1	14.2	0.64	0.0	0.87	40.5	651(79)	707(119)	- ^a
HMPA	38.8	10.6	1.05	0.0	0.87	40.9	656(84)	693(101)	746(107)

^aInsoluble.

(correlation coefficient of experimental versus predicted results), where Y_{pred} : predicted, Y_{exp} : experimental, Y_{mean} : mean values of the target properties (λ_{\max}), respectively. PRESS is an important cross-validation parameter as it is a good approximation of the real predictive error of the models. Its value being less than SSY points out that the model predicts better than chance and can be considered statistically significant. As the results showed in Table 4, the present models have PRESS \ll SSY.

To be reasonable model, PRESS/SSY should be smaller than 0.4. In our case, PRESS/SSY is 0.022 indicating that the DN model for the complex is significant. To confirm our finding, λ_{\max} values predicted by Eq. (1) are compared with

the obtained λ_{\max} values. Within the experimental error, the value agrees well with donor number of solvents. Plots λ_{\max} (experimental) versus λ_{\max} (predicted) shown in Fig. 5 yield slopes that are close to 1 and reasonable correlation coefficients R_{pre} is obtained.

The solution color of compound 1 changes from green to blue as the DN of the solvent increase. However, the results show the position of the λ_{\max} values are shifted to lower energy as the donor number of the solvent increases indicating a negative solvatochromism or red shift. The diagram of regression analysis of λ_{\max} values against DN parameter of solvents (Fig. 6) confirms the good linear correlation of the complex with DN parameter and also

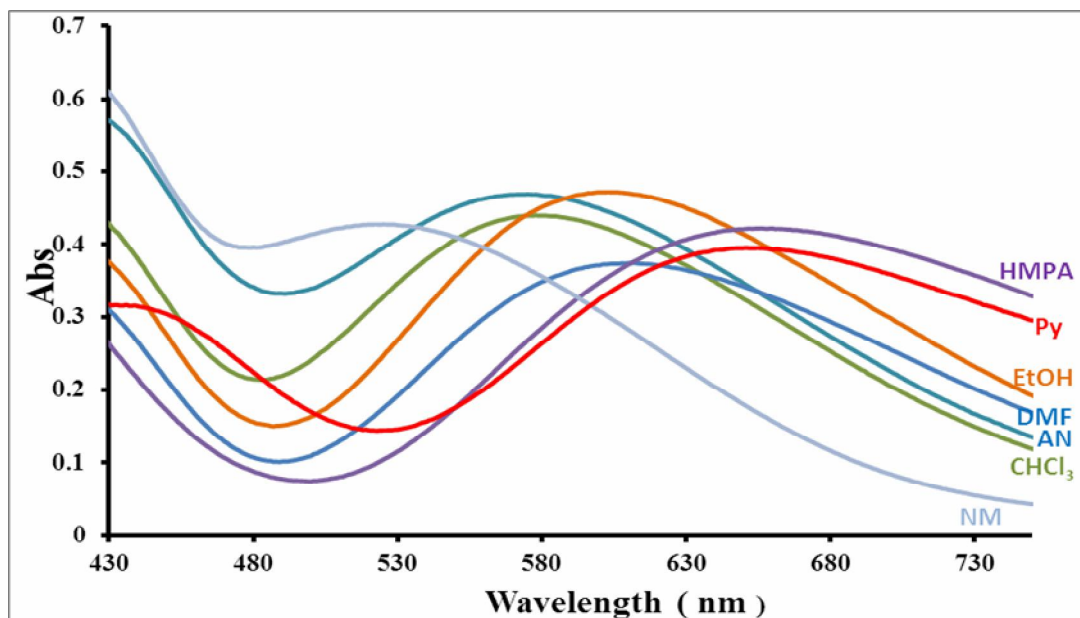


Fig. 4. Absorption spectra of complex 1 in selected solvents. Absorption spectra in other solvents are omitted for clarity.

Table 3. The Equation Resulted from the Linear Correlation of the λ_{\max} Values with DN of the Solvents^a

Complexes	Equations	F	R	S.E.	$\Delta\lambda_{\max}$ (nm)
1	$\lambda_{\max} = 3.471 (\pm 0.199) \text{DN}_{\text{solv}} + 522.366 (\pm 4.316)$	304	0.981	8.268	131

^aThe number of variables, n = 14.

Table 4. The Quality of the Obtained models by Means of Q^2 , PRESS and PRESS/SSY and Predictive Correlation Coefficient (R_{pre}) for Complex 1^a

Q^2	PRESS	PRESS/SSY
0.9780	1253.21	0.02175
$\lambda_{\max} \text{ experimental} = 0.9565 \lambda_{\max} \text{ predicted} + 25.335$		
$R_{\text{pre}} = 0.9707$		

^aThe number of variables, n = 14.

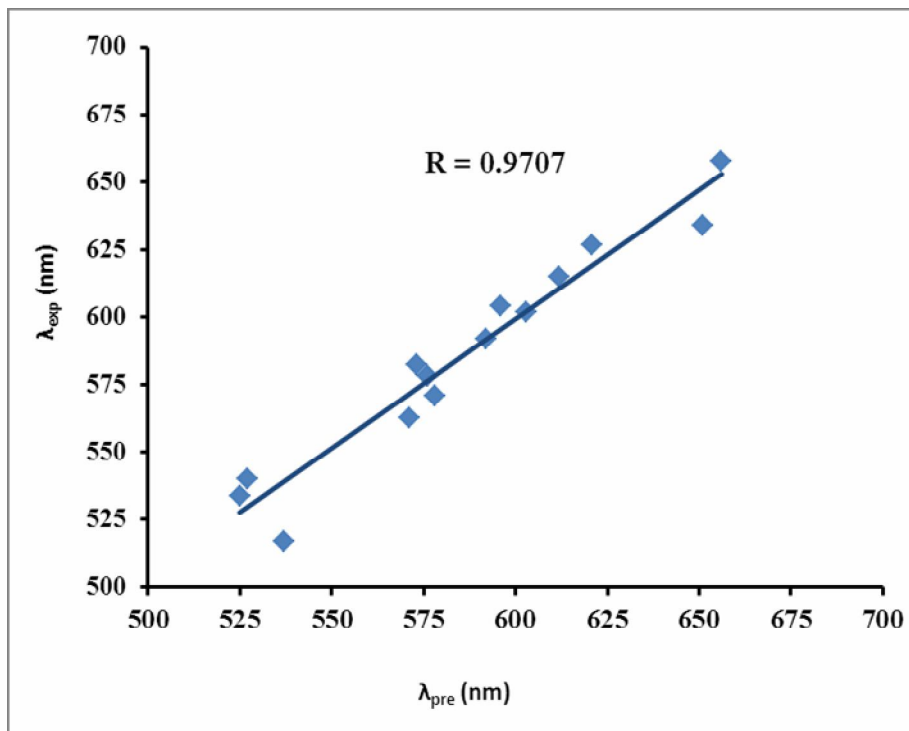


Fig. 5. The plots of observed λ_{max} values against calculated λ_{max} values for complex 1.

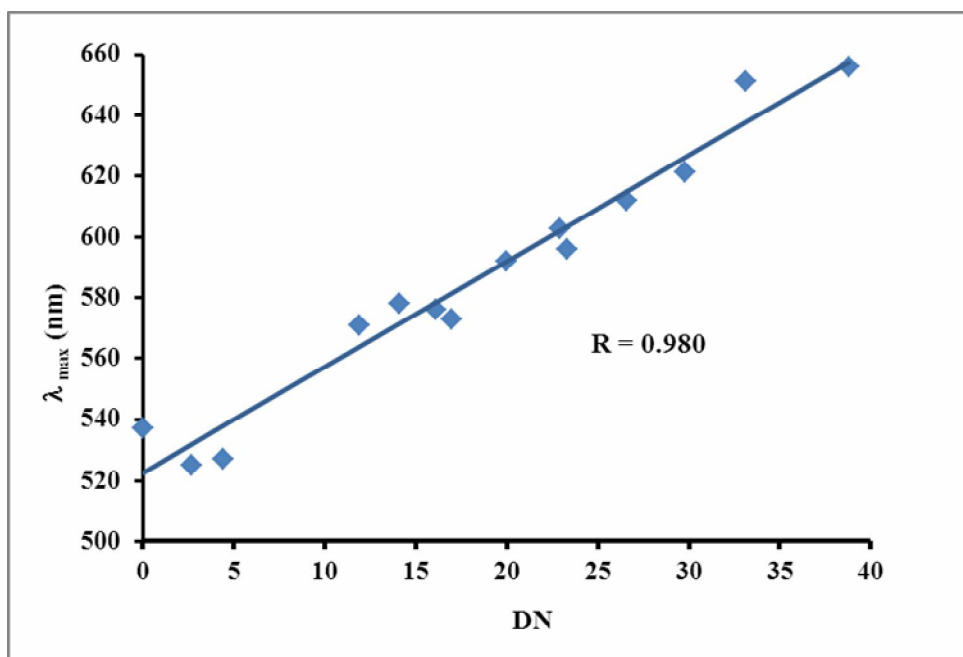


Fig. 6. Dependence of the λ_{max} values of compound 1 on the solvent DN values.

serves as a good evidence of the solvatochromic behavior of the complex.

In the solution, the metal center is attacked by solvent molecules to the axial sites of the complex by ejection of the weakly bonded counter ion ClO_4^- or water molecule. Therefore, all the d_{xy} , d_{yz} and d_{xz} orbitals of the Cu(II) ion are raised up by its interaction with polar solvent molecules approaching from above and below of the molecular plane, the broad d-d transition band of the complex moves to the red with the increase of the DN of the solvent. However in case $[(\text{tmen})\text{Cu}(\text{dike})\text{H}_2\text{O}]\text{X}$, where $\text{X} = \text{Cl}^-$ or Br^- , halide ion bonds to the axial site of the copper(II) ion but it is not so strong due to presence of Jahn-Teller effect in copper(II) ion with d^9 configuration. Thus, only the solvent molecule with high donor power such as ethanol, methanol, DMF, DMSO, Py and HMPA are able to remove it. These complexes are solvatochromic in limited solvents with high donor numbers.

CONCLUSIONS

Three new heteroleptic copper(II) complexes $[\text{Cu}(\text{dike})(\text{tmen})\text{H}_2\text{O}]\text{X}$ ($\text{X} = \text{ClO}_4^-$, Cl^- and Br^-) were prepared and were studied in solution. The complex where $\text{X} = \text{ClO}_4^-$ is more solvatochromic than others. Its solvatochromism was 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 this complex. The complex demonstrated negative solvatochromism due to coordination of solvent molecules with different donor power to the axial sites of the copper(II) ion which changed the geometry of the complexes from square planar to octahedron. It was also understood that the solvatochromic behavior of the complexes depends upon two main factors, the coordination ability of solvents and counter ions. In case where $\text{X} = \text{Cl}^-$ or Br^- , the halide anion bonds to the axial site of the copper(II) ion firmly and only solvent molecules with high donor power are able to remove it. As a result, these complexes are solvatochromic in high DN solvents.

ACKNOWLEDGEMENTS

We are grateful for the financial support of University of Mazandaran of the Islamic Republic of Iran.

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