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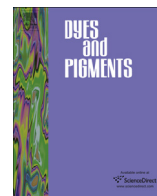


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Syntheses of dinuclear copper(II) complexes containing of tertiary diamine and amido groups with hydroxo bridges; chromotropic properties



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ABSTRACT

Two new symmetric dinuclear complexes type $[\text{Cu}(\text{L})(\mu\text{-OH})_2(\text{ClO}_4)_2]$, where either $\text{L} = N,N\text{-dimethyl}, N'\text{-3-propylamide-ethylenediamine}$ or $N,N\text{-diethyl}, N'\text{-3-propylamide-ethylenediamine}$ were synthesized and characterized on the basis of elemental analysis, conductance measurement, spectroscopic techniques and X-ray crystal analysis. The complexes show halochromism in aqueous solution. The pH effects on the visible absorption spectra of the two complexes were studied which act as pH-induced “off–on–off” switches through protonation and deprotonation in aqueous solution at room temperature. The dinuclear complexes were also observed to exhibit thermochromism, solvatochromism and ionochromism as a result of hemilability of amide groups. The solvatochromism of the complexes was investigated with different solvent parameter models using stepwise multiple linear regression method. The results suggested that the donor number parameter of the solvent has a dominant contribution to the shift of the d–d absorption band of the complexes.

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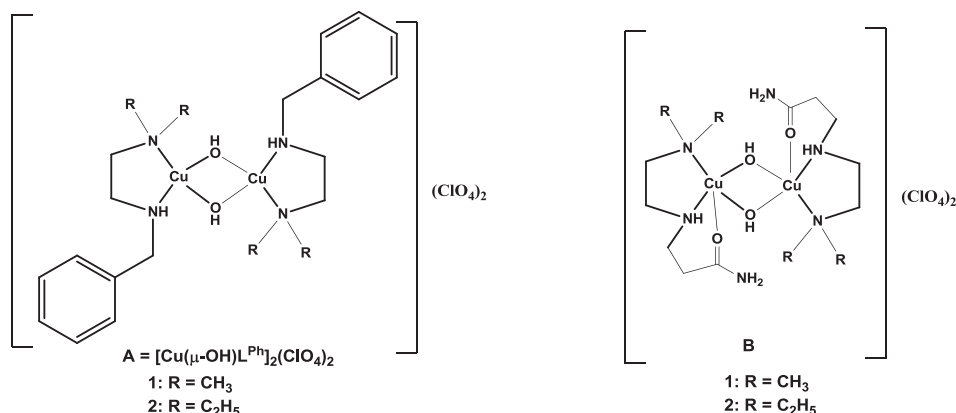
1. Introduction

Chromotropism may be defined as a reversible color change of the materials caused by the surrounding chemical or physical environment; the environment could be solvent (solvatochromism), temperature (thermochromism), pressure (piezochromism), light (photochromism), pH (halochromism), ion (ionochromism) or electrons (electrochromism) [1]. Chromotropism has attracted much attention because of the wide variety of potential applications as thermosensitive materials [2,3], imaging [4], photo-switching materials [5], sensor materials [6] molecular switches [7–10], pollutant sensors [11,12] and Lewis-acid–base color indicators [13]. A combination of metal-ion recognition moieties with appropriate ligands has been reported to afford metal-ion responsive chromotropic molecules [1]. Among chromotropic metal complexes, copper (II) ions with a combination of chelate ligands have been recognized as the most promising candidates for practical applications due to their high thermodynamic stabilities, accessibility of other oxidation states and also existence of simple and regular changes in their

electronic spectra according to the strength of the stress imposed to the system. In our previous study, a series of new homoleptic dinuclear copper(II) complexes with hydroxo bridges as shown A in Scheme 1 was prepared that demonstrated distinctive solvato- and thermochromism properties [14]. Our investigation also showed that in these homoleptic complexes the copper(II) centers are five-coordinated with square pyramidal structures that a water molecule or a counter ion coordinated on the apex of each copper(II) ions [15–17]. On the other hand, Chao and coworkers reported nickel(II) and copper(II) complexes containing amide groups that displayed spectral changes in the aqueous solution due to a pH dependent isomerization of the amide ligand [18]. This result motivated us to design a series of five-coordinated copper(II) complexes including chelate ligand with a hemilabile amide group attached to the amine nitrogen of the ethylenediamine derivatives in order to obtain metal complexes with versatile chromotropism properties. It should be pointed out that transfer of protons can be regarded as one of the simplest external stimulations and can induce the switching properties such as visible absorption for pH sensors. pH sensors are especially attractive since various living organism like enzyme function within a narrow pH gap that their actions or behavior can be explained as being “on–off” switching as a function of pH [19]. Halochromic polythiophene derivative in particular was used for

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Scheme 1. The complexes previously prepared (A) and the complexes under study (B).

the visual detection of CO₂ gas [20] or halochromic dyes was utilized in preparation of smart and interactive textiles [21]. However, the majority of pH sensors is based on organic molecules and less attention has been focused on metal complexes [22]. In this report, we present the design and synthesis of dinuclear copper complexes shown as B in Scheme 1. Additionally, an investigation was carried out in order to ascertain the effect of pH, temperature, solvent and also influence of pseudo halide anions on the electronic absorption spectra of the complexes. Based on our knowledge, this is the first time that a compound shows all these properties collectively. To function as chemical sensor devices these compounds can be encapsulated into zeolite cages [23] or by anchoring to the polymer backbones [24].

2. Materials and methods

2.1. Materials and measurements

$[Cu(\mu-OH)L^{Ph}]_2(ClO_4)_2$ was prepared according to our earlier reported procedure [14]. All solvents were spectral-grade and all other reagents were used as received. *Caution! Perchlorate salts are potentially explosive and should be handled with appropriate care.*

Elemental analyses were performed by LECO CHN-600 Elemental Analyzer. Absolute metal percentages were determined by a Varian-spectra A-30/40 atomic absorption-flame spectrometer. All the samples were dried to constant weight under a high vacuum prior to analysis. Conductance measurements were made at 25 °C with a Jenway 400 conductance meter on concentrations of 10.0×10^{-4} , 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 infinite dilute solution to obtain the molar conductance value. Infrared spectra (potassium bromide disks) were recorded using a Bruker FT-IR instrument. ¹H NMR spectra were measured with a Bruker 400 DRX Fourier Transform Spectrometer at room temperature. The electronic absorption spectra were measured using Braic2100 model and Spekol 2000 UV–Vis spectrophotometers. The buffer solution of pH = 8.5 for ionochromism study was prepared by mixing 100 mL of ammonium chloride (0.3 M) and 100 mL of aqueous ammonia solution (0.05 M).

2.2. Synthesis

2.2.1. Preparation of *N,N*-dimethyl-*N'*-3-propylamide-ethylenediamine (**L**¹)

Acrylamide (3.91 g, 55 mmol) and *N,N*-dimethyl-ethylenediamine (5.44 mL, 50 mmol) in methanol (25 mL) was refluxed for

3 h. The resulting solution was filtered to remove unreacted acrylamide. The solvent was then removed under reduced pressure. The pale yellow viscous oil was purified by vacuum distillation. The desired compound was obtained as pale yellow oil (7.40 g, 93%). Selected IR data (ν/cm^{-1}): 3360 (br. m, N–H str.), 2953 (m, C–H str. aliphatic), 2829 (m, N–CH₃ str.), 1668 (s, C=O str.), 1464 (m, C–N str.), 1411 (m, N–H bend.), 772 (m). ¹H NMR (400 MHz, CHCl₃), δ (ppm): 2.15 (s, 6H, CH₃), 2.34 (m, 4H, Me₂NCH₂– and HNCH₂CH₂C(O)NH₂), 2.21 (s, 1H, NH), 2.66 (t, 2H, $J = 5.6$ Hz, HNCH₂CH₂NMe₂), 2.84 (t, 2H, $J = 6.4$ Hz, –HNCH₂CH₂C(O)NH₂), 6.28 (s, 1H, –NH₂), 7.69 (s, 1H, –NH₂). ¹³C NMR (100 MHz, CHCl₃), δ (ppm): 33.79 (HNCH₂CH₂C(O)NH₂), 35.10 (–HNCH₂CH₂C(O)NH₂), 45.33 (CH₃), 46.55 (–HNCH₂CH₂N–), 58.40 (HNCH₂CH₂NMe₂), 175.48 (–C(O)NH₂).

2.2.2. Preparation of *N,N*-diethyl-*N'*-3-propylamide-ethylenediamine (**L**²)

The same procedure as **L**¹ was used for the preparation of ligand **L**², except that using *N,N*-diethyl-ethylenediamine instead of *N,N*-dimethylethylenediamine. The yield was 72% as pale yellow oil. Selected IR data (ν/cm^{-1}): 3339 (br. m, N–H str.), 2970 (m, C–H str. aliphatic), 2820 (m, N–Et str.), 1673 (s, C=O str.), 1449 (m, C–N str.), 1405 (m, NH bend.), 772 (m). ¹H NMR (400 MHz, CHCl₃), δ (ppm): 0.96 (t, 6H, $J = 7.2$ Hz, CH₃CH₂–), 2.34 (t, $J = 6.4$ Hz, Et₂NCH₂–), 2.47 (q, 4H, $J = 7.2$ Hz, CH₃CH₂–), 2.49 (t, 2H, $J = 6.4$ Hz, –HNCH₂CH₂NEt₂), 2.50 (s, H, NH), 2.63 (t, 2H, $J = 6.0$ Hz, –HNCH₂CH₂C(O)NH₂), 2.84 (t, 2H, $J = 6.0$ Hz, HNCH₂CH₂C(O)NH₂), 6.02 (s, 1H, –NH₂), 7.73 (s, 1H, –NH₂). ¹³C NMR (100 MHz, CHCl₃), δ (ppm): 11.59 (CH₃CH₂–), 35.38 (HNCH₂CH₂C(O)NH₂), 45.41 (Et₂NCH₂CH₂N–), 46.91 (CH₃CH₂–), 47.31 (HNCH₂CH₂C(O)NH₂), 52.28 (Et₂NCH₂CH₂N–), 175.71 (–C(O)NH₂).

2.2.3. Preparation of $[Cu(L^1)(\mu-OH)]_2(ClO_4)_2$, **1**

To the solution of diamine ligand **L**¹ (0.955 g, 6 mmol) in methanol (24 mL) were slowly added Cu(ClO₄)₂·6H₂O (1.11 g, 3 mmol) in methanol (6 mL). The resultant deep blue mixture was stirred for 30 min at room temperature. The desired compound precipitated from the solution as blue solid. The compound was recrystallized by diffusion of toluene into acetonitrile solution. The typical yield was 25%. The crystals were suitable for X-ray crystallography. Anal. calcd for C₁₄H₃₆N₆Cu₂Cl₂O₁₂ (MW = 678.48 g mol^{–1}): C, 24.78; H, 5.35; N, 12.39; Cu, 17.73; Found: C, 24.92; H, 5.25; N, 12.38; Cu, 17.63%. Selected IR data (ν/cm^{-1} using KBr disk): 3606 (w), 3531 (m, O–H str.), 3419 and 3282 (m doublet, NH₂ str.), 3163 (m, N–H str.), 2905 (w C–H str.), 1664 (s, C=O str.), 1467 (s, N–H bend.), 1118 (s, O–ClO₃ str.), 1087 (s, O–ClO₃ str.), 631 (s, O–ClO₃ bend.), 565 (w, Cu–O str.), 507 (w, Cu–N str.).

Table 1
Crystal data and structure refinement of $[\text{Cu}(\text{L}^1)(\mu\text{-OH})]_2(\text{ClO}_4)_2$.

| | |
|--|---|
| Empirical formula | $\text{C}_{14}\text{H}_{36}\text{Cu}_2\text{N}_6\text{O}_4 \cdot 2\text{ClO}_4$ |
| Formula weight | 678.48 |
| Color | Needle, blue |
| Temperature (K) | 293 (2) |
| Wavelength (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $\text{P}\bar{1}$ |
| Crystal size (mm) | $0.20 \times 0.11 \times 0.09$ |
| Unit cell dimensions | |
| <i>a</i> (Å) | 6.7993(2) |
| <i>b</i> (Å) | 9.8288(3) |
| <i>c</i> (Å) | 11.3800(4) |
| α (°) | 70.360(1) |
| β (°) | 74.535(1) |
| γ (°) | 74.613(1) |
| <i>V</i> (Å ³) | 677.28(4) |
| <i>Z</i> | 1 |
| Calculated density (Mg/m ³) | 1.663 |
| μ (mm ^{−1}) | 1.832 |
| <i>F</i> (0 0 0) | 350 |
| θ range for data collection (°) | 3.17–26.88 |
| Index ranges | $-8 \leq h \leq 8$ $-12 \leq k \leq 12$ $-14 \leq l \leq 14$ |
| Reflections collected/unique | 23,397/3110 [<i>R</i> (int) = 0.029] |
| Completeness to $\theta = 27.50$ | 99.8% |
| Absorption correction | Multi-scan |
| Refinement method | Full-matrix least-square ^a on <i>F</i> ² |
| Data/restraints/parameters | 3110/1/167 |
| <i>R</i> indices ^b [2806 with $I > 2\sigma(I)$] ^b | $R_1 = 0.0363$, $wR_2 = 0.1038$ |
| Goodness-of-fit ^c on <i>F</i> ² | 1.045 |
| <i>R</i> indices (all data) | $R_1 = 0.0408$, $wR_2 = 0.1078$ |
| Largest diff. peak and hole, $e \text{ Å}^{-3}$ | 0.656 and −0.586 |

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

2.2.4. Preparation of $[\text{Cu}(\text{L}^2)(\mu\text{-OH})]_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, **2**

This complex was prepared by a similar method used for $[\text{Cu}(\text{L}^1)(\mu\text{-OH})]_2(\text{ClO}_4)_2$ except that L^2 was used in place of L^1 . The compound was obtained as blue crystals with typical yield of 32%. Anal. calcd for $\text{C}_{18}\text{H}_{44}\text{N}_6\text{Cu}_2\text{Cl}_2\text{O}_{12}$ (MW = 734.57 g mol^{−1}): C, 29.43; H, 6.04; N, 11.44; Cu, 16.89; Found: C, 29.82; H, 5.80; N, 11.68; Cu, 16.52%. Selected IR data (ν/cm^{-1} using KBr disk): 3626 (m, O–H str.), 3414 and 3284 (m, doublet, NH₂ str), 3223 (m, N–H str), 2972 (m C–H str.), 2924 (m C–H str.), 1665 (s, C=O str.), 1444 (m, N–H bend.) 1387 (s), 1117 (s, O–ClO₃ str.), 1089 (s, O–ClO₃ str.) 628 (m, O–ClO₃ bend.), 567 (w, Cu–O str.), 507 (w, Cu–N str.).

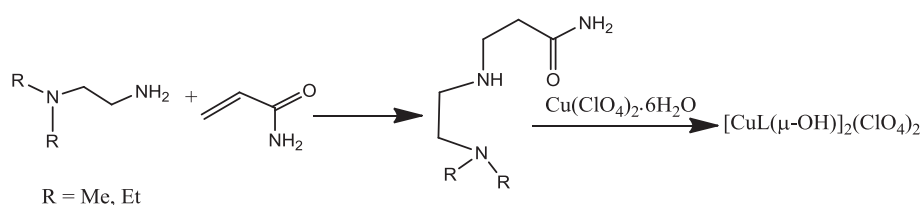
2.3. X-ray structure determination

The X-ray measurements of $[\text{Cu}(\text{L})(\mu\text{-OH})]_2(\text{ClO}_4)_2$ were made on a Bruker Apex-II CCD single crystal diffractometer at room temperature by using graphite-monochromated Mo-K α radiation. Data were collected and reduced by SMART and SAINT software [25] in the Bruker packages. The structure was solved by direct method [26,27] and subsequent Fourier difference

techniques and refined using full-matrix weighted least-squares procedure on *F*² [28] with anisotropic thermal parameters for all non-hydrogen atoms. Several hydrogen atoms were located on the final difference map, the ligand H atoms were included in the refinement via the “riding model” method with the X–H bond geometry and the H isotropic displacement parameter depending on the parent atom X. The position and isotropic displacement parameter of the OH-bridge hydrogen have been free refined with only the O–H bond distance restrained to the usual value 0.9 Å by literature. The chlorine displacement ellipsoids are very large due to a significant rotational disorder of the perchlorate anion but each attempt to treat it by the suitable overlap of two rotated conformations was unsuccessful. The last difference Fourier maps has shown the largest electron density residuals around the disordered perchlorate anion. A summary of crystal data and structure determination is reported in Table 1.

2.4. MLR analysis in solvatochromism study

All the absorption maxima reported were taken from experimental curves of d–d transition of the complexes. Multivariate statistical methods have been used in the classification and selection of solvents. Empirical parameters of solvent polarity were used as basic data sets. These parameters can be obtained directly from the literature [29–31]. The extraction of chemical information contained in such a data set can be carried out by statistical method of Multiple Linear Regression analysis (MLR) using the SPSS/PC software package [32]. In this approach, the stepwise procedure (SMLR) was used for selection of the most relevant solvent parameters. This method combines the forward and backward selection procedures. Due to the complication of inter-correlations, the variance explained by certain variables will change when new variables enter to the equation. Sometimes a variable that is qualified to enter losses some of its predictive validity when other variables are entered. If this occurs, the stepwise method will remove the weakened variable. A final set of selected equations was tested for stability and validity through a variety of statistical methods [33]. The choice of equation suitable for further consideration was made by using four criteria, namely, multiple correlation coefficients (*R*), standard error (S.E.), *F*-statistic and the number of variables (*n*) in the model. The best multiple linear regression model is one that has high *R* and *F*-values, low standard error, least number of variables and high prediction ability. 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 SE. The solvent parameters considered in this study for interpreting solute–solvent interactions are hydrogen bonding ability “ α ”, electron pair donating ability “ β ”, polarity/polarizability parameter “ π^* ”, Gutmann’s donor number “DN”, Mayer and Gutmann’s acceptor number “AN” as well as Dimorth and Richardt’s “*E*_T30”. The following solvents were used for solvatochromism study: nitromethane (NM), acetonitrile (AN), water (H₂O), dimethylformamide (DMF), dimethylsulfoxide

**Scheme 2.** Synthetic outline for preparation of ligands and complexes.

(DMSO), pyridine (Py) and hexamethylphosphorictriamide (HMPA).

3. Results and discussion

3.1. Synthesis

The ligands were prepared in good yield by Michael addition of *N,N*-dialkylethylenediamine to acrylamide in methanol under reflux. Consequently, the treatment of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with the appropriate ligand in mole ratios of 1:2 in methanol at room temperature led to the formation of desired complexes in moderate yields (Scheme 2).

3.2. Characterization

3.2.1. IR spectra

The free ligands have indicator bands which are apparent with minor shift in the dinuclear complexes. Medium intense and narrow bands between 3400 and 3150 cm^{-1} are associated to the N–H and NH_2 stretching vibrations of the amide and amine groups respectively, those are broader in the free ligands. Additionally, upon formation of the chelate rings in the complexes, the C=O vibration of the amide moiety, which appeared as a strong band around 1670 cm^{-1} in free ligands, moved to around 1660 cm^{-1} . The IR spectra of the free ligands showed bands with strong to medium intensities between 2820 and 2760 cm^{-1} , which are characteristic of the C–H stretching vibrations of the N– CH_3 (or C_2H_5) group [34], provided that the lone-pair of electrons on the tertiary nitrogen atom is not involved in a bond but upon coordination, these bands disappeared. The presence of a sharp signal at around 3600 cm^{-1} in both complexes can be assigned to the O–H stretching frequency of the hydroxo bridges [35]. At lower frequency the complexes also exhibited bands around 565 and 507 cm^{-1} which are attributed to the $\nu(\text{Cu–O})$ and $\nu(\text{Cu–N})$ vibration modes, respectively [36]. Due to the larger dipole moment change for the Cu–O band compared to the Cu–N band, the $\nu(\text{Cu–O})$ band usually appears at higher frequency than the $\nu(\text{Cu–N})$ band [37]. The presence of the ClO_4^- group was declared by an intense band at around 1100 cm^{-1} and a medium band at 630 cm^{-1} which are attributed to the anti-symmetric stretching and anti-symmetric bending vibration modes, respectively [38].

3.2.2. Conductometric data

Molar conductance of the dinuclear complexes measured in some solvents with different polarities is presented in Table 2. The standard values of 1:2 electrolytes in the respective solvents are shown in the same table [39]. The conductivity data show that the complexes are almost consistent with 1:2 electrolytes.

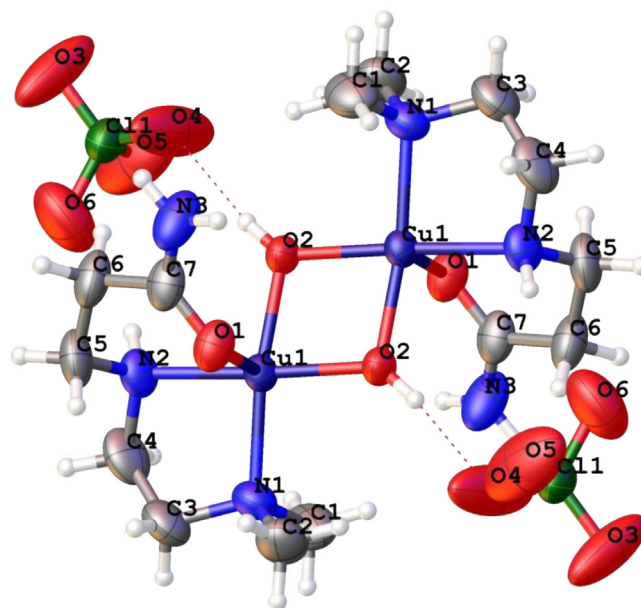
3.2.3. X-ray structure

A perspective view of the complex **1** with the atom numbering scheme is shown in Fig. 1. Selected bond lengths and angles are gathered in Table 3. The compound crystallized in the space group $\text{P}\bar{1}$. The structure of $[\text{Cu}(\text{L}^1)(\mu\text{-OH})_2](\text{ClO}_4)_2$ consists of a centrosymmetric Cu(II) dimer. Therefore, the crystallographic asymmetric

Table 2

The molar conductivity values (λ_{M}) of the complexes ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, at 25°C) in some solvents.

| Compound | H_2O | AN | DMF |
|-----------------|----------------------|---------|---------|
| 1 | 267 | 253 | 161 |
| 2 | 255 | 265 | 155 |
| 1:2 electrolyte | 235–273 | 220–300 | 130–170 |



^a O(2)–H(2) bond distance restrained to the usual value 0.9 \AA

Fig. 1. ORTEP view of $[\text{Cu}(\text{L}^1)(\mu\text{-OH})_2](\text{ClO}_4)_2$, **1**, placed on a crystallographic center of symmetry (the asymmetric unit is half complex)^a.

unit is constituted by half complex which therefore shows a perfect Ci symmetry at the solid state. The copper(II) ion has a square pyramidal geometry in which the basal plane is composed of two nitrogen atoms of tertiary (N1) and secondary (N2) amines and two oxygen donor of hydroxyl groups (O2, O2'). Among them two oxygen atoms are forms of hydroxo bridging anions. On the other hand, the fifth coordination site of the square pyramid in the complex is occupied by the oxygen atom (O1) of amide moiety of the ligand L^1 . The basal atoms are nearly coplanar; the deviations from the least-squares plane through the CuN_2O_2 atoms are N(1) -0.060 , N(2) 0.060 , O(2) 0.069 , O'(2) -0.068 , Cu(1) 0.165 \AA . According to Addison and Rao [40] the distortion of the square pyramidal geometry toward trigonal bipyramidal can be described by geometrical parameter $\tau = |\alpha - \beta|/60$, where α and β are the two largest L–M–L angles of coordination sphere. The τ values are zero for a regular square pyramidal geometry and unity for a regular trigonal bipyramidal one. The τ value for the coordination around the each copper atoms is 0.122 , confirming the square pyramidal geometry of the copper sites. The Cu sites are bridged by two $\mu\text{-Cu–OH}$ through basal coordination linkages. The Cu–O2–Cu angle is found to be $101.53(4)^\circ$. The bond distance of Cu–O2 and Cu–O2' are

Table 3

Selected bond lengths (\AA) and angles ($^\circ$) for complex **1**.

| Bond distances | | | |
|-------------------------------|------------|----------------------------|------------|
| Cu–O(2) ^a | 1.9206(18) | Cu–N(2) | 2.022(2) |
| Cu–O(2) | 1.9268(19) | Cu–O(1) | 2.352(2) |
| Cu–N(1) | 2.027(2) | Cu–Cu ^a | 2.9815(5) |
| O(1)–C(7) | 1.244(4) | N(3)–C(7) | 1.310(4) |
| Bond angles | | | |
| O(2)–Cu–O(2) ^a | 78.40(8) | N(1)–Cu–N(2) | 86.39(11) |
| O(2)–Cu(1)–N(2) | 97.53(9) | O(2) ^a –Cu–O(1) | 96.71(8) |
| O(2) ^a –Cu(1)–N(2) | 173.27(9) | O(2)–Cu–O(1) | 91.25(9) |
| O(2) ^a –Cu–N(1) | 96.31(9) | N(2)–Cu–O(1) | 88.69(9) |
| O(2)–Cu–N(1) | 165.87(10) | N(1)–Cu–O(1) | 102.44(10) |
| O(1)–C(6)–C(7) | 121.6(3) | O(1)–C(7)–N(3) | 121.8(3) |

^a 1 – X, 1 – Y, 2 – Z.

Table 4
Hydrogen bonds for $[\text{Cu}(\text{L}^1)(\mu\text{-OH})]_2(\text{ClO}_4)_2$ (D, donor atom; A, acceptor atom).

| D–H...A | <i>d</i> (D–H) Å | <i>d</i> (H...A) Å | <i>d</i> (D...A) Å | D–H...A (°) |
|--------------------------------|------------------|--------------------|--------------------|-------------|
| N(3)–H(3A)...O(1) ^a | 0.86 | 2.20 | 3.023(4) | 161.3 |
| N(3)–H(3B)...O(5) ^b | 0.86 | 2.25 | 3.095(5) | 168.7 |
| N(2)–H(2A)...O(6) | 0.91 | 2.30 | 3.134(5) | 152.2 |
| O(2)–H(2)...O(4) | 0.845(18) | 2.095(19) | 2.934(4) | 172(4) |

Symmetry transformations used to generate equivalent atoms.

^a $-X, 1-Y, 2-Z$.

^b $-1+X, +Y, +Z$.

1.9268(19) Å and 1.9206(18) Å, respectively. The N2 nitrogen is chiral and therefore the dimer complex is a meso-form having opposite chirality in the two centrosymmetric moiety. Intradimer Cu...Cu separation is 2.9815(5) Å. The bond length of Cu–O(1) is 2.353(2) Å which is within the range of 2.2–2.9 Å, known as the axial Cu–O bond length, and hence the amide groups may weakly coordinate in the complex. The distance shows that the forces holding amide group in the complex are relatively weak and can be driven out from the coordination sphere by solvent molecules in solution, which will be more sensible bonded with the increase in

their donor powers, leading to the observed solvatochromism. The closest interdimer Cu...Cu separation is 6.799(12) Å. Details about hydrogen bonding are shown in Table 4. Hydrogen bonding interaction between the hydrogen atoms of the bridged hydroxo groups (O(2)–H(2)) with perchlorate anions (O(4)) and hydrogen atoms of the amide (N(3)–H(3A)) and oxygen atom of amide group (O(1)) stabilizes the dimeric structure (dotted lines in Fig. 2) and form 1D chain that extend along the crystallographic 'a' axis. Molecular packing is mainly determined by several weak hydrogen bonds involving perchlorate oxygen atoms, secondary and tertiary amine as well as other heteroatoms which are responsible for the observed packing (Fig 3).

3.3. Halochromism

The electronic absorption spectra of dinuclear complexes **1** and **2** in aqueous solution show the d–d transitions at 624 and 632 nm, respectively, which are consistent with the square pyramidal geometry of Cu(II) ion [41]. The electronic absorption spectra of the complexes are sensitive to the pH of the solution, so that the original blue color of the solution turns to purple upon addition of a

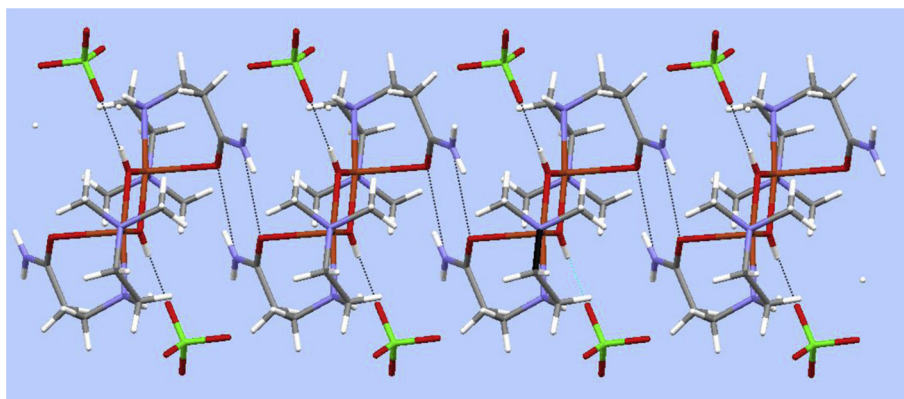


Fig. 2. Hydrogen bonding of $[\text{Cu}(\text{L}^1)(\mu\text{-OH})]_2(\text{ClO}_4)_2$, **1** along the 'a' axis.

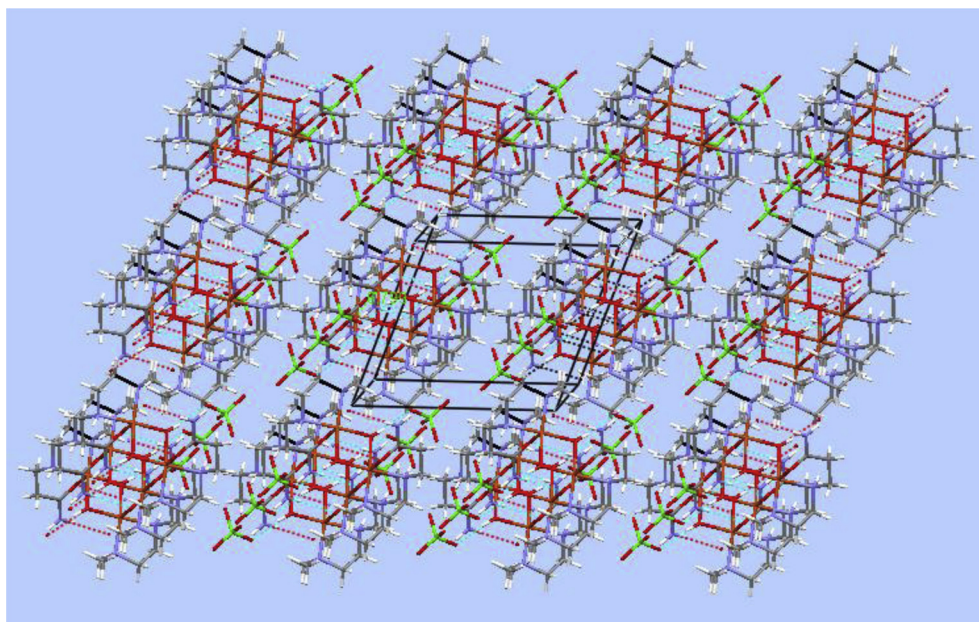


Fig. 3. Crystal packing of $[\text{Cu}(\text{L}^1)(\mu\text{-OH})]_2(\text{ClO}_4)_2$, **1** along the 'a' axis.

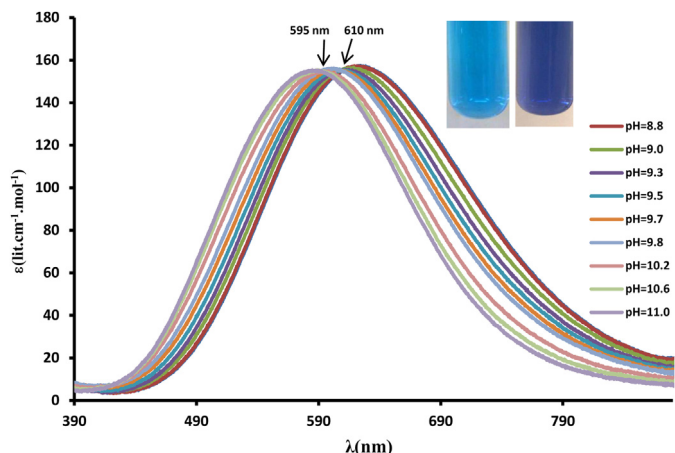


Fig. 4. Visible absorption spectra of complex **1** (4.0×10^{-3} mol dm $^{-3}$) in water at 25 °C. The pH values are denoted on the figure.

base (NaOH, 0.1 M). This phenomenon is totally reversible. To investigate the color changes, the visible spectra of the complexes were studied in pH ranges 8 to 11. These results are shown in Fig. 4. There are two isosbestic points at 595 and 610 nm in complex **1** and 578 and 597 nm in complex **2** which became visible in different pH scales. As the pH of the solution increased with addition of the base, the absorption bands shifted toward lower wavelength due to ionization of the amide protons and following the Cu–O to Cu–N bond rearrangement. It seems that the first isosbestic point is due to ionization of the amide protons and the second isosbestic point belongs to the reversible switching of the coordination modes Cu–O to Cu–N as shown in Scheme 3. The blue shift in the absorption maxima of the complexes with increasing the pH of the solution shows that the nitrogen atom of the deprotonated amide moiety is a stronger donor than neutral amide. Such phenomena were observed by Choa in nickel and copper complexes and amide derived ligands [42,43]. This phenomenon was also observed by using weaker base such as ligand **L** or triethylamine. Titration of the complexes with NaOH demonstrated that $[\text{Cu}(\mu\text{-OH})\text{L}]_2^{2+}$ releases two protons around pH = 10.3 (Fig. 5). In contrast, for the related complex $[\text{Cu}(\mu\text{-OH})\text{L}^{\text{Ph}}]_2^{2+}$ no proton release is observed at pH below 11. Thus, the acidity of the complexes cannot be explained by deprotonation of hydroxo bridges and/or the secondary amine since the coordinated hydroxo group and secondary amine should have similar pK_a values in the structurally related complexes $[\text{Cu}(\mu\text{-OH})\text{L}^{\text{Ph}}]_2^{2+}$ shown in Scheme 1A. Interestingly, when the pH of the solution was decreased to 2.0 by addition of perchloric acid (0.1 M) the original blue color of the solution diminished. The decolorization was along with red shift and decrease in intensity of the d–d band. The original blue color of the copper (II) complexes redeveloped by increasing the pH of the solution to around 8 with addition of a base. Spectrophotometric titration of $[\text{Cu}(\mu\text{-OH})\text{L}]_2^{2+}$

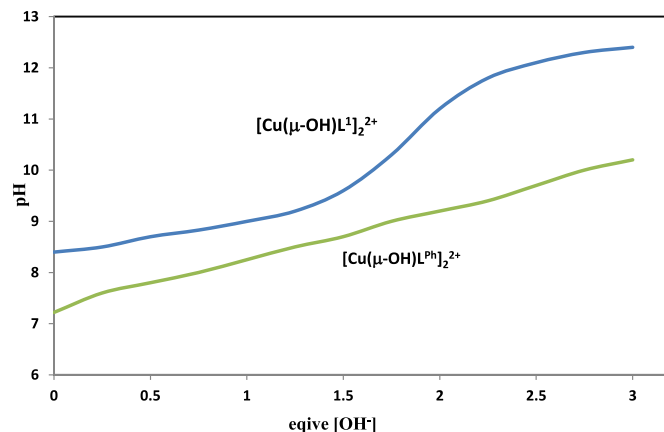
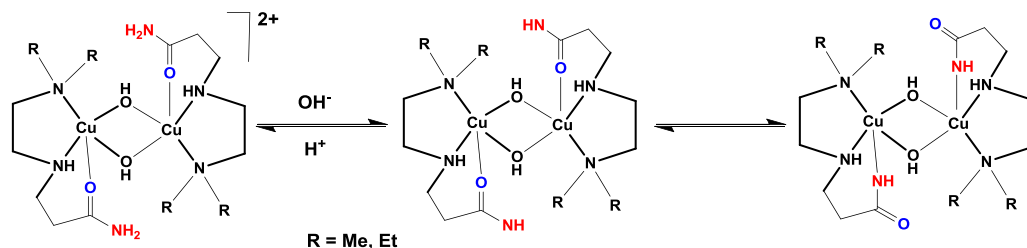


Fig. 5. pH titration of complexes $[\text{Cu}(\text{L}^1)(\mu\text{-OH})_2(\text{ClO}_4)_2]$ and dinuclear complex $[\text{Cu}(\mu\text{-OH})\text{L}^{\text{Ph}}]_2(\text{ClO}_4)_2$ (4 mM in H $_2$ O) with NaOH (0.10 M).

with perchloric acid at $\lambda_{\text{max}} = 624$ nm (Fig. 6) displayed that decolorization occurred with consumption of eight equivalents protons. It is perhaps due to protonation of all of the amine, amide and bridging OH $^-$ groups and formation of protonated ligand and mononuclear copper(II) complexes. Such a phenomenon is observed for the related dinuclear complex $[\text{Cu}(\mu\text{-OH})\text{L}^{\text{Ph}}]_2^{2+}$. In an complementary experiment an aqueous solution of copper(II) perchlorate was acidified and the ligand **L**, **L**^{Ph} or ethylenediamine was then added to the resultant solution. The blue color of the solution abruptly decolorized regardless of the nature of diamine ligands. However, decolorization was not observed in absence of diamine ligands.

3.4. Solvatochromism

The complexes **1** and **2** are soluble in solvents with high dielectric constant and demonstrate distinctive solvatochromism. The presence of a strong Jahn–Teller effect on the Cu(II) ions made them good solvatochromic probes. The origin of the color changes in the compounds is attributed to the shift in the d–d transition of the copper(II) ions as a result of solvent–solute interactions. The visible spectral changes of the complexes in the selected solvents are shown in Fig. 7. The observed λ_{max} values of the complexes along with the molar absorption coefficients (ϵ) and their respective solvent parameter values are illustrated in Table 5. Based on the results illustrated in the table, the effect of the substituent attached to the tertiary amine on the d–d transition of the complexes is insignificant. The solvatochromism property of the complexes is possibly due to the dissociation of the weak amide–copper bonds from the coordination sphere that facilitates the approach of the solvent molecules above and below the chelate plane to the copper (II) centers. The relationship between the energy of the d–d transitions of the complexes and the solvent parameters has been



Scheme 3. Interconversion of complexes triggered by acid and base (pH = 8.5–11.0) in aqueous solution.

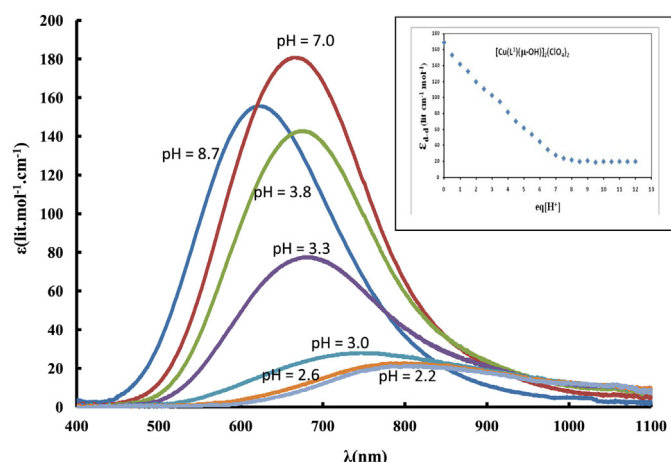


Fig. 6. The pH dependent visible spectrum of **1** in aqueous solution at 25 °C. The inset graph shows the decrease of 627 nm absorbance on titration of **1** (4 mM in H₂O) with HClO₄.

investigated by SMLR technique. As a result, Eq. (1) has been considered as the base equation, in which λ_{\max} values are taken from Table 5 and λ_{\max}^0 is the value of the absorption energy in an inert solvent (1,2-dichloroethane) and a , b , c , d , e and f values are the regression coefficients describing the sensitivity of the property λ_{\max} to the different solvent parameters like DN, AN, E_T30 , β , α and π^* , and solute/solvent interaction mechanisms.

$$\lambda_{\max} = \lambda_{\max}^0 + a \text{ DN} + b \text{ AN} + c E_T30 + d\beta + e \alpha + f \pi^* \quad (1)$$

By using the SMLR method, this equation would be changed and the solvent parameters will be added or removed by program until

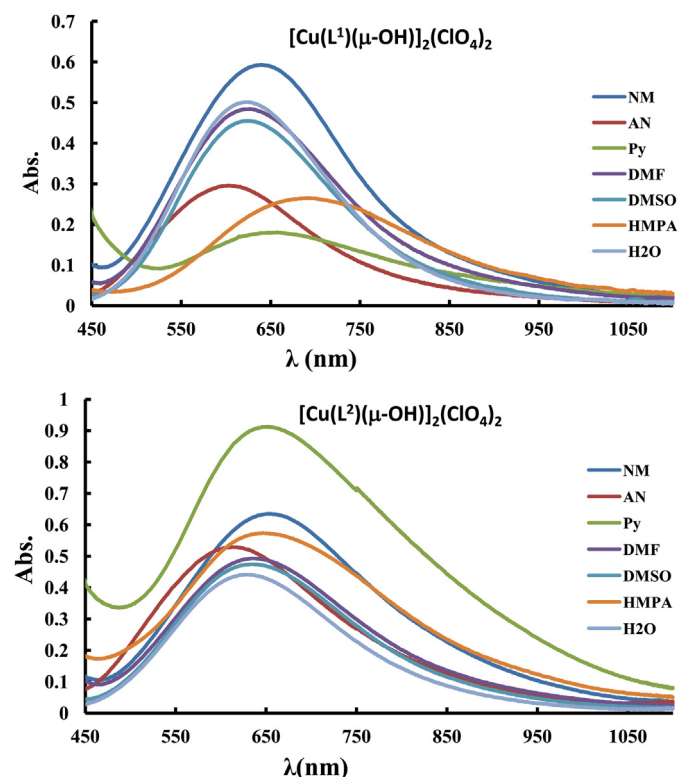


Fig. 7. Absorption spectra of complexes **1** and **2** in selected solvents.

Table 5

The solvent parameter values^a and electronic spectra of the complexes in various solvents: λ_{\max}/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$).

| Solvent | DN | AN | $E_T(30)$ | β | α | π^* | Complex 1 | Complex 2 |
|------------------|------|------|-----------|---------|----------|---------|-----------|-----------|
| NM | 2.7 | 20.5 | 46.3 | 0.0 | 0.13 | 0.85 | 635 (208) | 657 (228) |
| AN | 14.1 | 18.9 | 45.6 | 0.40 | 0.19 | 0.75 | 595 (208) | 610 (208) |
| H ₂ O | 19.5 | 54.8 | 63.1 | 0.47 | 1.17 | 1.09 | 620 (177) | 626 (188) |
| DMF | 26.6 | 16.0 | 43.8 | 0.69 | 0.00 | 0.88 | 619 (184) | 628 (179) |
| DMSO | 29.8 | 19.3 | 45.1 | 0.76 | 0.00 | 1.00 | 621 (194) | 632 (180) |
| Py | 33.1 | 14.2 | 40.5 | 0.64 | 0.00 | 0.87 | 637 (185) | 648 (163) |
| HMPA | 38.8 | 10.6 | 40.9 | 1.05 | 0.00 | 0.87 | 660 (208) | 653 (200) |

^a These values are taken from Refs. [29–31].

certain statistical criteria are met and the best model is obtained. In both complexes the results confirm the dominant contribution of the DN (donor number) parameter in the solvatochromism of the complexes (Table 6). The positive sign of the coefficient indicates a red shift as the donor number of the solvents increases. Although the emptiness of one of the axial sites of the complexes and also facile removal of the coordinated amide group on the other site of the chelate plane lead to approach of the solvents molecules to the metal center with no difficulty, but each solvent has its own basicity strength due to their electron donating power. An increase in DN of the solvents means more power and more ability of the solvent molecule to coordinate to the copper(II) centers. Due to approach of the polar solvent molecules to the axial position of the complexes, a strong repulsion occurs between electron in the d_{z^2} orbital of the copper(II) ions and the electron pair of the solvents that causes the required energy for transferring the electrons to $d_{x^2-y^2}$ orbital declines. Accordingly, the position of this band decreases nearly linearly with the increase of the electron pair donating power of the solvents. Regression analysis of the band maxima of the dinuclear complexes against the electron pair donating power of the solvents is shown in Fig. 8. An obvious exception from this general trend is found in the λ_{\max} values of nitromethane that is far away from linearity trend obtained in Fig. 8. This inconsistency in the absorption maxima can be ascribed to the low donor number of nitromethane (2.7) which hinders the amide groups to be replaced by solvent molecules. As a result, the complexes are not solvatochromic in nitromethane. However, the high dielectric constant of nitromethane (28.5) resulted in solvation of the complexes in this solvent. This was supported by the similarity of the solid-state spectra of the complexes with those in nitromethane that display almost similar λ_{\max} values (632 and 658 nm for complexes **1** and **2**, respectively). As a result, the data in nitromethane were eliminated in the SMLR investigation. Although the basicity nature of the solvents such as pyridine can give rise to deprotonation of the amide groups and could be responsible in color change of solution, this effect on the solvatochromism of the complexes is negligible because, the deprotonated amide groups and/or NH-coordinated amide groups are substituted by solvent molecules. This is also confirmed by lack of contribution of other solvent parameter than DN in the model obtained by SMLR method (see Table 6).

Table 6

The equations resulted from the linear correlation of the λ_{\max} values with DN of the solvents.^a

| Complexes | Equations | F | R | S.E. |
|-----------|---|----|------|------|
| 1 | $\lambda_{\max} = 2.21$ $(\pm 0.46)\text{DN}_{\text{solvent}} + 586.55(\pm 13.03)$ | 23 | 0.92 | 9.31 |
| 2 | $\lambda_{\max} = 1.66$ $(\pm 0.26)\text{DN}_{\text{solvent}} + 588.03(\pm 7.22)$ | 42 | 0.96 | 5.16 |

^a The number of variables, $n = 6$.

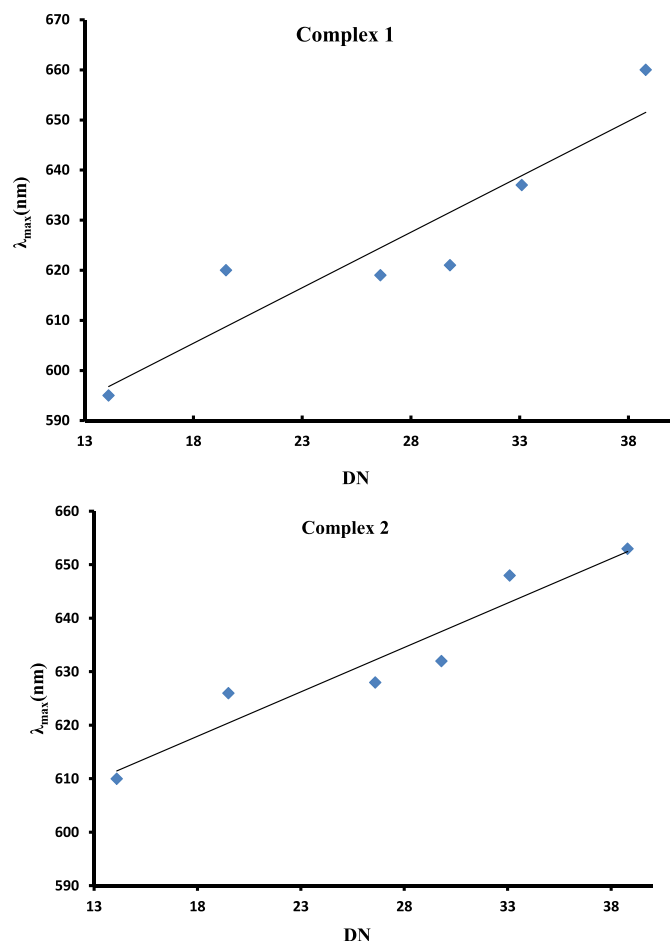


Fig. 8. Dependence of the λ_{\max} values of complexes **1** and **2** on the solvent DN values.

3.5. Thermochromism

UV–vis absorption spectra of the complexes in DMSO were recorded at temperatures in the range 25–130 °C (Fig. 9). At room temperature, two bands are observed at 260 and 627 nm. The former band is accompanied with a shoulder at 315 nm. The shoulder is assigned to a metal-to-ligand charge transfer (MLCT) involving the amide chelate ligand transition, and the second one is due to a d–d transition of the copper(II) ion. Upon heating, the original blue color of the solution turns to green and the band at 627 nm and the shoulder underwent red shifts while band at 260 nm remained constant. However, at 130 °C the shoulder shifted to 325 nm and tails into visible region while the d–d band moved to 560 nm. We attributed the observed red shift to the substitution of DMSO molecules with weakly coordinated amide moieties. The hemilability of the amide groups along with Jahn–Teller effect that is imposed by the copper(II) ion (with d^9 electron configuration) made the amide groups susceptible for bond rupture at high temperature and further substitution by solvent molecules (DMSO). This phenomenon is an irreversible process due to tight bond formation between DMSO and Cu(II) and the presence of significant amount of solvent molecules around the copper centers. This phenomenon was also observed in other polar solvents.

3.6. Ionochromism

Ionochromic materials, similar to photochromic, thermochromic and other chromic materials, alter color in the presence of a factor.

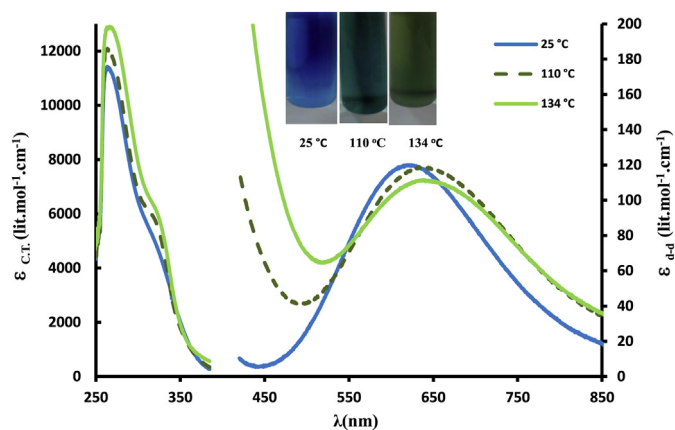


Fig. 9. Temperature dependence of the UV–vis absorbance of a DMSO solution of **1**.

The factor which causes color change in ionochromic substances is ions. A flow of ions through an ionochromic material results in a reaction/color change from the material. Ionochromic substances are suitable for detection of charged particles. These compounds can be used as pM indicators for complexometric titrations [44].

Interaction between the complexes and different halides and pseudo halides were investigated by visible spectroscopy at a concentration of $2.0 \times 10^{-3} \text{ mol L}^{-1}$ of complexes in the buffer solution ($\text{pH} = 8.5$). Variation of absorption spectra of the complexes upon addition of different anions including Cl^- , Br^- , I^- , CN^- , OCN^- , SCN^- , N_3^- and NO_2^- are shown in Fig. 10. The spectra show no obvious change in the absorption maxima upon the addition of the anions Cl^- , Br^- and NO_2^- , while a visible spectral change have been observed by addition of other anions and the variation in the color changes are significant. The color change might be due to substitution of the weakly coordinated amide groups by the anions which causes change in ligand field strength around the copper(II) ions. However, in case where CN^- was used the color of the solution gradually turns to colorless. The dependence of the absorption spectra of complex **1** in aqueous solution on the concentration of cyanide anion was investigated by the absorption spectroscopy titration method (Fig. 11). Upon the addition of CN^- salt, the d–d band gradually underwent a hypochromic shift (decrease in

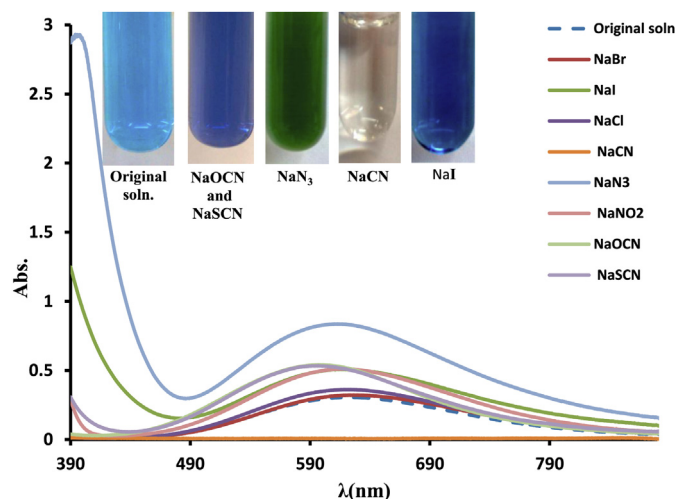


Fig. 10. The absorption spectra of complex **1** ($2.0 \times 10^{-3} \text{ mol L}^{-1}$) upon addition of NaCl, NaBr, NaI, NaCN, NaOCN, NaSCN, NaN_3 and NaNO_2 in aqueous solution.

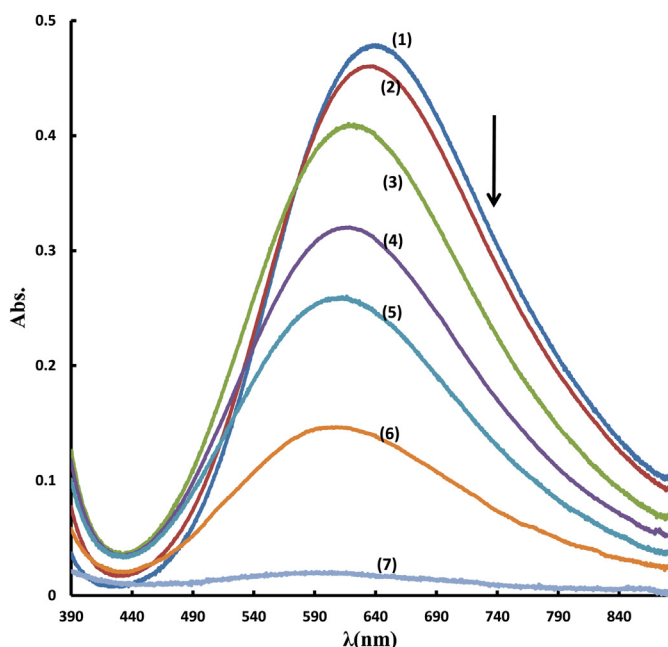


Fig. 11. The color changes of complex **2** (2.0×10^{-3} mol L $^{-1}$) upon addition of NaCN salt in aqueous solution. The NaCN concentration is (1) 0.0, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 5.0 and (7) 6.0 equiv, respectively.

intensity) along with a hypsochromic shift (blue shift) such that when the molar proportion of the complex and CN $^{-}$ was arrived at 1:6, the band disappeared and the solution become colorless. This behavior can be explained by strong coordination power of the cyanide anion that enables it to destroy the original complex by formation of copper(II) cyanide complex that rapidly decomposes into copper(I) cyanide and cyanogen [45]. The hypsochromic shift of the d–d band is attributed to the increasing concentration of Cu I CN moieties at the expense of [Cu II (L 1)(μ -OH)] $_2^{2+}$. The diminution of the intensity of the band is also consistent with decreasing amounts of colored [Cu II (L 1)(μ -OH)] $_2^{2+}$ and formation of copper(I) species. These results indicated that the dinuclear complexes are highly sensitive and selective toward cyanide and moderately sensitive to the iodide and pseudo halides. Anion competition was carried out by mixing anions NaY (Y = Cl $^{-}$, Br $^{-}$, I $^{-}$, CN $^{-}$, OCN $^{-}$, SCN $^{-}$, N $_3^{-}$ and NO $_2^{-}$) (6 equivalents) in buffer solution (pH = 8.5) of the complexes at room temperature. It is concluded that no any designated anions compete effectively with CN $^{-}$ in accordance with decolorization of the resulting solution.

4. Conclusion

Two new dinuclear copper(II) complexes containing hemilabile amide groups were prepared and characterized. X-ray structure determination of [Cu(L 1)(μ -OH)] $_2$ (ClO $_4$) $_2$ showed that the structure around the copper(II) ions is square pyramidal. Visible absorption spectra of the complexes change reversibly over the pH range 2.0–11.0. These complexes act as pH-induced off–on–off absorption switch through protonation and deprotonation of the coordinated amide groups in aqueous solution. The complexes show ionochromic behavior, and the color of the solution changed from blue to colorless upon addition of halides and pseudo halides. The anion competition showed that cyanide anion competes effectively with other anions by changing the color of solution from blue to colorless. The complexes are solvatochromic in polar solvents and their solvatochromism were tested with different solvent parameter

models using the SMLR computational method. The obtained results suggested that the donor number parameter of the solvent has the dominant contribution to the shift of the d–d absorption band of the complexes. The d–d visible absorption band exhibits a red shift with increasing the donor number (DN) of the solvents. As a result, the complexes respond to combinations of stimuli (heat, solvent, pH and anion) mainly due to presence of hemilabile amide groups in the axial position of the complexes.

Acknowledgment

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Appendix A. Supplementary data

CCDC 965074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk. Supporting information: assigned 1 H NMR, 13 C NMR and IR spectra for ligands and complexes, 1 H NMR, 13 C NMR and IR spectra of compound **1** in dilute D $_2$ SO $_4$ and visible absorption spectra of complex **2** in basic aqueous solution.

References

- [1] Fukuda Y. Inorganic chromotropism basic concepts and applications of colored materials. Tokyo and Berlin: Kodansha and Springer; 2007.
- [2] 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 2005;78:1061–71.
- [3] Sato O. Optically switchable molecular solids: photoinduced spin-crossover, photochromism and photoinduced magnetization. Acc Chem Res 2003;36:692–700.
- [4] Ding K, Yang Z, Zhang YL, Xu JZ. Injectable thermosensitive chitosan/glycerophosphate/collagen hydrogel maintains the plasticity of skeletal muscle satellite cells and supports their in vivo viability. Cell Bio Int 2013;37:977–87.
- [5] Sato O, Hayami S, Einaga Y, Gu ZZ. Control of the magnetic and optical properties in molecular compounds by electrochemical, photochemical and chemical methods. Bull Chem Soc Jpn 2003;76:443–70.
- [6] Schanze KS, Schmehl RH. Applications of inorganic photochemistry in the chemical and biological sciences: contemporary developments. J Chem Educ 1997;74:633–5.
- [7] Kahn O, Martinez CJ. Spin-transition polymers: from molecular materials toward memory devices. Science 1998;279:44–8.
- [8] Real JA, Andrés E, Muñoz MC, Julve M, Granier T, Bousseksou A, et al. Spin crossover in a catenane supramolecular system. Science 1995;268:265–7.
- [9] Halder GJ, Kepret CJ, Mourabaki B, Murray KS, Cashion JD. Guest-dependent spin crossover in a nanoporous molecular framework material. Science 2002;298:1762–5.
- [10] Gou M, Guo G, Zhang JA, Men K, Song J, Luo F, et al. Time-temperature chromatic sensor based on polydiacetylene (PDA) vesicle and amphiphilic copolymer. Sens Actuators B 2010;150:406–11.
- [11] Meinershagen JL, Bein T. Solvatochromism of copper(II)(tetramethylethylenediamine)(acetylacetonate) complex encapsulated in EMT zeolite cages. Adv Mater 2001;13:208–11.
- [12] Sone K, Fukuda Y. Inorganic thermochromism. In: Inorganic chemistry concepts. Berlin: Springer; 1987 (Chapter 10).
- [13] Sone K, Fukuda Y. Ions and molecules in solution. Amsterdam: Elsevier; 1983.
- [14] Golchoubian H, Zarabi RZ. Syntheses, crystal structure and chromotropic properties of dinuclear copper(II) complexes of tertiary diamine with hydroxo bridge. Polyhedron 2009;28:3685–90.
- [15] Golchoubian H, Rezaee E. Synthesis, characterization and solvatochromism studies of two new mixed-chelate copper(II) complexes containing β -ketoamine and diamine ligands. Polyhedron 2013;55:162–8.
- [16] Golchoubian H, Moayyedi G, Bruno G, Amiri Rudbari H. Syntheses and characterization of mixed-chelate copper(II) complexes containing different counter ions; spectroscopic studies on solvatochromic properties. Polyhedron 2011;30:1027–34.
- [17] Golchoubian H, Afshar ZM, Moayyedi G, Bruno G, Amiri Rudbari H. Synthesis, characterization and solvatochromism investigation of mixed ligand chelate

- copper(II) complexes with acetylacetonate and three diamine ligands. *Chin J Chem* 2012;30:1873–80.
- [18] Gao F, Chen X, Sun Q, Cao JN, Lin JQ, Xian QZ, et al. Boosting the sensitivity of pH responsible luminescent switches of polypyridyl ruthenium(II) complexes by structural design. *Inorg Chem Commun* 2012;16:25–7.
- [19] Stryer L. *Biochemistry*. 3rd ed. New York: Freeman; 1988.
- [20] Yao Z, Hu X, Huang B, Zhang L, Liu L, Zhao Y, et al. Halochromism of a polythiophene derivative induced by conformational changes and its sensing application of carbon dioxide. *Appl Mater Interfaces* 2013;26:5783–7.
- [21] Schueren LV, Clerck K. Halochromic textile materials as innovative pH-sensors. *Adv Sci Technol* 2012;80:47–52.
- [22] Cheng F, Tang N, Chen J, Wang F, Chen L. pH-induced fluorescence switch of two novel tetranuclear Ru(II) polypyridyl complexes. *Inorg Chem Commun* 2011;14:852–5.
- [23] Meinershagen JL, Bein T. Solvatochromism of a copper(II) (tetramethylethylenediamine)(acetylacetonate)⁺ complex encapsulated in EMT zeolite cages. *Adv Mater* 2001;13:208–11.
- [24] Balaji T, El-Safty SA, Matsunaga H, Hanaoka T, Mizukami F. Optical sensors based on nanostructured cage materials for the detection of toxic metal ions. *Angew Chem* 2006;118:7360–6.
- [25] SMART, SAINT, version 5.060. and version 6.02. Madison and Wisconsin, WI: Bruker AXS Inc; 2007.
- [26] Burla MC, Caliendo R, Camalli M, Carrozzini B, Cascarano GL, DeCaro L, et al. An improved tool for crystal structure determination and refinement. *J Appl Cryst* 2005;38:381–8.
- [27] Sheldrick GM. SHELXL97, program for crystal structure refinement; 2008. Germany.
- [28] SHELXT LN, version 5.10. Madison, WI: Bruker Analytical X-ray Inc.; 2008.
- [29] Gutmann V. The donor-acceptor approach to molecular interactions. New York: Plenum; 1978.
- [30] Linert W, Gutmann V. Structural and electronic responses of coordination compounds to changes in the molecule and molecular environment. *Coord Chem Rev* 1992;117:159–83.
- [31] Shorter J. Correlation analysis of organic reactivity, with particular reference to multiple regression. Chichester: Wiley; 1982.
- [32] SPSS/PS, statistical package for IBMPC, version 13. Ontario: SPSS; 1998.
- [33] Riahi S, Mousavi MF, Shamsipur M. Prediction of selectivity coefficients of a theophylline-selective electrode using MLR and ANN. *Talanta* 2006;69:736–40.
- [34] Tsiamis C, Themeli M. Substituent and solvent effects in the spectra and structure of some mixed-ligand copper(II) chelates containing β -ketoenols. *Inorg Chim Acta* 1993;206:105–15.
- [35] Meek DE, Ehrhardt SA. Copper(II) complexes of secondary and tertiary N-substituted ethylenediamines. *Inorg Chem* 1965;4:584–7.
- [36] Raman N, Esthar S, Thangaraja C. A new Mannich base and its transition metal(II) complexes- Synthesis, structural characterization and electrochemical study. *J Chem Sci* 2004;116:209–13.
- [37] Nakamoto K, Ohkaku N. Metal isotope effect on metal-ligand vibrations. VI. Metal complexes of 8-hydroxyquinoline. *Inorg Chem* 1971;10:798–805.
- [38] Fukuda Y, Shimura A, Mukaida M, Fujita E, Sone K. Studies on mixed chelates – III: mixed copper(II) chelates with *N,N,N',N'*-tetramethylethylenediamine and β -diketones. *J Inorg Nucl Chem* 1974;36:1265–70.
- [39] Geary WJ. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord Chem Rev* 1971;7:81–122.
- [40] Addison AW, Rao TN, Reedijk J, Rijn JV, Verschoor GC. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane] copper(II) perchlorate. *J Chem Soc Dalton Trans* 1984;1349–56.
- [41] Jadeja RN, Shah JR, Suresh E, Paul P. Synthesis and structural characterization of some Schiff bases derived from 4-[[[(aryl)imino]ethyl]-3-methyl-1-(4'-methylphenyl)-2-pyrazolin-5-one and spectroscopic studies of their Cu(II) complexes. *Polyhedron* 2004;23:2465–74.
- [42] Chao MS, Lu HH, Tsai ML, Lin CM, Hsieh TH. Molecular switching of nickel(II) complexes using a hemilabile *N,N'*-bis(β -carbamoyl)ethyl-1,2-diaminocyclohexane ligand. *Inorg Chem Commun* 2009;12:1088–90.
- [43] Chao MS, Lu HH, Tsai ML, Lin CM, Hsieh TH. Reversible switching of coordination modes of nickel(II) complexes using a hemilabile 4,7-diazadecanediamide ligand. *Inorg Chim Acta* 2009;362:3835–9.
- [44] Malati MA. Experimental inorganic/physical chemistry: an investigative, integrated approach to practical project work. Albion: Horwood; 1999.
- [45] Brotherton TK, Lynn JW. The synthesis and chemistry of cyanogens. *Chem Rev* 1959;59:841–83.