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Solvatochromism Study on the Copper(II) Complexes Containing 3–Substituted Derivatives of Acetylacetonate Ligands

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Abstract: Solvatochromic properties of a series of bis(3–substituted derivatives of acetylacetone)copper(II) (X-acacH , X = Cl, H. CH₃) complexes were studied. All the complexes demonstrated negative solvatochromism. Among the complexes the Cu(Cl-acac)₂, demonstrated the most solvatochromism. A multi-parametric equation has been utilized to explain the solvent effect on the d-d transition of the complexes 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 solvatochromism of the compounds.
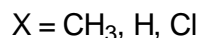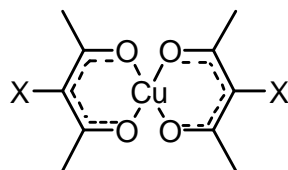
INTRODUCTION

The phenomenon of solvatochromism which refers to changes in electronic absorption spectra with solvent is one of the important topics in solution chemistry. Although most, if not all, complexes are solvatochromic to some extent, the term is usually applied to species that demonstrate shift in energy of at least a few hundred wavenumbers with variation in solvent. There are many useful application for this phenomenon in analytical and industrial purposes such as use in Lewis acid-base color indicator [1, 2], imaging [3-6], photo-switching [7-9] and sensor materials [10] and also utilizes to develop optical sensor materials to monitor pollutant levels in the environment [11, 12]. Among the solvatochromic metal complexes the 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. There are different solvent parameters to describe the interaction between 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) [13], Mayer and Gutmann's acceptor number, AN (the electron acceptor property of a solvent) [14], Dimroth and Reichardt's $E_T(30)$ (a measure of the ionization power of a solvent) [15], 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) [16] and π* (polarity/polarisability parameter of solvent) [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. Thus several computational methods for correlation of the experimentally observed quantities to the solvent properties have been developed to study the solvatochromic effect [18]. One of the statistical methods is stepwise multiple linear regression (SMLR).

We have been interested in the solvatochromism of the mixed-chelate copper(II) complexes incorporating diketonate ligands for a number of years [19-26]. During our studies it was found that bis(diketonate) copper(II)

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X = CH₃, H, Cl

Scheme 1: The complexes under study.

complexes show interesting solvatochromism. Although these kinds of complexes were prepared long time ago [27] and their structures were well established [28-30], based on our knowledge their solvatochromism have not been investigated yet. As a result, herein we report the solvatochromism study of [Cu(X-acac)₂] complexes in which X-acac stands for 3–substituted derivatives of acetylacetonate with different electronic properties as shown in Scheme 1.

Experimentl: The complexes of [Cu(X-acac)₂] were prepared according to published procedures [31]. 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.

The electronic absorption spectra were measured using a Braic2100 model UV-Vis spectrophotometer.

Data 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 [32]. 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). Multiple linear regression of a dependent variable Y_s, with a series of explanatory variable X_1, X_2, X_3, etc., in Equation (2) is a well-established model. The variable Y_s is the solvent-dependent property (v_{max} in this study) in a given solvent, Y_o the statistical quantity representing the value of the property in the reference solvent (dichloromethane), X_1, X_2, X_3, etc. (explanatory variable) represent independent but complementary solvent parameters which account for the solute-solvent interaction mechanism and a_1, a_2, a_3, etc. are the regression coefficients describing the sensitivity of property Y_s to the different solute-solvent interaction mechanism. That is suitable selection of bulk and molecular properties of solvents constitute of linear or multiple regression analysis model equations.

$$Y_s = Y_0 + a_1X_1 + a_2X_2 + a_3X_3 \ldots + a_nX_n \qquad (1)$$

The solvent properties investigated are Dimroth and Reichardt's $E_T(30)$, Kamlet and Taft's α, β, π*, Gutmann's donor DN and acceptor number AN.

In this report a stepwise multiple linear regression (SMLR) method was used to generate the best models of the solvent parameters using SPSS/PC software package [33]. The stepwise method involves three main steps 1) identifying an initial model, 2) changing the model at the previous step by adding or removing a parameter and 3) obtaining the best model when stepping is no longer possible and all the parameters reviewed and evaluated to specify which one contributes the most to the equation [34]. The variance of the data in this procedure plays a main role so that when a new parameter is entered into the equation its value changes. When the importance of a parameter with entering new data decreases the stepwise method removes the weakened parameter. This procedure continues till a final equation is obtained. The final equation is also tested for stability and validity of the results by the computer program itself. The appropriate equation is selected by considering four criteria, namely, multiple correlation coefficients (R), standard error (S.E.), F-statistic and the number of parameters in the model (N). The best model is the one with higher R and F-values, lower standard error, the least number of parameters and high ability for prediction [35]. 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.

RESULTS AND DISCUSSION

All the complexes are easily soluble in a wide range of organic solvents. The presence of a strong Jahn-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. The positions of the v_{max} values of the complexes along with the molar absorptivities are collected in Table 1. As the results illustrate, the energy change on the absorption spectra of compounds is as large as 4030 -3130 cm⁻¹ over the solvents studied. The greatest solvatochromic effect is displayed by complex [Cu(Cl-acac)₂] (4030 cm⁻¹).

Table 1: Electronic absorption maxima of the complexes in various solvents: $v_{max}/10^3\,cm^{-1}$ ($\varepsilon/M^{-1}cm^{-1}$)

Solvent	Cu(Cl-acac)$_2$	Cu(H-acac)$_2$	Cu(CH$_3$-acac)$_2$
Dichloromethane (DCM)	18.52 (40.4)	18.35 (32.7)	18.28 (60.5)
Nitrobenzene (NB)	18.32 (40.0)	18.25 (32.6)	18.02 (81.8)
Benzonitrile (BN)	16.45 (56.8)	16.23 (40.3)	16.08 (58.5)
Acetone (AC)	16.39 (62.0)	15.92 (46.8)	16.03 (65.7)
Tetrahydofuran (THF)	16.34 (61.4)	15.60 (45.3)	15.92 (60.3)
Ethanol (EtOH)	16.03 (52.2)	15.34 (40.3)	15.87 (57.5)
Methanol (MeOH)	16.00 (52.3)	15.06 (59.1)	15.72 (53.4)
Dimethylforamide (DMF)	15.67 (78.9)	15.20 (56.5)	15.46 (67.9)
Dimethylsulfoxide (DMSO)	15.29 (67.8)	14.93 (59.4)	15.80 (77.0)
Pyridine (Py)	14.88 (87.3)	14.53 (76.8)	15.65 (74.2)
Hexamethylphosphorictriam (HMPA)	14.49 (47.7)	14.73 (50.2)	15.15 (54.4)

Table 2: The solvent parameter values.

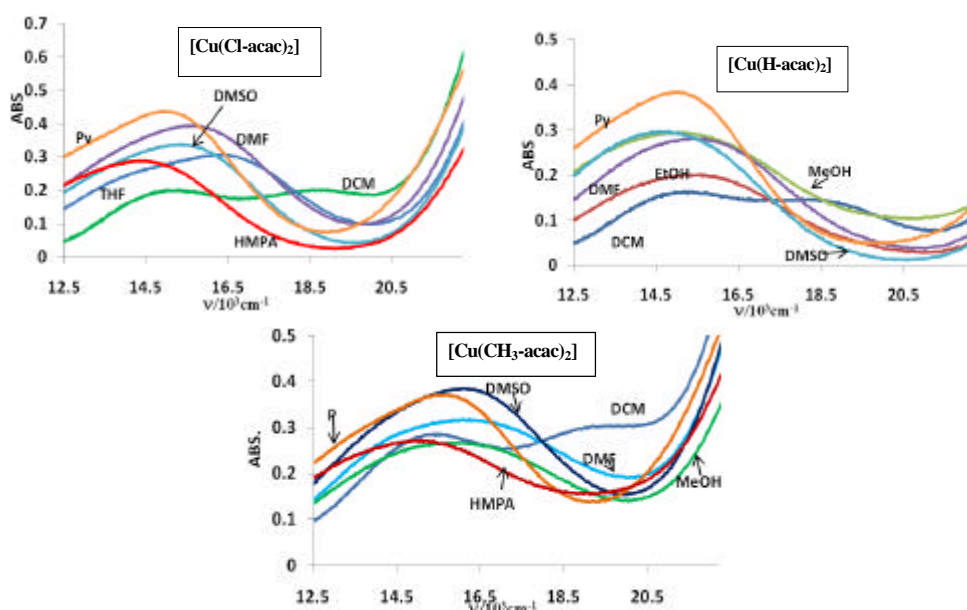| Solvent	DN	AN	β	α	E$_T$(30).	π*
DCM	0.0	20.40	0.10	0.13	40.7	0.82
NB	4.4	14.80	0.30	0.00	41.5	1.01
BN	11.9	15.50	0.37	0.00	41.5	0.90
Ac	17.0	12.50	0.43	0.08	42.2	0.71
THF	20.0	8.00	0.55	0.00	37.4	0.58
EtOH	22.9	37.10	0.75	0.86	51.9	0.54
MeOH	23.3	41.30	0.66	0.98	55.4	0.60
DMF	26.6	16.00	0.69	0.00	43.8	0.88
DMSO	29.8	19.30	0.76	0.00	45.1	1.00
Py	33.1	14.20	0.64	0.00	40.5	0.87
HMPA	38.8	10.6	1.05	0.00	40.9	0.87

Fig. 1: Absorption spectra of the complexes in selected solvents. Absorption spectra in other solvents are omitted for clarity.

To explore the solvent effects on the absorption spectra of the complexes, the absorption frequencies (v_{max}) were correlated with the solvatochromic Equation (1). Hence, The frequencies of the d-d absorption transition band (v_{max}) of each complexes in various solvents with their own solvent parameters shown in Table 2 were offered in Equation (1) 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, hydrogen bonding ability α, Reichardt's E$_T$(30) and π*.

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

Complexes	Equations	F	R	S.E.	Δv_{max} (cm^{-1})
Cu(Cl-acac)$_2$	$v_{max}/10^3$= -0.104($\pm$0.008)DN$_{solv}$ + 18.370($\pm$0.181)	184.274	0.976	0.286	4.03$\times$10^3
Cu(H-acac)$_2$	$v_{max}/10^3$= -0.105($\pm$0.013)DN$_{solv}$ + 18.001($\pm$0.300)	67.780	0.94	0.457	3.82$\times$10^3
Cu(CH$_3$-acac)$_2$	$v_{max}/10^3$= -0.076($\pm$0.013)DN$_{solv}$ + 17.762($\pm$0.302)	35.523	0.893	0.4788	3.13$\times$10^3

Table 4: The quality of the obtained models by means of Q^2, PRESS and PRESS/SSY and predictive correlation coefficient (R_{pre}).

Compound	Q^2	PRESS	PRESS/SSY
Cu(Cl-acac)$_2$	0.9223	1.23	0.077
	v_{max} experimental = 0.9812v_{max} predicted +0.3374		
	R_{pre} = 0.961		
Cu(H-acac)$_2$	0.8226	3.08	0.1773
	v_{max} experimental = 1.004 v_{max} predicted + 0.049		
	R_{pre} =0.912		
Cu(CH$_3$-acac)$_2$	0.715	2.91	0.285
	v_{max} experimental = 1.098 v_{max} predicted -1.502		
	R_{pre} =0.853		

$$v_{max} = v^{\circ}_{max} + a\,DN + b\,AN + c\,\beta + d\,\alpha + d\ E_T(30) + e\,\pi^*$$
(2)

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

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, [36] are presented in Table 4. The parameters in Table 4 are defined as: PRESS as the predictive residual error sum of squares, PRESS = $\sum(Y_{pred} - Y_{exp})^2$; SSY as the 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}: predicted, Y_{exp}; experimental, Y_{mean}; mean values of the target properties (v_{max}), respectively.

As the results showed in Table 4, good cross-validation Q^2 values were obtained ($Q^2 > 0.70$; $Q^2 = 0.72$ - 0.92). PRESS is 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 be reasonable model, PRESS/SSY should be smaller than 0.4. In our case, PRESS/SSY ranges between 0.285-0.077, indicating that

the DN model for complexes is significant. To confirm our finding, v_{max} values predicted by Equation (1) are compared with the obtained v_{max} values. Within the experimental error, the value agrees well with donor number of solvents. The plots obtained from v_{max} (experimental) against v_{max} (predicted) values are shown in Fig. 2.

According to the results obtained, the DN parameter of the solvent has a dominate contribution in Equation (1) for compounds 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 dz^2 orbital of the copper(II) ions and the electron pair of the solvents and hence decreasing the energy require to transfer 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.

In the series of the complexes the shifts induced in a given solvent depend upon the electronic properties of substituent group of X in X-acac 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. Introducing an electron-attracting (X = Cl) or electron-releasing (X = CH$_3$)
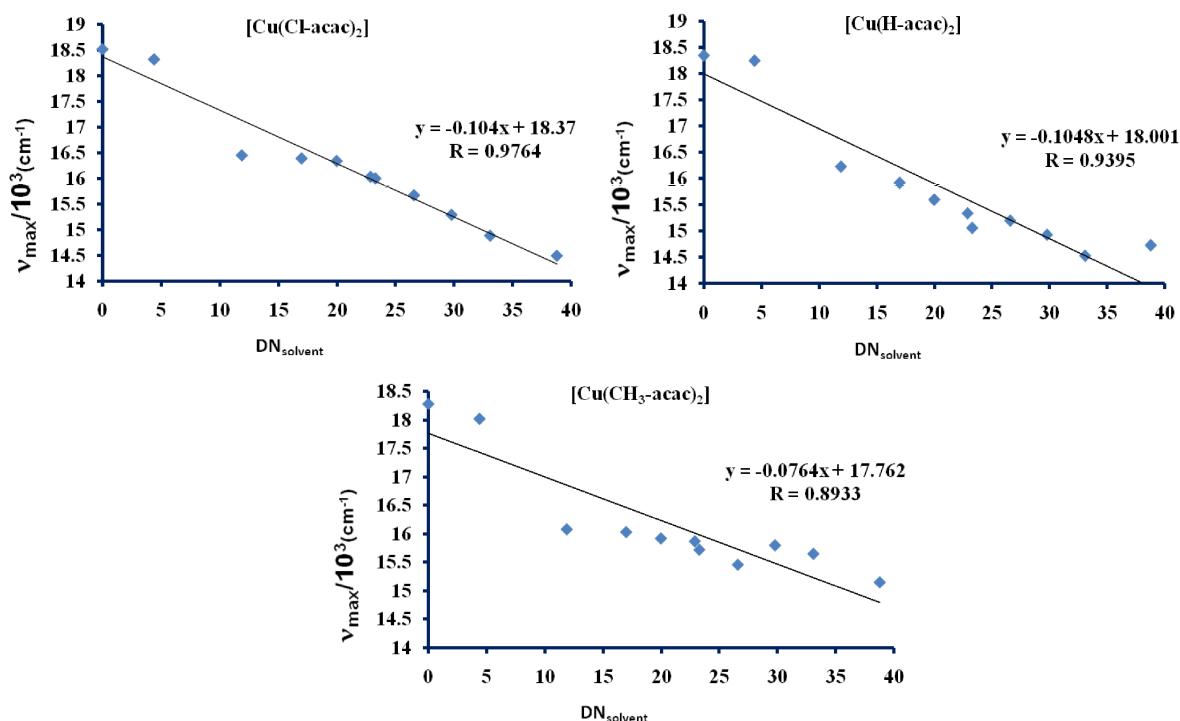
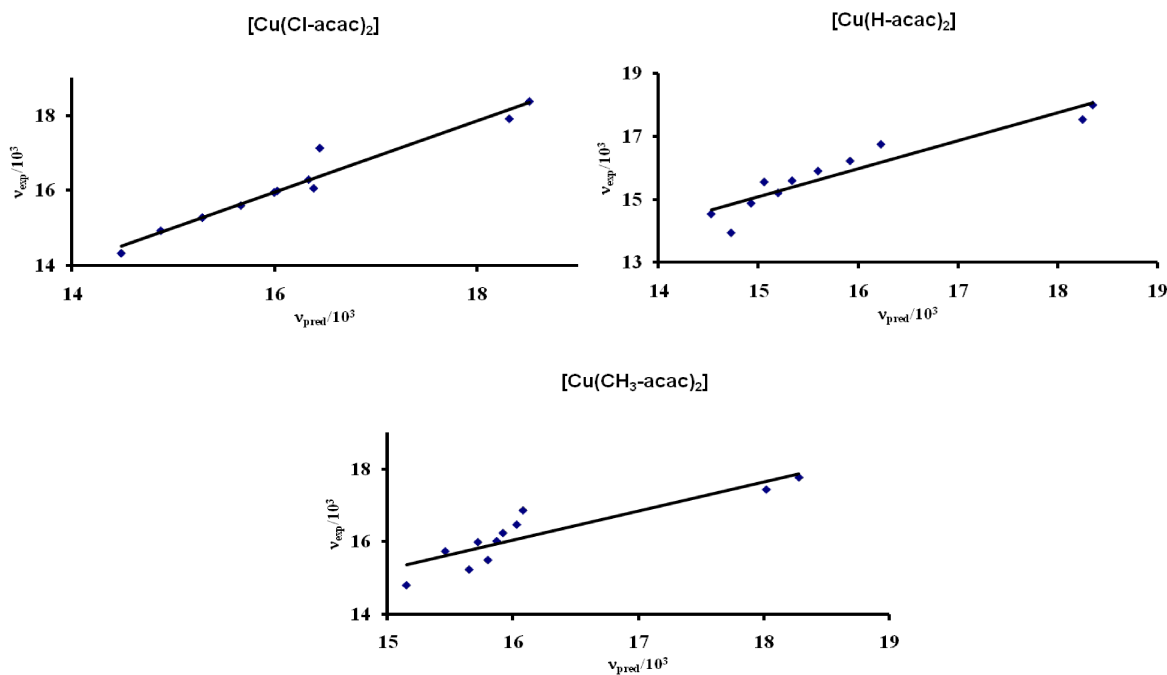Fig. 2: Dependence of the v_{max} values of complexes on the solvent DN values.

Fig. 3: The plots of the observed v_{max} values against the calculated v_{max} values for complexes.

substituent on the acac chelate alters the Lewis acidity of CuO_4 chromophore and consequently, its equatorial ligand field strength. In other words, presence of Cl-acac chelate 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 1 the v_{max} values in one particular solvent decreases in the following order of acac chelate. Cl-acac>H-acac>CH$_3$-acac.

It is clear from Fig. 1 that the spectra in non-coordinating solvents such as dichloromethane and nitrobenzene two absorption maxima are observed while in coordinating solvents only an absorption maximum with non-Gaussian profile is detected. Thus, it can be reasonable to assume a square planar geometry for complexes in non-coordinating solvents in which causes two d-d transitions as $d_{xy} \rightarrow d_{x^2-y^2}$ and $(d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2}$ whereas, in coordinating solvents an octahedral coordination geometry contributes to the molecular structure in solution, merging two absorption bands into a non-Gaussian profile as a result of the Jahn-Teller effect.

CONCLUSION

The solvatochromic properties of bis (diketonate) copper (II) complexes were studied in solution. Their solvatochromism behaviors were examined with different solvent parameters using SMLR computational method. The statistical evaluation of the data (R, S. E., F-test, Q^2 and PRESS/SSY) indicated that the DN parameter of the solvent plays the most important role in the solvatochromic behavior of the complexes. It was found that the solvatochromic behavior of the complexes depends upon two main factors, the coordination ability of solvents and the nature of electronic properties of the substituent of X in the X-acac moiety. All complexes demonstrated negative solvatochromism due to coordination of solvent molecules with different donor power to the axial site of the copper(II) ion in which resulted change in the geometry of the complexes from square planar to octahedron in solution. Among the complexes investigated the $Cu(Cl-acac)_2$, displayed highest Δv_{max} value ($\Delta v_{max} = (v_{max})_{DCM} - (v_{max})_{HMPA}$).

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REFERENCES

1. Sone, K., Y. Fukuda, H. Tanaka, H. Ohtaki and R. Tamamushi, 1983. Ions and Molecules in Solution; Elsevier (Eds.) Amsterdam, pp: 251.

2. Miyamoto, K., M. Sakamoto, C. Tanaka, E. Horn and Y. Fukuda, 2005. Syntheses, Structures, Spectroscopic Properties and Thermal Behavior of Nickel(II) Mixed-Ligand Complexes with *N,N,N',N'*-Tetramethylethylenediamine, Benzoylacetonate and a Halide Anion. Bull Chem. Soc. Jpn, 78(6): 1061-1071.

3. Yamamoto, R. and T. Maruyama, 1994. Jpn. Kokai Tokyo Koho, JP: 06073169.

4. Masuda, Y. and F. Inatsugu, 1975. Jpn. Kokai Tokyo Koho, JP: 50121176.

5. Golden, M.L., J.C. Yarbrough, J.H. Reibenspies, N. Bhuvanesh, P.L. Lee, Y. Zhang and M.Y. Darensbourg, 2004. In the Proceedings of the 2004, 228th ACS National Meeting, Philadelphia, PA, United State, August pp: 22-26.

6. Fontan, C.A. and R.A. Olsina, 1989, Talenta. 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene as a metallochromic indicator for the complexometric determination of Cu(II) with EDTA, 36(9): 945-949.

7. Sato, O., 2003. Optically Switchable Molecular Solids:? Photoinduced Spin-Crossover, Photochromism and Photoinduced Magnetization Acc. Chem. Res., 36(6): 692-700.

8. Marder, S.R. and J.W. Perry, 1994. Nonlinear Optical Polymers: Discovery to Market in 10 Years. Science. 263(5154): 1706-1707.

9. Sato, O., S. Hayami, Y. Einaga and Z.Z. Gu, 2003. Control of the Magnetic and Optical Properties in Molecular Compounds by Electrochemical, Photochemical and Chemical Methods. Bull. Chem. Soc. Jpn, 76(3): 443-470.

10. Schanze, K.S. and R.H. Schmehl, 1997. Applications of Inorganic Photochemistry in the Chemical and Biological Sciences - Contemporary Developments. J. Chem. Educ., 74(6): 633-636.

11. Sone, K. and Y. Fukuda, 1987. Inorganic Thermochromism in: Inorganic Chemistry concepts, Springer: Berlin/Heidelberg.

12. Meinershagen, J.L. and T. Bein, 2001. Solvatochromism of a Copper(II) (Tetramethylethylenediamine)-(acetylacetonate)$^+$ Complex Encapsulated in EMT Zeolite Cages. Adv. Mater., 13(3): 208- 211.

13. Gutmann, V., 1978. The Donor-Acceptor Approach to Molecular Interactions, Plenum Press: New York.

14. Mayer, U., V. Gutmann and W. Gerger, 1975. The acceptor number - A quantitative empirical parameter for the electrophilic properties of solvents. Monatsh. Chem., 106(6): 1235-1257.

15. Reichardt, C., 1994. Solvatochromic Dyes as Solvent Polarity Indicators . Chem. Rev., 94(8): 2319-2358.

16. Marcus, Y., 1993. The properties of organic liquids that are relevant to their use as solvating solvents .Chem. Soc. Rev., 22(6): 409-416.

17. Laurence, C., P. Nicolet, M. T.Dalati, J.L.M. Abboud and R. Notario, 1994. The Empirical Treatment of Solvent-Solute Interactions: 15 Years of .pi.* .J. Phys. Chem. 98(23): 5807-5816.

18. Dorohoi, D.O., A. Airinei and M. Dimitriu, 2009. Intermolecular interactions in solutions of some amino-nitro-benzene derivatives, studied by spectral means, Spectrochim. Acta, 73(2): 257-262.

19. Golchoubian, H. and E. Rezaee, 2009. Chromotropism of a new mixed chelate copper(II) complex J. Mol. Struct., 927(1-3): 91-95.

20. Movahedi, E. and H. Golchoubian, 2006. Substituent and solvent effects in the spectra of new mixed-chelate copper (II) complexes containing N,N' disubstituted ethylenediimine and acetylacetonate ligands . J. Mol. Struct., 787(1-3): 167-171.

21. Asadi, H., H. Golchoubian and R. Welter, 2005. Synthesis, Structural and Solvent Influence Studies on Solvatochromic of Acetylacetonatocopper(II) with N,N'-Dibenzylic or Thiophene Derivatives of Ethylenediamine Complexes. J. Mol. Struct., 779(1-3): 30-37.

22. Golchoubian, H. and E. Rezaee, 2009. Substituent Effect in the (–position of Acetylacetonate on the Solvatochromic Property of Mixed-chelate Copper(II) Complexes Consisting of Diamine and Acetylacetonate Ligands. J. Mol. Struct., 929(1-3): 154-158.

23. Golchoubian, H. and R.Z. Zarabi, 2009. Syntheses, Crystal Structure and Chromotropic Properties of Dinuclear Copper(II) Complexes of Tertiary Diamine with Hydroxo Bridge .Polyhedron, 28(17): 3685-6390.

24. Golchoubian, H., E. Rezaee, G. Bruno and H.A. Rudbari, 2011. Synthesis and solvatochromism studies of new mixed-chelate dinuclear copper(II) complexes with different counter ions. Inorg. Chim. Acta., 366(1): 290-297.

25. Golchoubian, H., O. Nazari and B. Kariuki 2011. Synthesis, Structure and Solvatochromism Studies on Copper (II) Complexes Containing Ethylenediamine, Pyridine and Imidazol Ligands. J. Chin. Chem. Soc., 58(2): 60-68.

26. Golchoubian, H., G. Moayyedi, G. Bruno and H.A. Rudbari, 2011. Syntheses and characterization of mixed-chelate copper(II) complexes containing different counter ions; spectroscopic studies on solvatochromic properties. Polyhedron 30(6): 1027-34.

27. Fernelius, W.C. and B.E. Bryant, 1957. Mixed benzohydroxamato-acetylacetonato metal complexes: spectral, thermal and photochemical behaviour. Inorg. Synth., 5: 105- 113.

28. Golchoubian, H., 2008. Redetermination of Crystal Structure of Bis(2.4-pentanedionato) Copper(II). Asian J. Chem., 20(1): 5834-5838.

29. Starikova, Z.A. and E.A. Shugam, 1969. Determination of Crystal Structure of Bis(2.4-pentanedionato) Copper(II). Zh. Strukt. Khim., 10 :290-293.

30. Lebrun, P.C., W.D. Lyon and H.A. Kuska, 1986. Crystal Structure of Bis(2,4-pentanedionate) Cu(II). J. Crystl. Spectro. Res., 16: 889-893.

31. Peacock, R.D., 1971. The preparation and investigation of bis(acetylacetonato) copper(II) . J. Chem. Educ., 48(2): 133-136.

32. Gutmann, V., 1968. Coordination Chemistry in Non-aqueous Solutions, Springer: Vienna.

33. SPSS/PS, 1998. Statistical package for IBMPC, Quiad software version 13, Ontario.

34. Darlington, R.B., 1990. Regression and Linear Models, McGraw-Hill: New York.

35. Riahi, S., M.F. Mousavi and M. Shamsipur, 2006. Prediction of selectivity coefficients of a theophylline-selective electrode using MLR and ANN, Talanta, 69(3): 736-740.

36. Roy, K. and P.P. Roy, 2009. Comparative chemometric modeling of cytochrome 3A4 inhibitory activity of structurally diverse compounds using stepwise MLR, FA-MLR, PLS, GFA, G/PLS and ANN techniques. Eur. J. Med. Chem., 44(7): 2913-2922.