



Universiteit
Leiden
The Netherlands

Copper (II) halide complexes with NNO tridentate ligand as chromotropic probes; synthesis, structural characterization and spectroscopic properties

Shirvan, A.; Golchoubian, H.; Siegler, M.A.; Bouwman, E.

Citation

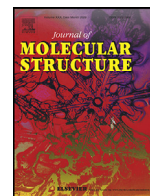
Shirvan, A., Golchoubian, H., Siegler, M. A., & Bouwman, E. (2021). Copper (II) halide complexes with NNO tridentate ligand as chromotropic probes; synthesis, structural characterization and spectroscopic properties. *Journal Of Molecular Structure*, 1243. doi:10.1016/j.molstruc.2021.130930

Version: Publisher's Version

License: [Licensed under Article 25fa Copyright Act/Law \(Amendment Taverne\)](#)

Downloaded from: <https://hdl.handle.net/1887/3564621>

Note: To cite this publication please use the final published version (if applicable).



Copper (II) halide complexes with NNO tridentate ligand as chromotropic probes; synthesis, structural characterization and spectroscopic properties

Atie Shirvan^{a,*}, Hamid Golchoubian^{a,*}, Maxime A. Siegler^b, Elisabeth Bouwman^c

^a Department of Chemistry, University of Mazandaran, Babol-sar, 47416-95447, Iran

^b Department of Chemistry, Johns Hopkins University, 3400 N. Charles Street, Baltimore, MD 21218, United States

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, Netherlands

ARTICLE INFO

Article history:

Received 26 January 2021

Revised 21 May 2021

Accepted 15 June 2021

Available online 19 June 2021

Keywords:

Solvatochromism

Thermochromism

Halochromism

Copper

ABSTRACT

This study reports chromotropism of two newly synthesized copper(II) complexes of formula $[\text{CuLCl}_2]$ and $[\text{CuLBr}_2] \cdot \text{MeOH}$ where $L = N-(2\text{-pyridylmethyl})-1\text{-hydroxypropylamine}$. The structure of the complexes was investigated by infrared spectroscopy, electronic absorption spectroscopy, elemental analysis, molar conductance measurements, and thermal analysis. Single Crystal X-ray structure determination reveals both complexes to adopt a distorted square-pyramidal geometry. Their chromotropic properties were investigated using electronic absorption spectroscopy. The complexes are solvatochromic in solvents with different polarities. The aqueous solutions of the complexes exhibit a variety of colors in the pH range of 1.8 to 11.4 showing that the compounds are halochromic. The complexes are also thermochromic and show reversible color changes in different temperatures in dimethyl sulfoxide solutions. The solution study reveals that the observed chromotropism originates from structural changes of the complexes in different conditions.

© 2021 Elsevier B.V. All rights reserved.

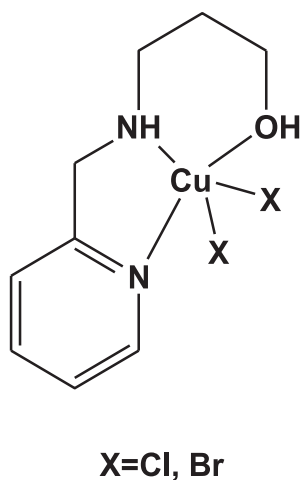
1. Introduction

The design and preparation of novel materials with chromotropic properties have gained increasing importance due to their potential applications in various areas. Chromotropic materials are able to exhibit discernible color changes upon exposure to various external stimuli such as temperature, pressure, different ions, pH, electric field, irradiation and/or polarity of the solvents [1,2]. Due to the optical response which lies within the visible region, the chromotropic compounds can generate simple and immediate visual signals and thus can be utilized efficiently as sensors and indicators [3-5]. Furthermore, investigation of chromotropism behavior of the compounds in solution and scrutinizing the mechanism of their color change, may lead to understanding of their possible solute-solution interactions in the various surrounding media. Consequently, this could provide valuable data for scientists in chemistry and biochemistry to choose the best reaction conditions such as solvent, temperatures and pH range [6]. Examples of chromotropic organic, organometallic and coordination compounds have been reported with diverse origins of their

color changes [7-9]. Copper(II) complexes with strong Jahn-Teller effects form a family of chromotropic metal complexes whose color change arises from changes in their d-d transitions. Most of these complexes contain four- or five-coordinate copper(II) centers stabilized with diamine and/or diketone ligands. Spectroscopic studies on these complexes demonstrated that the interaction of the solvent molecules with the axial positions of the complexes cause a shift in the d-d transitions and thus a substantial solvatochromism is observed in solvents with different polarities [10-12]. The design of complexes with two or more chromotropic features can be highly beneficial. The presence of labile metal-ligand bonds in the coordination sphere is a feasible approach to increase the sensitivity of the complexes to environmental changes [13]. Earlier studies show that the structure and spectroscopic properties of copper complexes containing chloride and/or bromide ions change upon heating or increasing the polarity in the solution [14]. Therefore, copper halide complexes with the proper combination of chelating ligands are expected to exhibit thermo and solvatochromic behavior [15,16]. Tridentate chelating ligands containing NNO donating atoms are of special interest because of the potential biological activities [17]. Besides, the multidentate ligands have the advantage of enhancing the stability of the resulting complexes due to the chelating effect. In this study, a tridentate NNO ligand contain-

* Corresponding authors.

E-mail address: h.golchoubian@umz.ac.ir (H. Golchoubian).



Scheme 1. Complexes under study.

ing hydroxyl and secondary amine moieties was used in connection with their ability to undergo deprotonation-protonation processes, which could potentially cause the formation of the complexes with pH-induced color change i.e. halochromism. In this regard, the two mononuclear copper(II) halide complexes shown in **Scheme 1** were synthesized and characterized, with the ligand *N*-(2-pyridylmethyl)-1-hydroxypropylamine. Their structural features, as well as their spectroscopic sensitivity to external stimuli were evaluated, and the complexes were shown to exhibit thermochromic, solvatochromic, and halochromic properties.

2. Experimental

2.1. General procedures

The ligand *N*-(2-pyridylmethyl)-1-hydroxypropylamine (**L**) was synthesized according to the procedure reported by Gentshev et al. [18]. All chemicals were purchased from commercial sources and used without further purification. The solvents employed for chromatopism studies were of spectroscopic grade.

IR spectra were recorded on a PerkinElmer UATR spectrum equipped with a single reflection diamond. UV-Vis spectra were acquired with JASCO V-750 double beam spectrophotometer with 1 cm quartz cells. Conductance measurements were performed at room temperature using a Jenway 400 conductivity meter on 1.00×10^{-3} M samples in selected solvents. Elemental analysis were performed by a PerkinElmer model 2400 elemental analyzer. Thermal analysis was carried out on a Bahr Thermo analyse STA 504 instrument in an argon atmosphere.

2.2. Synthesis

2.2.1. Preparation of complex $[\text{CuLCl}_2]$, **1**

A solution of CuCl_2 (0.536 g, 4 mmol) in methanol (8 mL) was added to a solution of **L** (0.66 g, 4 mmol) in methanol (10 mL). The resulted greenish-blue solution was stirred for 4 h at room temperature. After one day, the obtained blue crystals were collected by filtration and recrystallized by diffusion of diethyl ether into a methanol solution. Yield: 65% (0.78 g). Selected IR data (ν/cm^{-1}): 3147 (s); 3074 (m); 2946 (m); 1610 (s); 1573 (m); 1479 (m); 1463 (m); 1447 (s); 1421 (s); 1327 (s); 1284 (s); 1067(s); 1047 (s); 957 (s); 770 (s); 541 (m); 420 (m). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{Cl}_2\text{CuN}_2\text{O}$ (MW = 300.67 g mol $^{-1}$): C, 35.95; H, 4.69; N, 9.32%; Found: C, 35.97; H, 4.46; N, 9.29%.

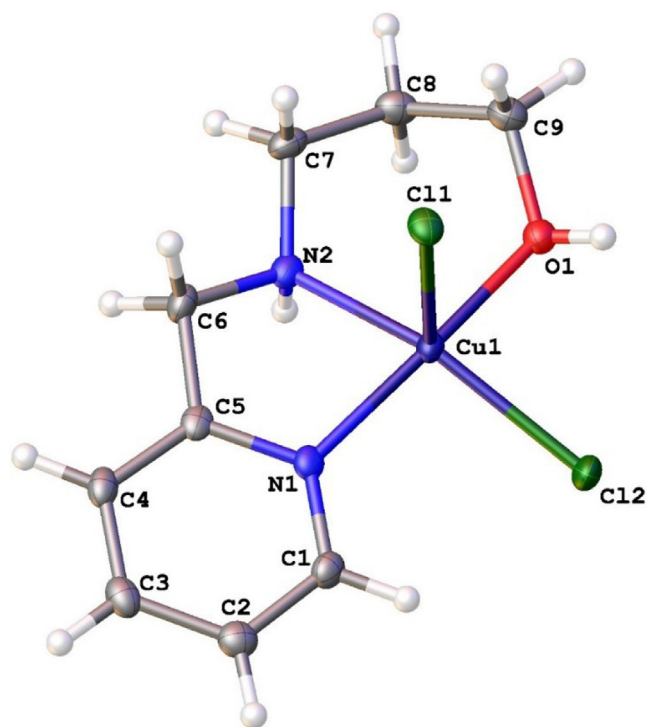


Fig. 1. Displacement ellipsoid plot (50% probability) of $[\text{CuLCl}_2]$, **1** at 110(2) K.

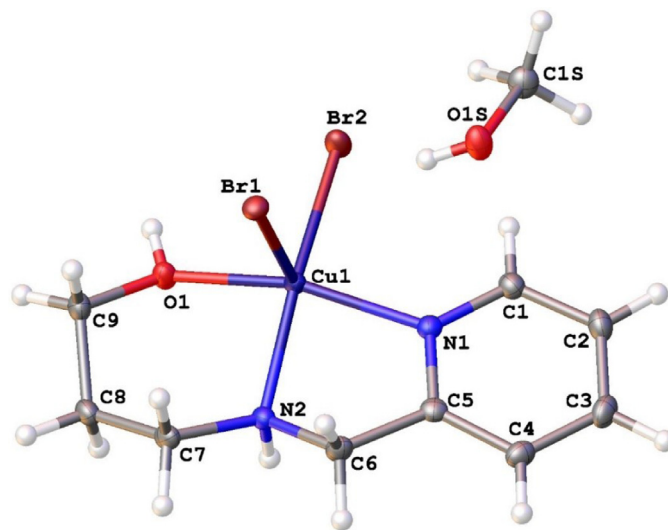


Fig. 2. Displacement ellipsoid plot (50% probability) of $[\text{CuLBr}_2]$, **2** at 110(2) K.

2.2.2. Preparation of complex $[\text{CuLBr}_2] \cdot \text{MeOH}$, **2**

This compound was synthesized by the same reaction procedure described for $[\text{CuLCl}_2]$, except that CuBr_2 (0.90 g, 4 mmol) was used in place of CuCl_2 . The desired complex was obtained as blue crystals with a typical yield of 43% (0.66 g). Selected IR data (ν/cm^{-1}): 3163 (s,); 3079 (s); 2862 (m); 1607 (s); 1569 (m); 1475 (m); 1446 (m); 1432 (s); 1422 (s); 1284 (s); 1053(s); 1028 (s); 951 (s); 778 (s); 541 (m); 418 (s). Anal. Calcd for $\text{C}_9\text{H}_{14}\text{Br}_2\text{CuN}_2\text{O}$ (MW = 389.57 g mol $^{-1}$): C, 27.75; H, 3.62; N, 7.19%; Found: C, 27.33; H, 3.20; N, 6.55%.

Table 1
Crystal data and structure refinement for **1** and **2**.

	1	2
Empirical formula	C ₉ H ₁₄ Cl ₂ CuN ₂ O	C ₉ H ₁₄ Br ₂ CuN ₂ O•CH ₄ O
Formula weight	300.66	421.62
Color, morphology	Light blue, small block	Blue, small block
Temperature (K)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /n
Unit cell dimensions		
<i>a</i> (Å)	7.95176 (19)	7.41692 (15)
<i>b</i> (Å)	10.9791 (2)	12.7280 (2)
<i>c</i> (Å)	13.2995 (3)	15.1141 (3)
β (°)	97.926 (2)	93.4959 (18)
Volume (Å ³)	1150.00 (4)	1424.15 (5)
<i>Z</i>	4	4
Calculated density (g cm ⁻³)	1.737	1.966
μ (mm ⁻¹)	2.34	7.14
F (0 0 0)	612	828
Crystal size (mm ³)	0.17 × 0.15 × 0.06	0.20 × 0.17 × 0.11
θ range for data collection (°)	3.19–27.67	3.12–27.67
Index ranges	–10 ≤ <i>h</i> ≤ 10 –14 ≤ <i>k</i> ≤ 14 –17 ≤ <i>l</i> ≤ 17	–9 ≤ <i>h</i> ≤ 9 –16 ≤ <i>k</i> ≤ 16 –19 ≤ <i>l</i> ≤ 19
Reflections collected/unique(<i>R</i> _{int})	17,148/2644(0.029)	21,215/3275(0.029)
Data completeness	100%	99.9%
Refinement method	Full matrix least-squares on F ²	Full matrix least-squares on F ²
Data/restraints/parameters	2644/2/142	3275/3/165
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0210, <i>wR</i> ₂ = 0.0491	<i>R</i> ₁ = 0.0159, <i>wR</i> ₂ = 0.0374
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0237, <i>wR</i> ₂ = 0.0506	<i>R</i> ₁ = 0.0181, <i>wR</i> ₂ = 0.0381
Goodness-of-fit on F ²	1.04	1.06
Largest diff. peak and hole (e Å ⁻³)	0.66 and –0.33	0.39 and –0.32

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex 1		Complex 2	
<i>Bond distances</i>		<i>Bond distances</i>	
Cu(1)–N(1)	1.9995(14)	Cu(1)–N(1)	2.0127(14)
Cu(1)–N(2)	2.0389(14)	Cu(1)–N(2)	2.0287(14)
Cu(1)–Cl(1)	2.4901(4)	Cu(1)–Br(1)	2.7251(3)
Cu(1)–Cl(2)	2.2794(4)	Cu(1)–Br(2)	2.3947(3)
Cu(1)–O(1)	2.0071(13)	Cu(1)–O(1)	1.9887(12)
<i>Bond angles</i>		<i>Bond angles</i>	
Cl(1)–Cu(1)–O(1)	94.05(4)	Br(1)–Cu(1)–O(1)	98.77(4)
Cl(1)–Cu(1)–N(1)	95.17(4)	Br(1)–Cu(1)–N(1)	97.50(4)
Cl(1)–Cu(1)–N(2)	96.37(4)	Br(1)–Cu(1)–N(2)	92.41(4)
Cl(1)–Cu(1)–Cl(2)	109.073(17)	Br(1)–Cu(1)–Br(2)	102.395(9)
Cl(2)–Cu(1)–N(1)	96.55(4)	Br(2)–Cu(1)–N(1)	96.71(4)
N(1)–Cu(1)–N(2)	81.73(6)	N(1)–Cu(1)–N(2)	82.00(5)
N(2)–Cu(1)–O(1)	91.40(6)	N(2)–Cu(1)–O(1)	88.16(5)
O(1)–Cu(1)–Cl(2)	85.97(4)	O(1)–Cu(1)–Br(2)	88.74(4)
N(2)–Cu(1)–Cl(2)	154.53(4)	N(2)–Cu(1)–Br(2)	165.17(4)
N(1)–Cu(1)–O(1)	169.06(5)	N(1)–Cu(1)–O(1)	161.31(5)

Table 3
The electronic absorption maxima of complexes **1** and **2** in selected solvents at room temperature.

solvent	Complex 1		Complex 2	
	λ_{\max} (nm)	ϵ (L cm ⁻¹ mol ⁻¹)	λ_{\max} (nm)	ϵ (L cm ⁻¹ mol ⁻¹)
NB	749	106	711	111
MeOH	698	162	703	127
NM	757	107	749	102
DMF	776	180	774	218
EtOH	708	130	714	188
H ₂ O	682	107	681	102
Ac	731	159	765	150
Py	784	197	704	165
DMSO	741	147	734	188
$\Delta\lambda$	102		93	

Table 4
Molar conductivity values (Λ m) of **1** and **2** (Ω^{-1} cm² mol⁻¹) at 25 °C in different solvents ^a.

	NB	EtOH	MeOH	DMF	H ₂ O
Compound 1	1	21	90	61	262
Compound 2	4	27	104	72	254
1:1 electrolytes	20–30	35–45	80–115	65–90	118–131
1:2 electrolytes	50–60	70–90	160–220	130–170	235–273
1:3 electrolytes	70–80	^b	^b	200–240	408–435

^a Standard values are given from Ref. [29].^b The standard value is not reported.

2.3. Single crystal X-ray crystallography

All reflection intensities were measured at 110 K for **1** and **2** using a SuperNova diffractometer (equipped with Atlas detector) with Mo *K* α radiation ($\lambda = 0.71073$ Å) under the program CrysAlisPro (Version CrysAlisPro 1.171.39.29c, Rigaku OD, 2017). The same program was used to refine the cell dimensions and for data reduction. The two structures were solved with the program SHELXS-2018/3 (Sheldrick, 2018) and was refined on *F*² with SHELXL-2018/3 (Sheldrick, 2018) [19]. Numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions (unless otherwise specified) using the instructions AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 *U*_{eq} of the attached C atoms. The H atoms attached to N2, O1 and O1S (only for **2**) have been located via difference Fourier maps, and their coordinates were refined pseudo-freely using the DFIX instructions in order to keep the *N* – *H* and *O* – *H* bond distances within acceptable ranges. Both structures are ordered. Detailed information on structure de-

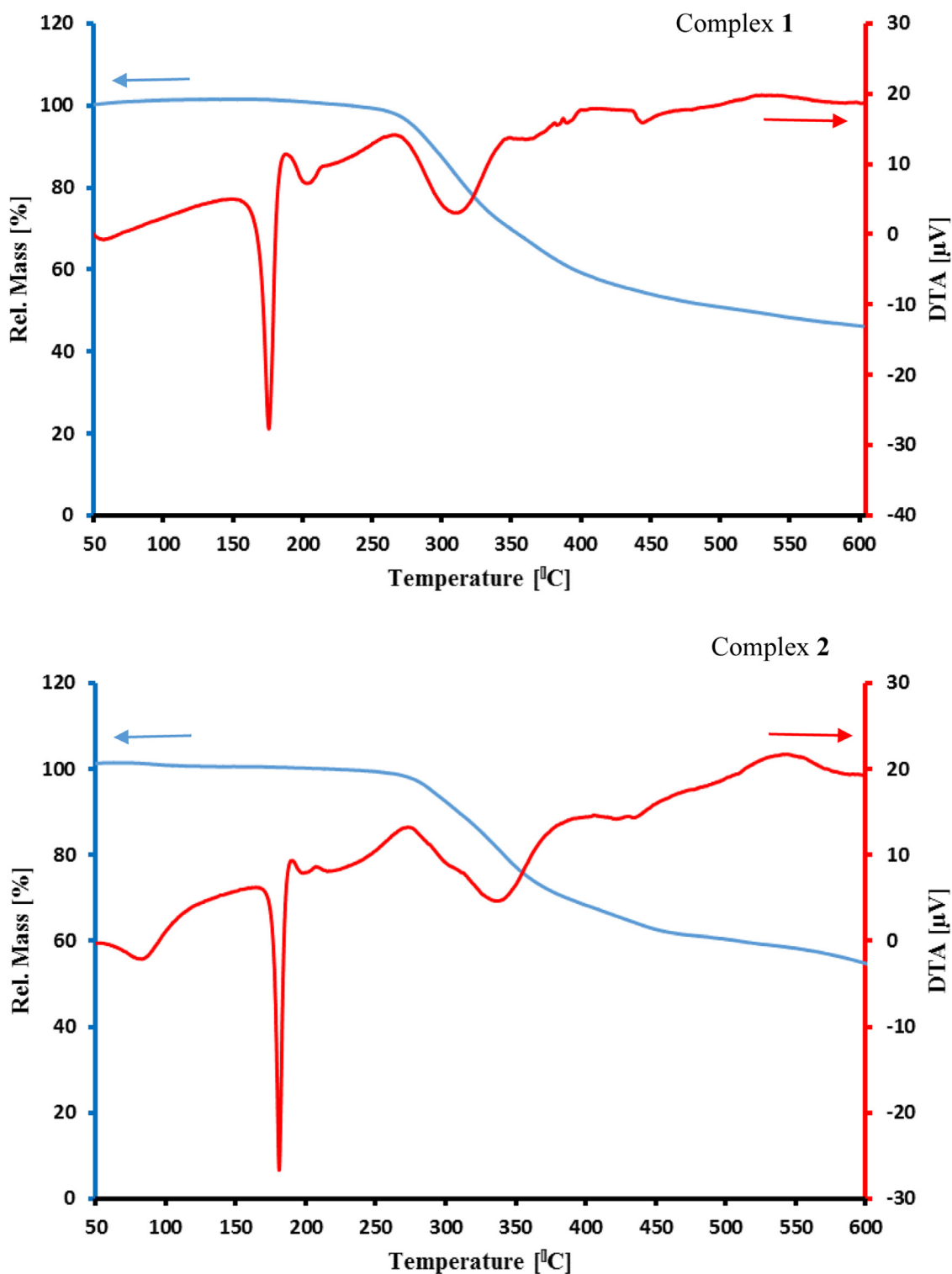


Fig. 3. TGA and DTA curves of **1** and **2**.

termination and crystal data for complexes **1** and **2** are presented in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The mononuclear copper complexes $[\text{CuLCl}_2]$ and $[\text{CuLBr}_2] \cdot \text{MeOH}$ were synthesized by the reaction of copper(II)

halide salts with *N*-(2-pyridylmethyl)-1-hydroxypropylamine in a molar ratio of 1:1 in methanol at ambient temperature. The proposed formulation of the complexes has been confirmed by spectroscopic and analytical data. The infrared spectra of the compounds **1** and **2** exhibit comparable signals due to their similar structures as was confirmed by single crystal X-ray crystallography (Fig. S1 in supplementary content). The stretching vibrations of N-H and O-H groups appear as overlapping bands at 3074–3147

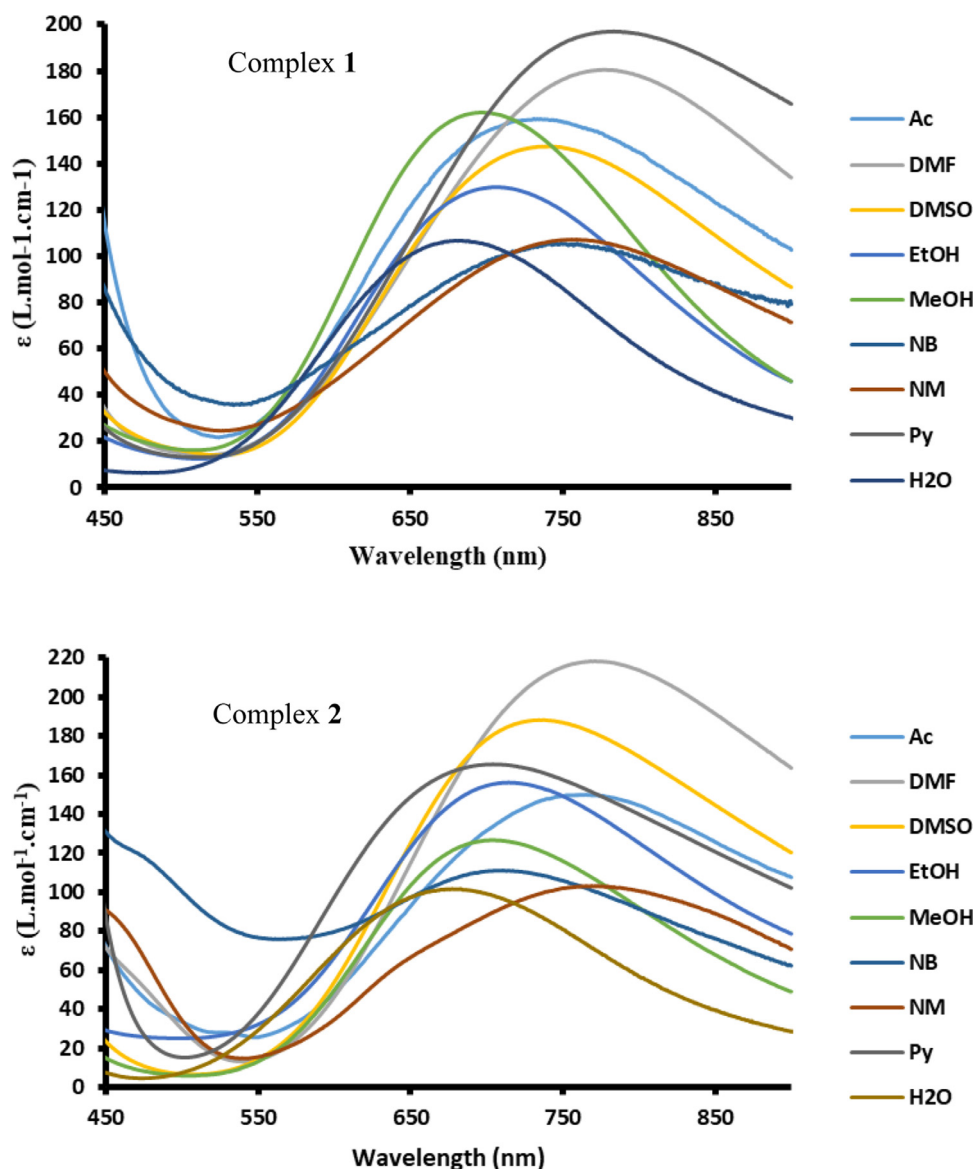


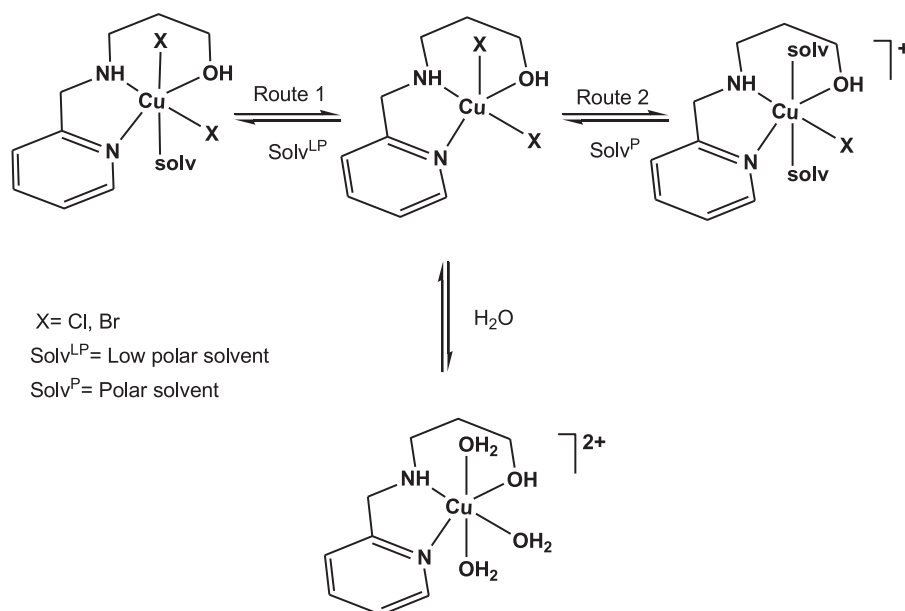
Fig. 4. Electronic absorption spectra of **1** and **2** in different solvents.

cm^{-1} and $3079\text{--}3163\text{ cm}^{-1}$ in the spectra of complexes **1** and **2**, respectively. In the IR spectrum of the free ligand these bands are broader and appear at higher frequencies (3283 cm^{-1}). This noticeable shift confirms that the secondary amine and alcohol groups of the ligand are coordinated to the copper center. The bands at 1610 cm^{-1} and 1573 cm^{-1} in complex **1** and 1607 cm^{-1} and 1569 cm^{-1} in complex **2** are attributed to $\text{C}=\text{N}$ and $\text{C}=\text{C}$ vibration modes of the pyridine ring [20]. Coordination of the chelating ligand to the copper(II) ion can be also substantiated by the appearance of the bands around 450 cm^{-1} and 540 cm^{-1} , which are attributed to Cu-N and Cu-O vibrations, respectively [21,22].

3.2. Description of structures

Both complexes crystallized in the monoclinic space group $P2_1/n$. A projection of the crystal structures of **1** and **2** along with the atom numbering scheme are shown in Figs. 1 and 2 and selected bond distances and angles are provided in Table 2. The copper metal centers in both mononuclear complexes adopt a five-coordinated N_2OX_2 ($\text{X}=\text{Cl}, \text{Br}$) environment. The three donor atoms

of **L** along with one halide ion are located in the basal plane of the square pyramid and the other halide ligand occupies the apical position. The geometrical parameter $\tau = |\alpha - \beta|/60$ where β and α are the two largest L-M-L bond angles in the coordination sphere, can be used to describe the distortion of square-pyramidal geometry (in which $\tau = 0$) towards a trigonal bipyramid (in which $\tau = 1$) [23]. The τ values of 0.24 for **1** and 0.06 for **2** confirm the distorted square-pyramidal geometries around the copper centers. The deviations from the least-square plane through the CuON_2X atoms are $\text{N}(1)\ 0.085$, $\text{N}(2)\ -0.231$, $\text{O}(1)\ 0.086$, $\text{Cl}(2)\ -0.199$, $\text{Cu}(1)\ 0.259\text{ \AA}$ in complex **1**, and $\text{N}(1)\ -0.066$, $\text{N}(2)\ -0.051$, $\text{O}(1)\ -0.065$, $\text{Br}(2)\ -0.050$, $\text{Cu}(1)\ 0.232\text{ \AA}$ in complex **2**. The tridentate ligand offers an N_2O donor set chelated to the copper ion, thereby forming two fused metallocyclic (5,6)-membered rings with N,N and N,O coordination angles of $81.73(6)^\circ$ and $91.40(5)^\circ$ in **1**, and $82.00(6)^\circ$ and $88.16(5)^\circ$ in **2**, respectively. The five-membered chelate rings in both complexes are puckered, so that the $\text{N}(1)\text{-C}(5)\text{-C}(6)\text{-N}(2)$ torsion angles are $18.4(2)^\circ$ and $28.4(2)^\circ$ in **1** and **2**, respectively. The six-membered chelate rings have chair conformations. The Cu-O bond lengths of $2.0071(13)$ and $1.9887(12)\text{ \AA}$ in **1** and **2** are in the normal range of copper-alcohol bond distances in equato-



Scheme 2. Proposed structural changes of 1 and 2 in different solvents.

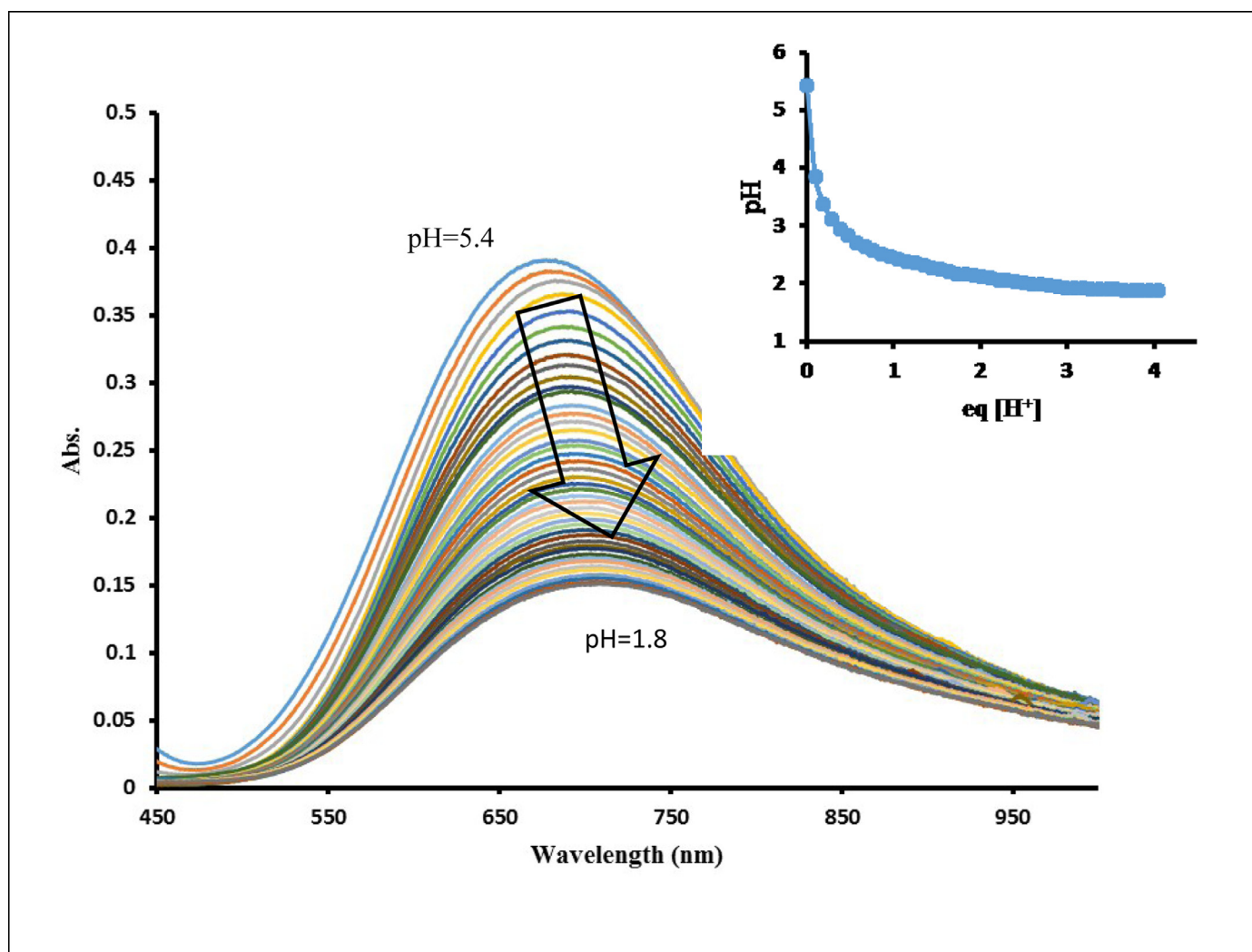
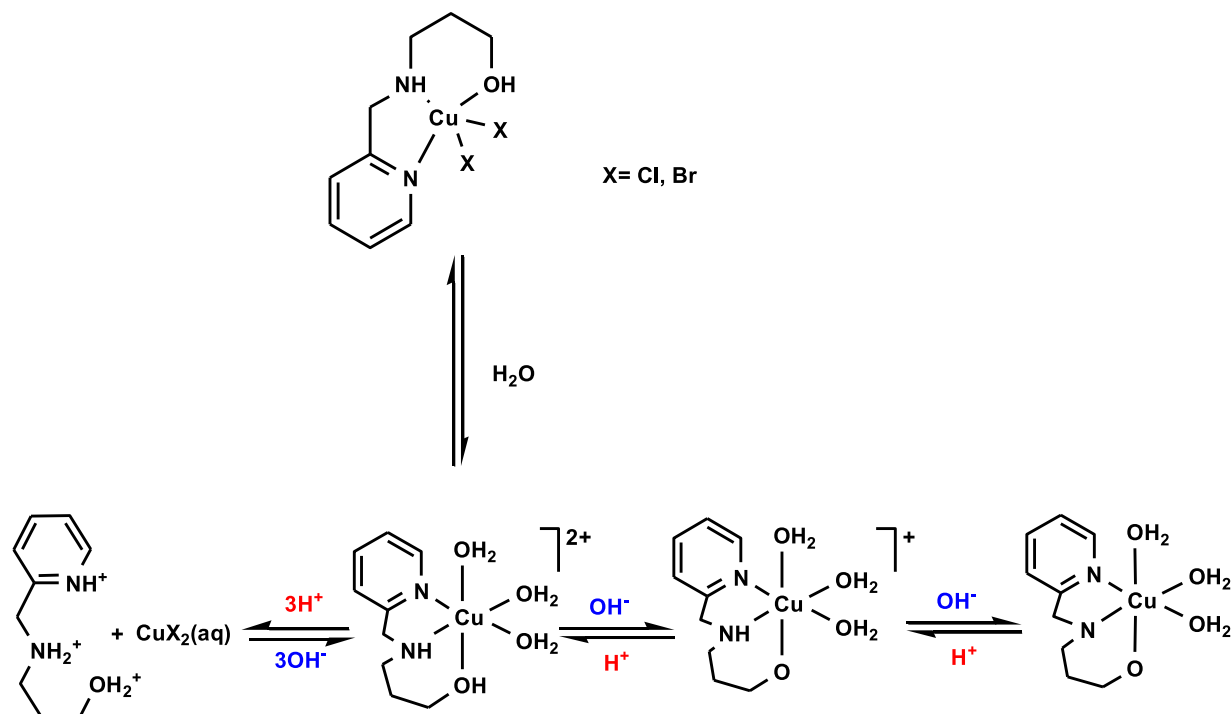


Fig. 5. The pH titration of 1 with HClO₄ (100 mM) in the pH range of 5.4–1.8.



Scheme 3. Interconversion of complexes **1** and **2** triggered by base and acid (pH=1.8–11.4) in aqueous solution.

rial positions [24]. In both complexes, the halide ion located in the apical site has longer Cu-X bond length than the equatorial halide ligand. The Cu-Cl(1) and Cu-Cl(2) bond lengths in **1** are 2.4901(4) and 2.2794(4) Å, respectively, whereas the corresponding Cu-Br bond lengths in **2** are 2.7251(3) and 2.3947(3) Å. The Cu-N bond lengths are in the range of 1.9995(14) to 2.0389(14) Å and are comparable to literature values [18,25,26]. In the crystal lattice of compound **1**, hydrogen bonding occurs between the hydroxyl group of the ligand and the equatorial chloride ion of a neighboring molecule (O(1)H(1A)•••Cl(2) = 3.1517(13) Å), by which a dimeric entity forms that is further linked to neighboring ones through hydrogen bonding between the secondary amine hydrogen and apical chloride ions (N(2)H(2A)•••Cl(1) = 3.2430(15) Å). In compound **2**, the crystal lattice is stabilized by the hydrogen bonding between the secondary amine and the apical bromide ion of a neighboring molecule (N(2)H(2A)•••Br(1) = 3.3866(14) Å), and furthermore by hydrogen bonding between the methanol molecule and the apical bromide as well as the hydroxyl group of the ligand (O(1S)H(1O1)•••Br(1) = 3.2715(13) Å; O(1)H(1A)•••O(1S) = 2.6542(18) Å). The crystal packing of compounds **1** and **2** are depicted in Figs. S2 and S3 in the supplementary content, respectively.

3.3. Thermal analysis

The thermal stabilities of the complexes were studied using thermal gravimetry (TG) and differential thermal analysis (DTA) in a temperature range of 25 to 600 °C under static argon atmosphere. The complexes have the same pattern of thermal decomposition due to their similar molecular formula and structures, as shown in Fig. 3. The endothermic signals which appeared in the DTA curves of **1** and **2** at 175 and 181 °C, respectively, are probably due to dissociation of the apical halogen ions which are coordinated loosely to the copper(II) ions. In both complexes decomposition of the organic ligand starts above 250 °C in two distinguishable stages. The first step is associated with the elimination of the methylpyridine moiety of ligand, which takes place between 250

and 350 °C in complex **1** and between 250 and 375 °C in complex **2**, as shown by the mass loss of 30.98% (calculated 31.64%) and 28.34% (calculated 23.68%) in **1** and **2**, respectively. This step is succeeded by the removal of the remaining aminopropanol moiety of the ligand with a mass loss of 22.87% (calculated 24.9%) and 17.25% (calculated 19.27%) in **1** and **2**, respectively. The residual mass at 600 °C is attributed to copper(II) chloride (observed 46.15%; calculated 44.71%) and copper(II) bromide (observed 54.41%; calculated 57.33%) in **1** and **2**, respectively.

3.4. Chromotropism study

3.4.1. Solvatochromism

The complexes are solvatochromic and show a range of color changes in solvents with different polarity including dimethylformamide (DMF), pyridine (Py), dimethylsulfoxide (DMSO), acetone (Ac), methanol (MeOH), ethanol (EtOH), nitromethane (NM), nitrobenzene (NB) and water. The λ_{\max} values of the visible absorption bands in different solvents are collected in Table 3 and the solvent-dependent electronic absorption spectra of **1** and **2** are shown in Fig 4. The observed solvatochromism arises from a shift in the d-d transition, which can be attributed to the structural changes of the complexes in different solvents. The d-d absorptions in all solvents appear as unsymmetrical broad bands at 700–800 nm with low intensities as is characteristic of octahedral complexes [27]. The crystallographic data showed that the complexes are square pyramidal in the solid state. However, in solution it is possible for solvent molecules to coordinate to the unoccupied apical position of the copper(II) ions, thus changing the structure to octahedral [1,28]. On other hand, the Jahn-Teller elongation in the Cu-X (X=Cl or Br) bonds make the apical halide ligands susceptible to dissociation and to be substituted by solvent molecules [14]. However, the probability of this phenomenon depends on the polarity and coordinating ability of the solvent molecule. In order to investigate this hypothesis, the molar conductance of the compounds in different solvents was determined and compared with the standard values [29] as presented in Table 4. In more

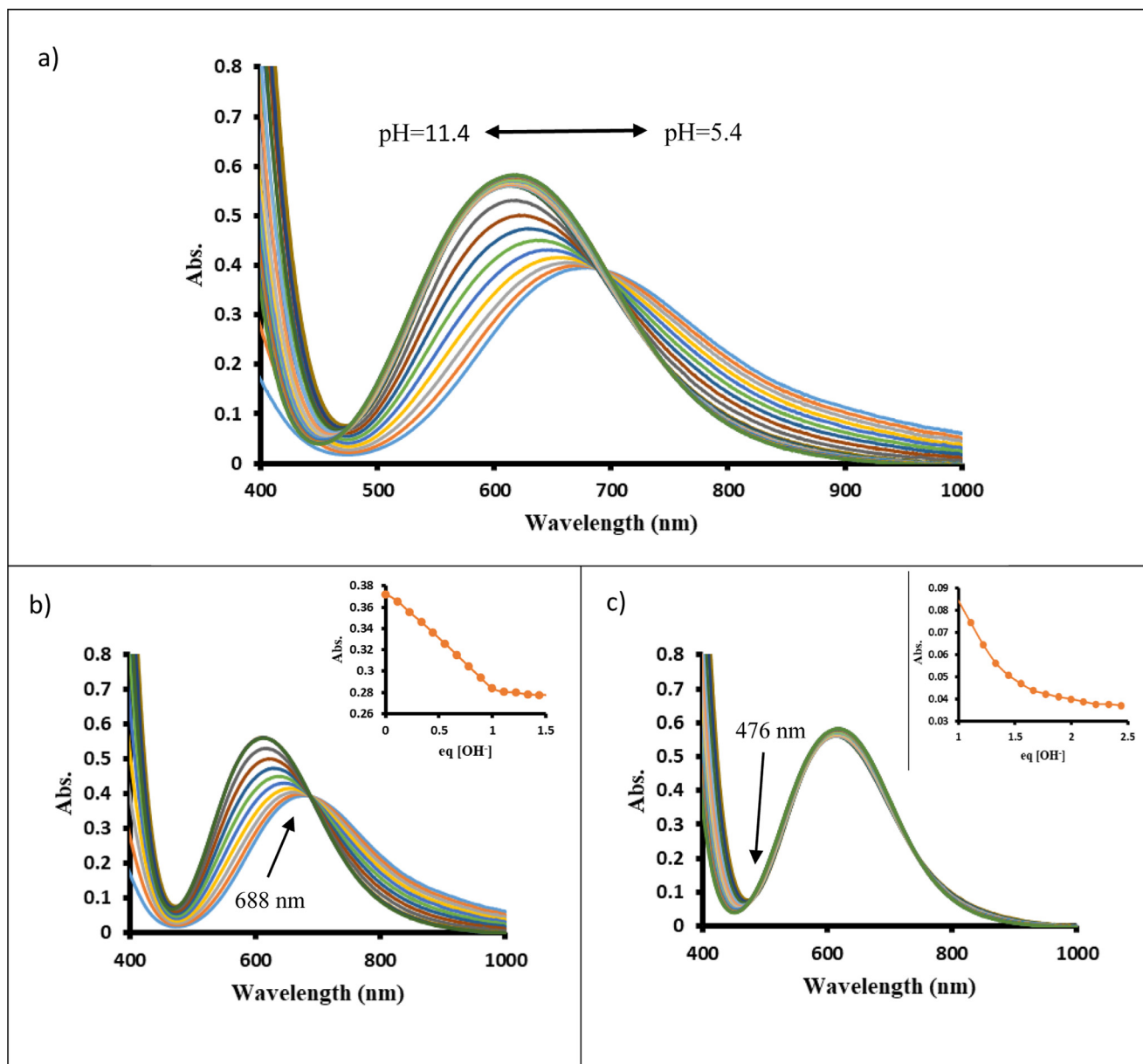


Fig. 6. The pH titration of **1** with NaOH (100 mM) in the pH range of 5.4–11.4 (a), spectroscopic titration of complex at 710 nm with NaOH (0.1 M) at pH range of 5.4–8.4 and presentation of isosbestic point at 688 nm (b), spectroscopic titration of complex at 460 nm with NaOH (0.1 M) at pH range of 8.4–11.4 and presentation of isosbestic point at 476 nm (c). Inset graphs of (b) and (c) show decrease in molar absorption values at 710 nm and 460 nm, respectively, during the titration.

polar solvents, the possibility of breaking of the Cu-X ($X = \text{Cl}$ or Br) bond increases and accordingly the molar conductance values of the solutions are enhanced. In solvents of low polarity the Cu-X ($X = \text{Cl}$ or Br) bonds remain intact and solvatochromism is associated with coordination of the solvent at the vacant site of the compounds (route 1 in Scheme 2) without considerable change in molar conductance value of the solution. In more polar solvents such as MeOH and DMF, the axial halide ligands are also replaced by solvent molecules as shown in route 2 of Scheme 2, as indicated by the increase of the molar conductance of the solutions to the standard value of a 1:1 electrolyte. In aqueous solution both halide ligands dissociate and are replaced with water molecules [15]. Since this reaction leads to the formation of the same cationic complex in both aqueous solutions of **1** and **2**, their color and electronic absorption spectra become the same (Fig. S4 in supplementary content). Meanwhile, the molar conductivity of the aqueous solution of **1** and **2** increase to the standard

range for 1:2 electrolytes, which is in harmony with the proposed mechanism.

3.4.2. Halochromism

The aqueous solutions of the complexes exhibit reversible color changes in response to pH changes. As discussed above, in aqueous solution the halogen ions dissociate and are substituted by water molecules, resulting in the formation of the same cationic complex $[\text{Cu}(\text{L})(\text{H}_2\text{O})_x]^{2+}$. Although halochromism of both compounds was carried out, the study of halochromism compound **1** is reported due to their similar identities and their halochromism behavior (see Figs. S5, S6). Upon decreasing pH of the solution from 5.4 (original pH) to 1.8 by the addition of an acid (HClO_4 100 mM), the blue color of the solution fades. This color change is reflected in the electronic absorption spectra as a reduction in the intensity of the absorption band along with a redshift in the absorption maxima (Fig 5). This phenomenon is probably due to proto-

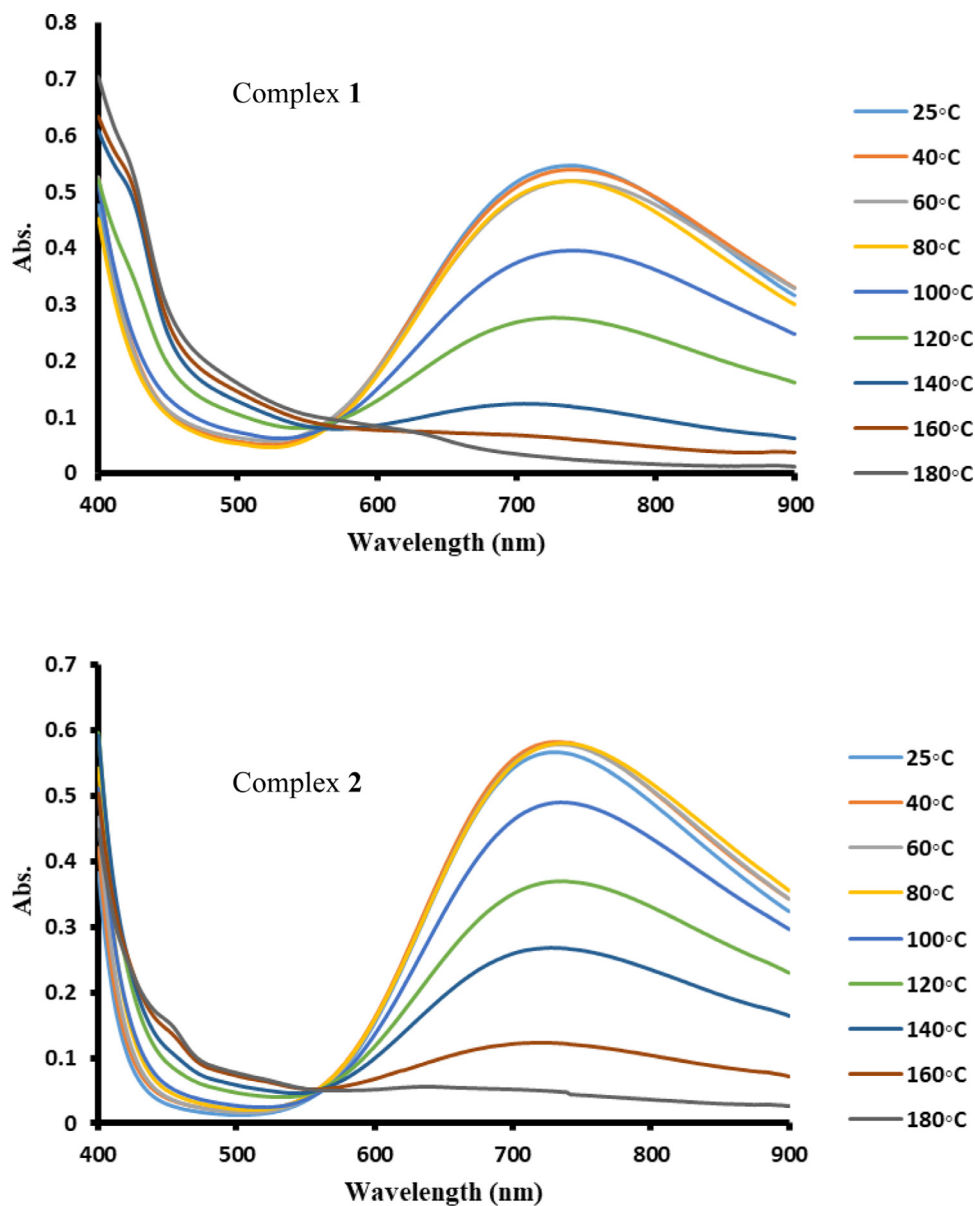


Fig. 7. Spectroscopic changes of DMSO solution of complexes **1** and **2** at different temperatures.

nation of the coordinated donor atoms, resulting in dissociation of the tridentate ligand and creation of the hydrated Cu(II) complex as shown in Scheme 3. Spectrophotometric titration of the complex with HClO₄ shows that this process is accompanied with consumption of three equivalent of protons (inset Fig 5), which agrees with the proposed mechanism.

Alkalization of the solution using a base (NaOH 100 mM) causes a change in the color of the solution from blue to purple. The changes in the spectra upon addition of the base in the pH range of 5.4–11.4 (Fig 6a) show a blue shift in the absorption maxima from 682 to 613 nm along with the development of two isosbestic points at 688 and 476 nm (Figs 6b and 6c). As shown in Figs 6b and 6c, spectroscopic titration of the solution with the base indicates consumption of two equivalents of hydroxide ions (the first in pH range of 5.4–8.4 and the second in the pH range of 8.4 to 11.4). These observations indicate that the observed halochromism caused by the addition of base arises from the deprotonation of the OH and NH groups of the chelating ligand with two subsequent equilibria that are shown in Scheme 3.

3.4.3. Thermochromism

The thermochromic behavior of the complexes was studied in DMSO solution. The complexes exhibit continuous color change from blueish green to pale yellow upon heating the solution from room temperature to the boiling point of the solvent. The spectroscopic changes of complexes **1** and **2** in DMSO solution in the temperature range of 25–180 °C are shown in Fig 7. The observed thermochromism may be attributed to the gradual substitution of halide anions and chelating ligands by solvent molecules and the formation of solvated copper(II) ions. The molar conductance of the heated solutions increases to higher values due to the dissociation of anionic ligands. Due to the centrosymmetric structure of the resulting [Cu(DMSO)₆]²⁺ in the solution [30], the d-d transitions are Laporte forbidden and consequently the intensity of the d-d adsorption bands decrease and the color of the solutions fade upon heating. This phenomenon is totally reversible and the original color of solutions reappears by cooling the solutions to room temperature. However, due to the presence of a significant amount of solvent molecules around the cop-

per (II) ions, re-coordination of the ligands in reverse reaction takes place slowly, and it requires two days to regain the original color.

4. Conclusion

Two mononuclear copper(II) complexes containing the tridentate ligand *N*-(2-pyridylmethyl)-1-hydroxypropylamine and halide ions (Cl and Br) were synthesized and their structures were crystallographically characterized. The complexes are nearly isostructural, have the same thermal behavior and are colored due to the d-d transition of copper(II) ions. The complexes are chromotropic in solution and display color changes in various solvents, different pH ranges and also at different temperatures. Spectroscopic and conductometric studies reveal that structural changes are responsible for the observed chromotropic shifts. The solvent effect on structures of the complexes mainly arises from the unsaturated coordination sphere of the copper(II) ion and lability of the Cu-X (X=Cl, Br) bonds in polar solvents. The halochromism that is observed in the pH range of 1.8 to 11.4 is attributed to protonation and deprotonation of the secondary amine, alcohol and pyridine groups of the ligand. The exchange of the solvent molecules for the coordinated ligands at higher temperatures causes the thermosensitivity of the compounds in DMSO solution and results color changes that are visible with the naked eye. Since the structural features of the chloride and bromide copper(II) complexes are the same, they exhibit similar chromotropic behavior. These mononuclear complexes are multi-chromic and respond reversibly to the combination of stimuli which can be simply detected by nondestructive spectroscopic methods.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

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

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130930.

References

- [1] Y. Fukuda, *Inorganic Chromotropism*, Springer Verlag, 2007.
- [2] W. Linert, Y. Fukuda, A. Camard, Chromotropism of coordination compounds and its applications in solution, *Coord. Chem. Rev.* 218 (2001) 113–152, doi:10.1016/S0010-8545(01)00359-9.
- [3] I.I. Ebralidze, N.O. Laschuk, J. Poisson, O.V. Zenkina, Chapter 1 - Colorimetric Sensors and Sensor Arrays, in: O.V. Zenkina (Ed.), *Nanomaterials Design for Sensing Applications*, Ed., Elsevier, 2019, pp. 1–39.
- [4] T.A. Khattab, B.D.B. Tiu, S. Adas, S.D. Bunge, R.C. Advincula, Solvatochromic, thermochromic and pH-sensory CDHF-hydrazone molecular switch: response to alkaline analytes, *RSC Adv* 6 (2016) 102296–102305, doi:10.1039/C6RA24113A.
- [5] A. Pakolpakçıl, B. Osman, E.T. Özer, Y. Şahan, B. Becerir, G. Gökaltay, E. Karaca, Halochromic composite nanofibrous mat for wound healing monitoring, *Mater. Res. Express* 6 (2020) 1250–1253, doi:10.1088/2053-1591/ab5dc1.
- [6] A.R. Katritzky, D.C. Fara, H. Yang, K. Tamm, T. Tamm, M. Karelson, Quantitative Measures of Solvent Polarity, *Chem. Rev.* 104 (2004) 175–198, doi:10.1021/cr020750m.
- [7] J. Chen, L. Ao, C. Wei, C. Wang, F. Wang, Self-assembly of platinum(ii) 6-phenyl-2,2'-bipyridine complexes with solvato- and iono-chromic phenomena, *Chem. Commun.* 55 (2019) 229–232, doi:10.1039/C8CC06770H.
- [8] S.K. Panja, J-type aggregation and thermochromic behavior of a Schiff base in solution: role of keto-enol tautomerization, *Spectrochim. Acta, Part A* 229 (2020) 117860, doi:10.1016/j.saa.2019.117860.
- [9] A.S. Klymchenko, Solvatochromic and Fluorogenic Dyes as Environment-Sensitive Probes: design and Biological Applications, *Acc. Chem. Res* 50 (2017) 366–375, doi:10.1021/acs.accounts.6b00517.
- [10] H. Golchoubian, G. Moayyedi, H. Fazilati, Spectroscopic studies on Solvatochromism of mixed-chelate copper(II) complexes using MLR technique, *Spectrochim. Acta, Part A* 85 (2012) 25–30, doi:10.1016/j.saa.2011.08.042.
- [11] I. Warad, S. Musameh, I. Badran, N.N. Nassar, P. Brandao, C.J. Tavares, A. Barakat, Synthesis, solvatochromism and crystal structure of trans-[Cu(Et₂NCH₂CH₂NH₂)₂.H₂O](NO₃)₂ complex: experimental with DFT combination, *J. Mol. Struct.* 1148 (2017) 328–338, doi:10.1016/j.molstruc.2017.07.067.
- [12] S.-i. Noro, N. Yanai, S. Kitagawa, T. Akutagawa, T. Nakamura, Binding Properties of Solvatochromic Indicators [Cu(X)(acac)(tmen)](X= PF₆⁻ and BF₄⁻, acac= Acetylacetonate, tmen= N, N, N', N'-Tetramethylethylenediamine) in Solution and the Solid State, *Inorg. Chem.*, 47 (2008) 7360–7365. https://doi.org/10.1021/ic800685z
- [13] M. Mauro, Dynamic Metal-Ligand Bonds as Scaffolds for Autonomously Healing Multi-Responsive Materials, *Eur. J. Inorg. Chem.* (2018) 2090–2100 2018, doi:10.1002/ejic.201800226.
- [14] I. Warad, S. Musameh, A. Sawafta, P. Brandão, C. José Tavares, A. Zarrouk, S. Amereih, A. Al Ali, R. Shariah, Ultrasonic synthesis of Oct. trans-Br₂Cu(N ∩ N)₂ Jahn-Teller distortion complex: xRD-properties, solvatochromism, thermal, kinetic and DNA-binding evaluations, *Ultrason. Sonochem.* 52 (2019) 428–436, doi:10.1016/j.ultrsonch.2018.12.019.
- [15] A. Shirvan, H. Golchoubian, E. Bouwman, Syntheses and chromotropic behavior of two halo bridged dinuclear copper(II) complexes containing pyridine-based bidentate ligand, *J. Mol. Struct.* 1195 (2019) 769–777, doi:10.1016/j.molstruc.2019.06.034.
- [16] R. Nazari, H. Golchoubian, G. Bruno, Mononuclear copper (II) complexes containing chelating ligand of 2-methyl-N-(pyridine-2-yl-methyl) propane-2-amine as chromotropic probes, *J. Iran. Chem. Soc.* 16 (2019) 1041–1052, doi:10.1007/s13738-018-01577-z.
- [17] P. Yang, D.-D. Zhang, Z.-Z. Wang, H.-Z. Liu, Q.-S. Shi, X.-B. Xie, Copper(ii) complexes with NNO ligands: synthesis, crystal structures, DNA cleavage, and anticancer activities, *Dalton Trans* 48 (2019) 17925–17935, doi:10.1039/C9DT03746B.
- [18] P. Gentschev, N. Möller, B. Krebs, New functional models for catechol oxidases, *Inorg. Chim. Acta* 300–302 (2000) 442–452, doi:10.1016/S0020-1693(99)00553-8.
- [19] G.M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst. C*, 71 (2015) 3–8. https://doi.org/10.1107/S2053229614024218
- [20] C.A. Wegermann, P. Strapasson, S.M.M. Romanowski, A. Bortoluzzi, R.R. Ribeiro, F.S. Nunes, S.M. Drechsel, Synthesis, characterization and catalytic activity toward dye decolorization by manganese (II) mononuclear complexes, *Applied Catalysis A: General* 454 (2013) 11–20, doi:10.1016/j.apcata.2012.12.036.
- [21] A. Djouhra, O. Ali, R.-R. Ramiro, M. Emilia, A selective naked-eye chemosensor derived from 2-methoxybenzylamine and 2,3-dihydroxybenzaldehyde - synthesis, spectral characterization and electrochemistry of its bis-bidentates Schiff bases metal complexes, *Spectrochim. Acta, Part A* 184 (2017) 299–307, doi:10.1016/j.saa.2017.05.022.
- [22] K. Nakamoto, N. Ohkaku, Metal isotope effect on metal-ligand vibrations. VI. Metal complexes of 8-hydroxyquinoline, *Inorg. Chem.* 10 (1971) 798–805, doi:10.1021/ic50098a027.
- [23] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, 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.* 7 (1984) 1349–1356, doi:10.1039/DT9840001349.
- [24] A. Nimmermark, L. Öhrström, J. Reedijk, Metal-ligand bond lengths and strengths: are they correlated? A detailed CSD analysis, *Z. Kristallogr. Cryst. Mater.* 228 (2013) 311–317, doi:10.1524/zkri.2013.1605.
- [25] I. Chakraborty, M. Pinto, J. Stenger-Smith, J. Martinez-Gonzalez, P.K. Mascharak, Synthesis, structures and antibacterial properties of Cu(II) and Ag(I) complexes derived from 2,6-bis(benzothiazole)-pyridine, *Polyhedron* 172 (2019) 1–7, doi:10.1016/j.poly.2019.02.001.
- [26] J.W. Shin, D.-W. Kim, J.-W. Jeon, D. Moon, Crystal structure of {2-methyl-2-[(pyridin-2-ylmethyl) amino] propan-1-ol-κ³N, N', O} bis (nitrate-κ³O) copper (II) from synchrotron data, *Acta Cryst. E* 75 (2019) 150–153, doi:10.1107/S2056989018018352.
- [27] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Vol.33 aus, *Studies in Physical and Theoretical Chemistry*, Elsevier, Amsterdam, Oxford, New York, Tokio, 1984.
- [28] U. El-Ayaan, F. Murata, Y. Fukuda, in: *Invited Review Thermochromism and Solvatochromism in Solution, Highlights in Solute-Solvent Interactions*, Springer, Berlin, Germany, 2002, pp. 43–58.
- [29] W.J. Geary, The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coord. Chem. Rev.* 7 (1971) 81–122, doi:10.1016/S0010-8545(00)80009-0.
- [30] I. Persson, P. Persson, M. Sandström, A.-S. Ullström, Structure of Jahn-Teller distorted solvated copper(ii) ions in solution, and in solids with apparently regular octahedral coordination geometry, *J. Chem. Soc., Dalton Trans.* 7 (2002) 1256–1265, doi:10.1039/B200698G.