

# Dinuclear Copper(II) Complex of Containing *N,N*-diisopropyl,*N'*-3-propylamide-ethylenediamine, and Dihydroxo Bridge; Solvatochromic and Thermo-chromic

Heidarian, Asieh; Golchoubian, Hamid\*<sup>+</sup>

Department of Chemistry, University of Mazandaran, Babolsar, I.R. IRAN

**ABSTRACT:** The synthesis and characterization of a dinuclear  $[LCu(\mu-OH)_2CuL](ClO_4)_2$ , complex with a tridentate *N,N*-diisopropyl,*N'*-3-propylamide-ethylenediamine hemilabile ligand (abbreviated L) is reported. The dinuclear complex was characterized by elemental analysis, molar conductance, thermal analysis, and spectral studies. In the complex, both copper centers are 5-coordinated and bridged through two hydroxo groups. Thermo- and solvatochromic behaviors of the complex were investigated by visible spectroscopy. Its reversible thermo-chromism (blue  $\leftrightarrow$  green) in acetonitrile solution is due to dissociation and re-coordination of Cu-O(amide) moiety. The solvent-dependent absorption maxima,  $\lambda_{max}$ , was studied by a Stepwise Multiple Linear Regression (SMLR) analysis to determine the best model describing the resulting positive solvatochromism. The statistical results demonstrated that among different solvent parameters, Donor Number (DN) is a dominant parameter that is responsible for the redshift in the d-d absorption band of the complex by increasing its values.

**KEYWORDS:** Dinuclear complex; Solvatochromism; Thermo-chromism; Tridentate ligand; Hydroxy bridge.

## INTRODUCTION

Development of molecular devices responding to an external stimulus such as solvent (solvatochromism), temperature (thermo-chromism), pressure (piezochromism), light (photochromism), or electrons (electrochromism) have received much attention due to their wide potential applications in biological systems [1] molecular switches [2], thermosensitive [3], imaging [4], photo-switching [5], sensor materials [6] pollutant sensor [7] and Lewis-acid-base color indicator [8]. However, most of these activities have been primarily focused on organic molecules

and much less attention have been carried out on transition metal complexes. It was found that a combination of appropriate metal-ion and ligands provide metal-ion responsive chromotropic molecules [9,10]. Chromotropism defines as a reversible color change of the materials caused by the surrounding chemical or physical motivations as mentioned above. So far, the majority of chemotropism studies were focused on organic molecules and less attention have been involved to metal complexes. Miao *et al.* prepared Zinc(II) complex that shows reversible

\* To whom correspondence should be addressed.

+ E-mail: h.golchoubian@umz.ac.ir

1021-9986/2022/3/866-874

9/\$/6.04

thermochromism and shows selective sensing to  $\text{NH}_3$  gas [11]. On the other hand, Ohno and coworkers reported platinum(II) complex that the Pt–Pt intramolecular interaction induced luminescence vapochromism and thermochromism [12]. A multifunctional ZMOF based on an unorthodox polytopic ligand prepared by Kurup et al. demonstrated reversible thermochromism [13]. Also, an antiparasitic activity influenced by thermochromism was recently reported [14]. Also, 2-picolylamine-Ni(II) complex exhibited chemotropism [15]. Among chronotropic metal complexes whose color changes are attributed to d–d transitions, the copper(II) ion is the most encouraging candidate for practical applications because of having various geometrical structures, several coordination numbers, and the presence of a strong Jahn–Teller effect [16]. However, it has low intensities due to some degree of the forbidden nature of the d–d transition. This drawback can be partly improved by the symmetric dinuclear complexes. On the other hand, polydentate ligands were found to be promising nominees due to the high thermodynamic stability of the metal complexes, especially during an applied stimulus, because of their strong chelate effect. One class of polydentate ligands is the polyamine ligand which shows robust stability with late transition metals [17–19]. The incorporation of amide moieties in diamine ligands makes such ligands appropriate candidates to demonstrate hemilabile properties [20,21]. The hemilabile phenomenon in this class of ligands is significantly due to the inert nature of the amine moiety and the liability of the amide group. Their metal complexes have the potential to show reversible thermochromism properties at elevated temperatures. Recently we prepared mono- and dinuclear copper(II) complexes with diamine ligands that were chronotropic [22–24]. Herein, we synthesized a three dentate ( $\text{N}_2\text{O}$ ) ligand containing a hemilabile amide group attached to the amine nitrogen of the ethylenediamine derivative ligand and its five-coordinated copper(II) complexes that demonstrated solvato- and thermochromism properties.

## EXPERIMENTAL SECTION

### Material and measurements

All reagents were purchased from Merck and Fluka and used without further purification. The solvents used in the solvatochromism study were spectroscopic grade and as follows: nitromethane (NM), acetone (Ac),

acetonitrile (AN), methanol (MeOH), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and pyridine (Py). The elemental analyses were carried out at a LECO 600 CHN elemental analyzer. Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on the concentration of  $1.00 \times 10^{-3}$  M sample in selected solvents. Simultaneous TG and DTA analyses were carried out with a Stanton Redcroft, STA-780 series TG/DTA Thermal Analyzer employing an aluminum crucible under  $\text{N}_2$  atmosphere with a heating rate of 10 °C/min in the temperature range 24–600 °C. The IR spectra were obtained by using IR-grade KBr disks on FT-IR spectrophotometer in the range of 4000–400  $\text{cm}^{-1}$ . The electronic spectra were recorded in a Braic2100 model UV–Vis spectrophotometer using 1 cm quartz cells.

### Preparation of *N,N*-diisopropyl,*N'*-3-propylamide-ethylenediamine (L):

A mixture of acrylamide (1.78 g, 25 mmol) and 2-(diisopropylamino)ethyleamine (3.48 g, 20 mmol) in methanol (20 mL) was refluxed for 3h. The unreacted acrylamide was filtered off from the resulting solution. The solvent was removed under reduced pressure. The crude yellow oil was purified by vacuum distillation resulting in a pale-yellow oil. The resultant yellow oil was then dissolved in water (12 mL), the solution made alkaline by KOH (0.1 M) to raise the pH to 13, and was extracted with dichloromethane (6 × 6 mL). The combined  $\text{CH}_2\text{Cl}_2$  fractions were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent under reduced pressure resulted in the desired product as a yellow oil. The yield was 40% (1.72 g). Selected IR data ( $\text{v}/\text{cm}^{-1}$ ): 3341, 3193 (br. m, N-H str.), 2966 (m, C-H str. aliphatic), 2831 (m, N-CH- str.), 1674 (s, C=O str.), 1461 (m, C-N str.), 1393 (m, N-H bend.).  $^1\text{H}$  NMR (400 MHz in  $\text{CDCl}_3$ ),  $\delta$  (ppm): 0.91 (s, 6 H,  $(\text{CH}_3)_2\text{CH}$ -), 0.92 (s, 6 H,  $(\text{CH}_3)_2\text{CH}$ -), 2.30 (t, 2 H,  $J=6.0$  HZ,  $(\text{CH}_3)_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}$ -), 2.46 (s, 1 H,  $\text{NH}$ ), 2.50 (m, 4 H,  $-\text{NCH}_2\text{CH}_2\text{NH}$ - and  $-\text{NHCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}_2$ ), 2.80 (t, 2 H,  $J=6.0$  HZ,  $-\text{NHCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}_2$ ), 2.91 (m, 2 H,  $J=6.8$  HZ,  $(\text{CH}_3)_2\text{CHN}$ -), 6.23 (s, 1 H,  $\text{NH}_2$ ), 7.82 (s, 1 H,  $\text{NH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz in  $\text{CDCl}_3$ ),  $\delta$  (ppm): 20.76 ( $(\text{CH}_3)_2\text{CH}$ -), 35.31 ( $-\text{NHCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}_2$ ), 43.85 ( $-\text{NCH}_2\text{CH}_2\text{NH}$ -), 45.49 ( $-\text{NCH}_2\text{CH}_2\text{NH}$ -), 47.91 ( $(\text{CH}_3)_2\text{CH}$ -), 48.58 ( $-\text{NHCH}_2\text{CH}_2\text{C}(\text{O})\text{NH}_2$ ), 175.79 ( $-\text{C}(\text{O})\text{NH}_2$ ).

### Preparation of $[LCu(\mu-OH)_2CuL](ClO_4)_2$

The ligand L (0.645 g, 3 mmol) was dissolved in methanol (12 mL) and a solution of  $Cu(ClO_4)_2 \cdot 6H_2O$  (1.148 g, 3 mmol) in methanol (6 mL) were slowly added. The resulting greenish-blue solution was stirred for 20 min at ambient temperature. The desired compound precipitated from the solution as a violet solid which turns green after drying in a vacuum. The compound was recrystallized by diffusion of toluene into an acetonitrile solution that yielded violet crystals (1.068 g, 45%). Anal. calcd for  $C_{22}H_{52}N_6Cu_2Cl_2O_{12}$  (MW=790.68 g/mol): C, 33.42; H, 6.63; N, 10.63; Found: C, 33.51; H, 6.73; N, 10.67%. Selected IR data ( $\nu/cm^{-1}$  using KBr disk): 3676 (w, O-H str.), 3416 and 3285 (m, doublet,  $NH_2$  str), 3160 (m, N-H str), 2977 (m, C-H str.), 2926 (m, C-H str.), 1666 (s, C=O str.), 1460 (m, N-H bend.), 1118 (s, O- $ClO_3$  str.), 1083 (s, O- $ClO_3$  str.), 629 (m, O- $ClO_3$  bend.), 570 (w, Cu-O str.), 497(w, Cu-N str.).

### SMLR analysis

Multiple Linear Regression (MLR) is a statistical method used to analyze the correlation between a single response variable (dependent variable) with more controlled variables (independent variables) by means of Eq. (1). In this study, the response variable is absorption maxima ( $Y=\lambda_{max}$ ) while the empirical parameters of the solvent polarity ( $X_n$ ) are controlled variables and SPSS/PC software package was utilized to analyze the data [25]. The  $a_1, a_2, \dots, a_n$  are the regression coefficients explaining the sensitivity of the property Y to the different solute/solvent interactions and  $Y_0$  is the statistical quantity corresponding to the absorption maxima in the gas phase or in an inert solvent.

$$Y = Y_0 + a_1X_1 + a_2X_2 + \dots + a_nX_n \quad (1)$$

The aim of the analysis is to predict the most appropriate parameters in solvent-solute interaction. The Stepwise Multiple Linear Regression (SMLR) methods is used to generate a suitable model for predicting the effective solvent parameters using the SPSS/PC software package [25]. There are three methods in MLR that are forward selection, backward elimination, and stepwise regression. All these methods can be classified into stepwise-type processes. In this study, only the stepwise regression method was used. The stepwise regression method is a combination of forwarding selection and

backward elimination. This method provides the best feasible model over three basic steps, identifying an initial model, varying the model at the previous step by adding or eliminating a parameter and attaining the best model while stepping is no longer possible, and reviewing and assessing all the parameters to identify which one participates the most in the equation, this method provides the best conceivable model [26]. Four standard aspects are applied to verify the stability and validity of the achieved model, multiple correlation coefficients (R), Standard Error (S.E.), F-statistic, and the number of parameters in the model. The model with high R and F-values, low standard error, and the least number of parameters are found to be good models for prediction [27].

**CAUTION!** Although no difficulties were experienced during our research, perchlorate salts are potentially explosive compounds therefore, they should be handled carefully.

## RESULTS AND DISCUSSION

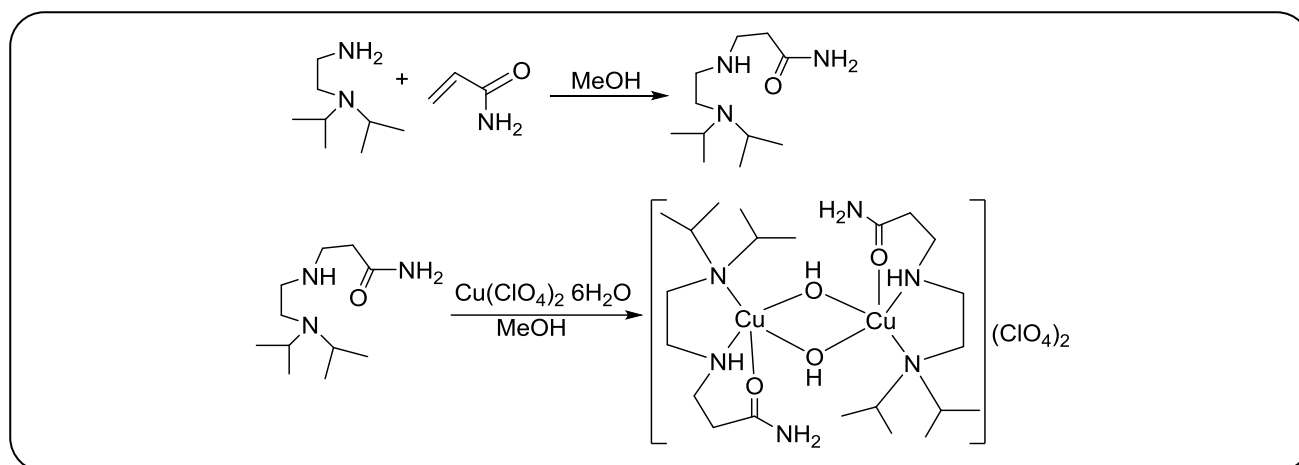
### Synthesis

The ligand was prepared in good yield by Michael's addition of *N,N*-diisopropylethylenediamine to acrylamide in methanol under reflux conditions. Accordingly, the treatment of  $Cu(ClO_4)_2 \cdot 6H_2O$  with the ligand in 1:1 mole ratio in methanol at room temperature resulted in the formation of a dinuclear complex in moderate yield (Scheme 1). It was established that the ligands containing diamine nitrogen-donor atoms with bulky substituents destabilize the formation of homoleptic bis-diamine complexes, but a bridging  $\mu$ -hydroxo dinuclear complex generates [28].

### Characterization

#### IR spectra

The IR spectra of the free ligand and complex are shown in supplementary content (Figs. S1 and S2). The free ligand has characteristic bands that are observed with minor shifts in the complex. The strong band observed in the IR spectrum of the free ligand at  $1674\text{ cm}^{-1}$ , showing a C=O amide group was shifted to higher frequencies ( $1666\text{ cm}^{-1}$ ) upon complexation. The narrow and intense band at  $3193\text{ cm}^{-1}$  and a broad and intense band at  $3341\text{ cm}^{-1}$  are associated with stretching vibrations of the amine (N-H) and amide ( $NH_2$ ) free ligand, respectively. Upon the formation of the chelate rings in the complex, the former band moves to the lower energy ( $3160\text{ cm}^{-1}$ ). As the lone



Scheme 1: The syntheses of the ligand and dinuclear complex.

pair of electrons of the donor nitrogen atom becomes involved in the metal-ligand bond, the transfer of electron density to the metal, and the subsequent polarization of the ligand involve electron depopulation of the N-H bond which culminates in a shift to lower energy [29]. However, the amide (NH<sub>2</sub>) stretching vibrations appear almost in the same region as the free ligand showing free from coordination in the dinuclear complex. The IR spectra of the free ligand and complex displayed bands with medium intensities at around 2900 and 2971 cm<sup>-1</sup> that are associated with the C-H stretching vibrations of the N-C(isopropyl) group [20]. The appearance of a band with medium intensity at 3285 cm<sup>-1</sup> in the complex can be assigned to the O-H stretching frequency of the hydroxo bridge [30]. At lower frequency, the complex demonstrated bands at 596 and 510 cm<sup>-1</sup> that are attributed to the ν(Cu-O) and ν(Cu-N) vibrational modes, respectively [31]. Owing to the larger dipole moment change for the Cu-O band compared to the Cu-N band, the vibrational Cu-O band usually appears at a higher frequency than the Cu-N band [31]. The uncoordinated perchlorate ion (T<sub>d</sub>) has four three fundamental vibrational modes (A<sub>1</sub>, E, 2T<sub>2</sub>) and two of them (2T<sub>2</sub>) are IR active in the IR region. These two vibrational modes are attributed to the anti-symmetric stretching (1100 cm<sup>-1</sup>) and anti-symmetric bending (620 cm<sup>-1</sup>) vibrational modes, respectively [32]. In a unidentate perchlorate, with C<sub>3v</sub> symmetry, each of these modes is split into an A<sub>1</sub> mode and an E mode, both of which are infrared-active. Also, in a symmetric bidentate perchlorate, of C<sub>2v</sub> symmetry, each E mode is further split into a B<sub>1</sub> and a B<sub>2</sub> mode, which suggests the presence of three infrared-active bands. In the dinuclear complex,

the number of the vibrational band associated with perchlorate did not change but the band positions were shifted to 1118 and 629 cm<sup>-1</sup> which reveals the perchlorate ions are uncoordinated [32].

#### Conductometric data

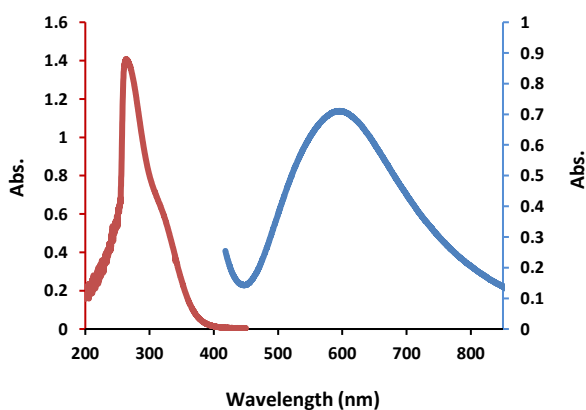
The molar conductance values of the complex in solvents of acetonitrile and dimethylformamide along with the standard values of 1:1 and 1:2 electrolytes in the respective solvents are presented in Table 1 [33]. It can be perceived that in both solvents the molar conductivity values of **1** with counter ions of ClO<sub>4</sub><sup>-</sup> are in the range of 1:2 electrolytes and consistent with the suggested structural formula.

#### Electronic spectrum

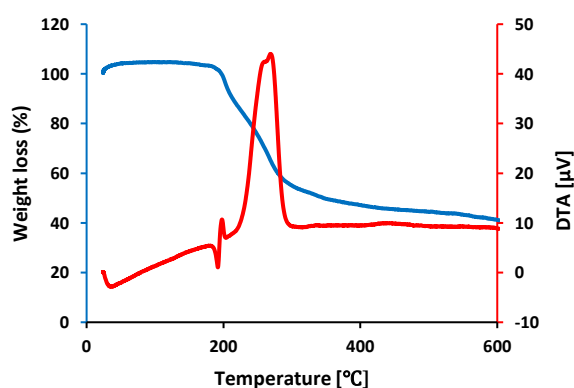
The electronic absorption spectrum of the complex in the solvent of acetonitrile (Fig. 1) shows a strong absorption band at around 265 nm, due to metal to ligand charge transfer transition. The shoulder observed at around 310 nm can be attributed to LMCT transition of the Cu-O-Cu skeleton [34]. In the visible region, the complex displays a single broad d-d band at 593 nm, which corresponds to a distorted square pyramidal geometry around the copper(II) centers. This band is due to the transition of an electron from d<sub>z<sup>2</sup></sub> orbital to the upper level of d<sub>x<sup>2</sup>-y<sup>2</sup></sub> in the copper(II) ion centers of the compound. Single broadband in the region 550–690 nm is quite common for typical copper(II) complexes with square pyramidal or distorted square pyramidal geometries [35]. Alternatively, trigonal bipyramidal complexes of copper(II) display absorbance maxima above 800 nm along with a higher energy shoulder [30].

**Table 1: The molar conductivity values ( $\Lambda_M$ ) of the complex ( $\Omega^{-1} \text{ cm}^2 / \text{mol}$ , at  $25^\circ \text{ C}$ ) in solvents.**

Compound	AN	DMF
$[\text{LCu}(\mu\text{-OH})_2\text{CuL}](\text{ClO}_4)_2$	258	163
1:1 electrolyte	120-160	65-90
1:2 electrolyte	220-300	130-170



**Fig. 1: The electronic absorption spectrum of the complex in solvent of acetonitrile.**



**Fig. 2: The TGA-DTA curves of the complex.**

#### Thermal analysis

The thermal stability and thermal behavior of the complex were studied by thermogravimetric analysis in a nitrogen atmosphere from 24 to 600 °C at a heating rate of 10 °C /min. TGA-DTA analysis of the complex exhibits that the compound is stable in a temperature range of 24-190 °C and then follows a similar type of decomposition pattern as shown in Table 2. The DTA curve (Fig. 2) reveals an endothermic process devoid of any weight loss from 184 to 194 °C due to the dissociation

of weak Cu–O(amide). Then, the compound starts losing OH bridging groups along with  $2\text{H}^+$  as  $2\text{H}_2\text{O}$  in a temperature range 195-203 °C, and then the ligand decomposes in several steps as shown in Table 2. Finally, the thermogram shows a continuous weight loss of the formation of two molecules of  $\text{Cu}(\text{ClO})_2$  with a mass loss of 42.1% (calc. 42.1%). Further heating was avoided due to the explosive nature of perchlorate ions.

#### Thermochromism

UV-vis absorption spectra of the complex in acetonitrile at a temperature range 25 to 93 °C are shown in Fig. 3. Upon heating, the initial blue color of the solution becomes green and the band at 593 nm goes through redshift while the band at 265 nm keeps on constant. However, at above 85° C the shoulder at 310 nm shifts to low energy and tails into the visible region while the d-d band loses its intensity. The observed redshift might be assigned to the substitution of acetonitrile molecules by weakly coordinating the amide groups. The hemilability of the amide groups together with the presence of the Jahn-Teller effect in the copper(II) ion with  $d^9$  electron configuration make the amide groups susceptible to bond rupture at elevated temperature and further substitution by solvent molecules. This phenomenon is a reversible process so that after cooling the solution to room temperature, the detached amide moieties re-coordinate to the copper centers, and the original blue color re-develops. This phenomenon was also observed in other polar solvents such as DMSO. To confirm the proposed mechanism a structurally related complex ( $[\text{L}^{\text{Ph}}\text{Cu}(\mu\text{-OH})_2\text{CuL}^{\text{Ph}}]^{2+}$ ) with no amide group was examined in acetonitrile [36]. As is shown in Fig. S3 the visible spectrum of  $[\text{LCu}(\mu\text{-OH})_2\text{CuL}](\text{ClO}_4)_2$  in elevated temperature is almost identical to the room temperature spectrum of  $[\text{L}^{\text{Ph}}\text{Cu}(\mu\text{-OH})_2\text{CuL}^{\text{Ph}}](\text{ClO}_4)_2$ .

#### Solvatochromism

The complex is soluble in different organic solvents and demonstrates remarkable color changes. The visible absorption spectra of the complex in selected organic solvents were illustrated in Fig. 4. The color change is attributed to the shift in d-d electronic transition of the copper(II) centers caused by the coordination of solvent molecules with different coordination power to the unoccupied coordination sites of the copper(II) centers.

Table 2: TGA results obtained for the complex.

Temp. (°C)	Fragment loss	Mass loss (%)	
		Experimental	Calculated
195-203	-2H <sub>2</sub> O	4.6	4.6
210-247	2 (CH <sub>2</sub> -CH <sub>2</sub> C(O)-NH <sub>2</sub> )	18.5	18.3
255-296	2(CH <sub>3</sub> -CH-CH <sub>3</sub> )	21.1	21.6
330-600	2(N-CH <sub>2</sub> -CH <sub>2</sub> -NH)	14.4	14.6

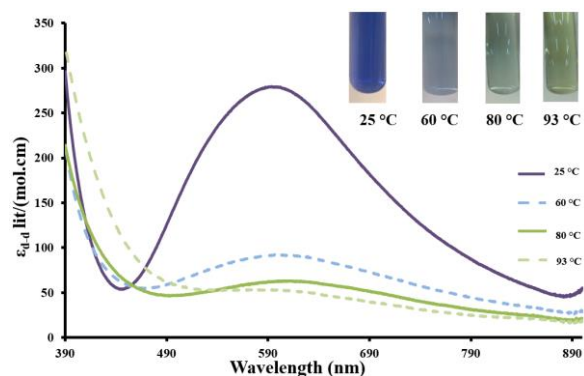


Fig. 3: Temperature dependence of the visible absorbance of the complex in acetonitrile.

Ongoing from nitromethane to pyridine as the solvent, a redshift of  $\Delta\lambda = 75$  nm is observed (Table 3). The obtained  $\lambda_{\max}$  values in different solvents were utilized in the correlation analysis. To ascertain the corresponding contributions of the different solvent properties on  $\lambda_{\max}$ , a SMLR investigation was employed. The six general empirical scales of solvent parameters cover Gutmann's donor number (DN), Mayer and Gutmann's acceptor number (AN), Dimroth and Reichardt's  $E_T(30)$ , Kamlet and Taft's  $\beta$  (electron pair donating ability),  $\alpha$  (hydrogen bonding ability) and  $\pi^*$  (polarity/polarizability) [37] were applied in the solvatochromic equation (2) where  $\lambda_{\max}^0$  is the value of the absorption energy in an inert solvent, for instance, dichloromethane, and a, b, c, d, e, and f values are their corresponding regression coefficients [38,39].

$$\lambda_{\max} = \lambda_{\max}^0 + a DN + b AN + c E_T(30) + d \beta + e \alpha + f \pi^* \quad (2)$$

Therefore, by utilizing SPSS software the  $\lambda_{\max}$  values of the complex in different solvents accompanied by solvent parameters shown in Table 2 were delivered one

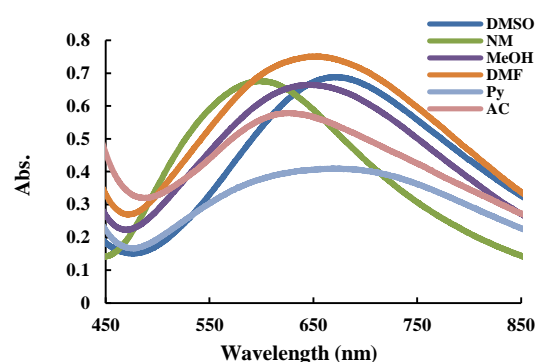


Fig. 4: Absorption spectra of the complex in selected solvents. Absorption spectra in other solvents are omitted for clarity.

by one to the statistical computer program. SMLR method evaluates the solvent parameters step by step causing a parameter being accepted, excluded, or exchanged until the final equation is completed. The obtained results are summarized in Table 4. The corresponding equation reveals that the donor number (DN) parameter controls the variation in absorption maxima in the complex and the involvement of other solvent parameters have a negligible contribution to solvatochromism. The high  $F$  and  $R$  values and low standard error (S.E.) confirm the accuracy of the equation. The diagram of absorption maxima ( $\lambda_{\max}$ ) versus DN of the solvents is illustrated in Fig. 5. Based on characterization results, the geometry of the copper(II) centers in the complex is a square pyramid with a vacant coordination site, which are available for a solvent molecule to change the geometry of copper(II) ion centers to the octahedron. In addition, the presence of a strong Jahn-Teller effect in the copper(II) center causes long bond length Cu-O(amide) in the axial position of the complex that is susceptible to being driven out by solvent molecules in the solution. This could be a possible mechanism in the observed solvatochromism phenomenon and in accord

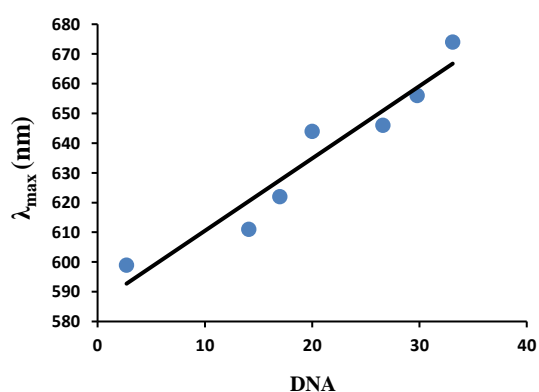
**Table 3: The solvent parameter values<sup>1</sup> and electronic spectra of the complex in various solvents:  $\lambda_{max}/nm$  ( $\epsilon/M^{-1} cm^{-1}$ ).**

Solvent	DN	AN	$E_T(30)$	$\beta$	$\alpha$	$\pi^*$	Complex 3
NM	2.7	20.5	46.3	0.0	0.13	0.85	599(276)
AN	14.1	18.9	45.6	0.40	0.19	0.75	611(272)
AC	17.0	12.5	42.2	0.43	0.08	0.71	622(285)
MeOH	20.0	41.3	55.4	0.66	0.98	0.60	644(184)
DMF	26.6	16.0	43.8	0.69	0.00	0.88	646(187)
DMSO	29.8	19.3	45.1	0.76	0.00	1.00	656(181)
Py	33.1	14.2	40.5	0.64	0.00	0.87	674(78)

<sup>1</sup>. These values are taken from Ref [37] Marcus.

**Table 4: The equations resulted from the linear correlation of the  $\lambda_{max}$  values with DN of the solvents.**

Equations	F	R	S.E.	$t_{DN}$
$\lambda_{max} = 3.561(\pm 0.68)DN_{solv} + 556.23(\pm 15.39)$	28	0.95	17.40	5.26

**Fig. 5: Dependence of the  $\lambda_{max}$  values of the complex on the solvent DN values.**

with the strength of the donor power of solvent molecules. As the solvent molecules approach from  $z$ -direction of the complex, the energy level of  $d$  orbitals changes. The solvent molecules interact much more with  $d_z^2$ ,  $d_{xz}$ , and  $d_{yz}$  than  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals, consequently, a typical octahedral  $d$  orbital splitting is made. Destabilization of orbitals with  $z$ -character and reduction of the energy of the two other orbitals causes a redshift in the  $d$ - $d$  band and observation of a positive solvatochromism.

## CONCLUSIONS

A dinuclear copper(II) complex containing a tridentate ligand of  $N,N$ -diisopropyl, $N'$ -3-propylamide-ethylenediamine was prepared and characterized. The compound is thermo-

and solvatochromic. The observed reversible thermochromism is based on the breakage and the re-coordination of the weak coordination of Cu-O(amide) moiety of the hemilabile ligand with the variation of temperature. Its solvatochromism is based on geometry change from a square pyramidal to an octahedron due to the coordination of solvent molecules on the vacant site of copper(II) centers. The solvatochromism property of the complex was analyzed by six of the most important solvent parameters by SMLR. The obtained results show that donor number (DN) interaction preferably contributes to solvent-induced color changes. The introduction of amide functionality at the diamine ligand with high steric hindrance resulted in dinuclear coordinatively unsaturated structure in relation to visible absorption property, which makes this compound promising for investigating chromophore in terms of environmental effects relating to optical properties for the application.

## Acknowledgment

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

Received :Feb. 1, 2021 ; Accepted : Dec. 7, 2021

## REFERENCES

- [1] Tabacco M.B., Uttamlal M., McAllister M., Walt D.R., [An Autonomous Sensor and Telemetry System for Low-level pCO<sub>2</sub> Measurements in Seawater](#), *Anal. Chem.*, **71**(1): 154-161 (1999).

- [2] Gou M., Guo G., Zhang, J.A., Men K., Song J., Luo F., Zhao X., Qian Z., Wei Y.Q., Time-Temperature Chromatic Sensor Based on Polydiacetylene (PDA) Vesicle and Amphiphilic Copolymer, *Sensor Actuat B-Chem* **150(1)**: 406-411 (2010).
- [3] Miyamoto K., Sakamoto M., Tanaka C., Horn E., Fukuda Y., Syntheses, Structures, Spectroscopic Properties, and Thermal Behavior of Nickel(II) Mixed-Ligand Complexes with *N,N,N',N'*-tetramethylethylenediamine, benzoylacetate, and a Halide Anion, *Bull. Chem. Soc. Jpn.* **78(6)**: 1061-1071 (2005).
- [4] Ding K., Yang Z., Zhang Y. L., Xu J. Z., Injectable Thermosensitive Chitosan/-Glycerophosphate/Collagen Hydrogel Maintains the Plasticity of Skeletal Muscle Satellite Cells and Supports Their *in Vivo* Viability, *Cell Bio. Int.* **37(9)**: 977-987 (2013).
- [5] Sato O., Hayami S., Einaga Y., Gu Z.Z., Control of the Magnetic and Optical Properties in Molecular Compounds by Electrochemical, Photochemical and Chemical Methods, *Bull. Chem. Soc. Jpn.*, **76(3)**: 443-470 (2003).
- [6] Schanze K.S., Schmehl R.H., Applications of Inorganic Photochemistry in the Chemical and Biological Sciences: Contemporary Developments, *J. Chem. Educ.* **74**: 633-635 (1997).
- [7] Meinershagen J.L., Bein T., Solvatochromism of Copper(II)(tetramethylethylenediamine)(acetylacetate) Complex Encapsulated in EMT Zeolite Cages, *Adv. Mater.*, **13(3)**: 208-211 (2001).
- [8] Sone K, Fukuda Y. "Ions and Molecules in Solution", Elsevier, Amsterdam (1983).
- [9] Golchoubian H., Zarabi R. Z., Syntheses, Crystal Structure and Chromotropic Properties of Dinuclear Copper(II) Complexes of Tertiary Diamine with Hydroxo Bridge, *Polyhedron*, **28(17)**: 3685-3690 (2009).
- [10] Linert W., Fukuda Y., Camard A., Chromotropism of Coordination Compounds and its Applications in Solution, *Coord. Chem. Rev.*, **218**: 113-152 (2001).
- [11] Miao J., Nie Y., Xiong Z., Chai Y., Fu S., Yan H., Stimulus-responsive Reversible Thermochromism and Exciplex Emission of a Zn(II) Complex and Selective Sensing of NH<sub>3</sub> Gas, *Dalton T*, **48(15)**: 5000-5006 (2019).
- [12] Ohno K., Kusano Y., Kaizaki S., Nagasawa A., Fujihara T., Chromism of Tartrate-Bridged Clamshell-like Platinum (II) Complex: Intramolecular Pt-Pt Interaction-Induced Luminescence Vapochromism and Intermolecular Interactions-Triggered Thermochromism, *Inorg. Chem.* **57(22)**: 14159-14169 (2018).
- [13] Tom L., Kurup M. R. P. A Stimuli Responsive Multifunctional ZMOF Based on an Unorthodox Polytopic Ligand: Reversible Thermochromism and Anion Triggered Metallogelation. *Dalton T*, **48(44)**: 16604-16614(2019).
- [14] Méndez-Arriaga J. M., Oyarzabal I., Martín-Montes Á., García-Rodríguez J., Quirós M., Sánchez-Moreno M., First Example of Antiparasitic Activity Influenced by Thermochromism: Leishmanicidal Evaluation of 5, 7-dimethyl-1, 2, 4-triazolo [1, 5-a] pyrimidine Metal Complexes. *Med. I Chem.*, **16(3)**: 422-430 (2020).
- [15] Kazemi S., Golchoubian H. Structure and Chromotropic Properties of 2-Picolylamine-Ni (II) Complex. *Inorg. Chem. Res.*, **4(1)**:76-85 (2020).
- [16] Camard A., Ihara Y., Murata F., Mereiter K., Fukuda Y., Linert W., The use of Solvatochromic Mixed Copper (II) Chelates with *N,N,N',N'*-tetramethylethylenediamine and Tropolonato or Hinokitiolato Ligands, [Cu(trop/hino)(tmen)] B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, as Indicator for Lewis Basicity of Solvents and Low-Coordinating Anions, *Inorg. Chim. Acta.* **358(2)**: 409-414 (2005).
- [17] Aryannezhad M., Behmadi H., Saadati S.M., Poormorteza N., Amini Moghaddam Z., Synthesis and Characterization of Novel Photoactive Poly (ether-amide) Based on Highly Substituted Phenanthrimidazole, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **36(6)**: 69-76 (2017).
- [18] Nurchi V.M., Crisponi G., Sanna G., Pérez-Toro I., Niclos-Gutierrez J., Gonzalez-Perez M.J., Martín A.D., Complex Formation Equilibria of Polyamine Ligands with Copper (II) and Zinc (II), *J. Inorg. Biochem.* **194**: 26-33 (2019).
- [19] Fukuda Y., "Inorganic Chromotropism", Springer, Berlin (2007).
- [20] Chao M.-S., Lu H.-H., Tsai M.-L., Huang S.-L., Hsieh T.-H., Reversible Switching of Coordination Modes of Nickel (II) Complexes Using a Hemilabile 4,7-diazadecanediamide Ligand, *Inorg. Chim. Acta.* **362(10)**: 3835-3839 (2009).



- [21] Golchoubian H., Moayyedi G., Reisi N., Halochromism, Ionochromism, Solvatochromism and Density Functional Study of a Synthesized Copper (II) Complex Containing Hemilabile Amide Derivative Ligand, *Spectrochim. Acta Part A*, **138**: 913–924 (2015).
- [22] Golchoubian H., Tarahomi M., Rezaee E., Bruno G., Synthesis, Structural Characterization and Chromotropism of a Copper(II) Complex Containing Bidentate Ligand, *Polyhedron*, **85**: 635–642 (2015).
- [23] Golchoubian H., Rostami L., Synthesis, Crystal Structure and Chromotropism Study of Copper Complexes Containing Tridentate and Pseudo Halide Ligands; Amide Linkage Isomerism, *Inorg. Chim. Acta*, **462**: 215–222 (2017).
- [24] Koohzad S., Golchoubian H., Jagličić Z., Structural, Solvatochromism and Magnetic Properties of Two Halogen Bridged Dinuclear Copper (II) Complexes: a Density Functional Study, *Inorg. Chim. Acta*, **473**: 60–69 (2018).
- [25] SPSS/PS, “Statistical Package for IBMPC”, Quiad Software Version 13, Ontario, (1998).
- [26] Darlington R. B., “Regression and Linear Models”, McGraw-Hill, New York (1990).
- [27] Riahi S., Mousavi M. F., Shamsipur M., Prediction of Selectivity Coefficients of a Theophylline-Selective Electrode Using MLR and ANN, *Talanta* **69**(3): 736–740 (2006).
- [28] Murata F., Arakawa M., Nakao A., Satoh K., Fukuda Y., Syntheses, Crystal Structures and Chromotropic Properties of Nickel (II) Mixed Ligand Complexes Containing N-methyl-1, 4-diazacycloheptane and Various  $\beta$ -diketonates, *Polyhedron*, **26**(8): 1570-1578 (2007).
- [29] Tsiamis C., Themeli M., Substituent and Solvent Effects in the Spectra and Structure of some Mixed-Ligand Copper (II) Chelates Containing  $\beta$ -ketoenols, *Inorg. Chim. Acta*, **206**(1): 105-115 (1993).
- [30] Meek D. E., Ehrhardt S. A., Copper(II) Complexes of Secondary and Tertiary N-substituted Ethylenediamines, *Inorg. Chem.*, **4**(4): 584-587 (1965).
- [31] Raman N., Esthar S., Thangaraja C., A New Mannich base and its Transition Metal(II) Mcomplexes-Synthesis, Mstructural Characterization and Electrochemical Study, *J. Chem. Sci.*, **116**(4): 209-213 (2004).
- [32] Nakamoto K., Ohkaku N., Metal Isotope Effect on Metal-Ligand Vibrations. VI. Metal Complexes of 8-hydroxyquinoline, *Inorg. Chem.*, **10**(4): 798-805 (1971).
- [33] El Ayaan U., Murata F., El Derby S., Fukuda Y., Synthesis, Structural and Solvent Hnfluence Studies on Solvatochromic Mixed-Ligand Copper (II) Complexes with the Rigid Nitrogen Ligand: bis [N-(2,4,6-trimethylphenyl) imino] acenaphthene, *J. Mol. Struct.*, **692**(1-3): 209-216 (2004)
- [34] Banerjee S., Mondal S., Chakraborty W., Sen S., Gachhui R., Butcher R. J., Slawin A. M. Z., Mandal C., Mitra S., Syntheses, X-ray Crystal Structures, DNA Binding, Oxidative Cleavage Activities and Antimicrobial Studies of Two Cu (II) Hydrazone Complexes, *Polyhedron*, **28**(13): 2785-2793 (2009).
- [35] Lever A. B. P., “Inorganic Electronic Spectroscopy”, 2nd ed., Elsevier Science, Amsterdam (1984).
- [36] Golchoubian H., Moayyedi G., Reisi N., Halochromism, Ionochromism, Solvatochromism and Density Functional Study of a Synthesized Copper(II) Complex Containing Hemilabile Amide Derivative Ligand, *Spectrochim. Acta Part A*, **138**: 913–924 (2015).
- [37] Marcus Y., The Properties of Organic Liquids that are Relevant to Their Use as Solvating Solvents, *Chem. Soc. Rev.*, **22**(6): 409-416 (1993)
- [38] Hadjmohammadi M.R., Chaichi M.J., Yousefpour M., Solvatochromism Effect of Different Solvents on UV-Vis Spectra of Flouresceine and its Derivatives, *Iran. J. Chem. Chem Eng (IJCCE)*. **27**(4): 9-14 (2008)
- [39] Erdal Tümer, A., Edebali, S., Gülcü, Ş., Modeling of Removal of Chromium (VI) from Aqueous Solutions Using Artificial Neural Network, *Iran. J. Chem. Chem Eng (IJCCE)*., **39**(1): 163-175 (2020).