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Structural and chromotropism properties of copper(II) complexes containing a tridentate ligand

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Abstract

Two dinuclear complexes of $[LCu(Cl)(\mu-Cl)CuCl_3][LCu(Cl)(\mu-Cl)CuL(H_2O)]Cl, 1$ and $[LCu(Br)(\mu-Br)]_2Br, 2$, with a tridentate ligand of 3-((pyridin-2-ylmethyl)amino)propanamide, L, were prepared and characterized by physicochemical (elemental analyses, molar conductance measurements, thermogravimetry) and spectroscopic (IR, UV–vis) data. The crystal structures of compounds have been identified by single-crystal X-ray diffraction analyses and showed that the tridentate ligand L functions as an N₂O-donor via the nitrogen atoms of the secondary amine and pyridyl moieties together with the oxygen atom of the amide group. The structural geometry about the copper(II) ions is a distorted square pyramid. The compounds are chromotropic and their reversible chromotropism was investigated by utilizing spectral analysis. The halochromism was due to structural change and followed by ionization of the coordinated water molecules and deprotonation of the secondary amine moiety. It was discovered that the solvatochromism of the compounds arisen from the structural change followed by the solvation of the vacant sites of the complexes. The compounds demonstrated ionochromism and sensitivity and selectivity towards CN⁻ and N₃⁻ anions in the presence of other pseudo-halide anions.

Graphic abstract



Keywords Copper(ii) complex \cdot Chromotropism \cdot Tridentate ligand \cdot Dinuclear complex

Introduction

Copper(II) complexes comprising multi-dentate ligands have received substantial interest because of their potential applications in the field of structural chemistry (Venegas-Yazigi

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et al. 2010), biological systems (Liu et al. 2014), catalysis (Liu et al. 2018) and magnetism (Pardasani et al. 2017). One of the most interesting aspects of the chemistry of copper(II) with multi-dentate donor ligands is the phenomenon of chromotropism (Fukuda 2007). Chromotropism is the reversible color change in a substance that is attributable to the physical and chemical properties of its environment, such as solvent, temperature and pH, light, as well as the presence of ions and electrons. The most intriguing features of these type of copper complexes demonstrating chromotropism are due to structural change imposed with the environment. The development of an experimental correlation between the structural properties of metal complexes and their chromotropic properties are been seriously followed in many

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laboratories (Fukuda 2007; Linert et al. 2001; Bamfield 2002; Kryatova et al. 2012; Lumb et al. 2013; Golchoubian et al. 2015). Investigation of this type has yielded significant results in many complexes (Piromchom et al. 2014; Abou-Hussen and Linert 2009; Baho and Zargarian 2007). Copper(II) ion together with chelate ligands are known as the most promising candidates for practical applications of chromotropism owing to their high-level of thermodynamic stabilities, unsaturated coordination number as well as the presence of straightforward and steady shifts in their electronic spectra according to the power of the stimuli intruded into the system.

On the other hand, By this time a number of papers have been reported about dinuclear copper(II) complexes containing small anions such as hydroxide and halides (Venegas-Yazigi et al. 2010; Choubey et al. 2015; Thakurta 2009; Skorda et al. 2005; Xiang et al. 2006; Zhang et al 2012; Qian et al. 2013; Kapoor et al. 2004; Lumb et al 2013; Lee et al. 2005; Nethaji et al 2013; Du et al 2002; Schuitema et al 2002; Bernalte-Garcia et al. 2006; Yraola et al. 2008; Gungor and Kara et al. 2012). The study of this class of dinuclear complexes is complicated, partly due to their diverse structural features. The dinuclear complexes type [LCu(μ -X)₂CuL] where X is Cl⁻ or Br⁻, and L is a bi- and tridentate ligand are rich of structural diversity with a range of Cu-X distances and Cu-X-Cu angles depending on the nature of the chelating ligands (Kapoor et al. 2010; Lumb et al. 2013, Nethaji et al. 2013; Bu et al. 2001, 2002; Schuitema et al. 2002; Bernalte-Garcia et al. 2006; Lee et al. 2008; Yraola et al. 2008; Višnjevac et al. 2001; Gungor and Kara et al. 2012; Grove et al. 2001). Until now, a variety of bi- and tridentate ligands have been effectively developed to design the coordination sphere of the copper(II) center in bis(µ-halo)-bridged complexes (Bu et al. 2001; Bernalte-Garcia et al. 2006). However, the number of halo-bridged complexes including tridentate pyridine derivative ligands is very limited in the literature (Lee et al. 2005, 2008; Kapoor et al. 2010; Bu et al. 2001; Choubey et al. 2015; van Albada et al. 2004). We have currently been focusing our attention on five-coordinate metal complexes (Golchoubian et al. 2014, 2019; Shirvan et al. 2019). Herein, the synthesis of copper(II) complexes containing bridging halo ligand as illustrated in Fig. 1 are reported and their halochromism is investigated.

Experimental

Materials

The ligand was synthesized according to our published procedures (Rostami and Golchoubian 2017). All reagents and solvents were purchased from Merck and Aldrich and used without further purification. Microanalysis was performed with a Perkin Elmer Model 2400 elemental analyzer. Conductivities were measured in methanol, water and dimethylformamide solution 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. Then for each solvent, a curve was plotted by drawing the molar conductance versus concentration of sample. The curve was then extrapolated to an infinitive dilute solution to obtain the molar conductance value. IR spectra were recorded with a Bruker FT-IR spectrophotometer in the range 4000–500 cm⁻¹ using KBr pellets. Electronic absorption spectra were recorded with a Braic 2100 model UV-Vis spectrophotometer with 1 cm quartz cells in the range 200-800 nm. The pKa values of the complexes were determined spectrophotometrically by using Patterson method (Patterson 1999). The buffer solution of pH = 8.5 for ionochromism study was prepared by dissolving 54.4 g of sodium acetate in 50 ml of water, heating to 35 °C. After cooling, anhydrous acetic acid (10 mL) was slowly added and diluted to 100 mL with water.

X-ray crystal structure analysis

The data collection for compounds was carried with a Bruker APEXII CCD diffractometer, using

Fig.1 The structures of complexes under study



graphite-monochromatized MoK α (λ = 0.71073°A) radiation at 100 K. The data were integrated with SAINT V8.38A (Bruker 2005). The structure was solved by SHELXS-2015. Refinement by full-matrix least-squares methods based on F2 values against all reflections was performed by SHELXL-2015 (Sheldrick 2015), including anisotropic displacement parameters for all non-H atoms. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on the atoms to which they are attached. The molecular graphics were drawn with Olex2 (Dolomanov et al. 2009). Crystallographic data and details of the data collection and structure refinement are listed in Table 1

Chemicals

Preparation [LCu(Cl)(µ-Cl)CuCl₃][LCu(Cl)(µ-Cl)CuL(H₂O)]Cl, 1

To a solution of ligand, L (1.314 g, 7.331 mmol) in methanol (5 mL) was slowly added a solution of $CuCl_2 \cdot 2H_2O$ (1.294 g, 7.331 mmol) in methanol (15 ml). The resultant

Table 1 Crystal data and structure refinement of complexes 1 and 2

green reaction mixture was stirred for 3 h at room temperature. The dark green compound precipitated from the solution, which was purified by vapor diffusion of diethyl ether into the methanol solution. The crystals were suitable for X-ray crystallography. Yielded 1.936 g, 96% as green crystals (Scheme 1). Anal. Calcd. for $C_{27}H_{41}Cu_4N_9O_4Cl_8$ (MW = 1093.48 g mol⁻¹): C, 29.66; H, 3.78; N, 11.53; found C, 29.85; H, 3.78; N, 11.12. Select IR data ($\bar{\nu}/cm^{-1}$ using KBr disk): 3546 (br. O–H Str.), 3382 (m, NH₂ str.), 3248 (w), 3167 (m, N–H str.), 2924 (m, C–H str. aliphatic), 1651 (s, C=O str.), 1590 (s, C–N str.), 1456 (s, NH bend.), 1323 (m), 1033 (m), 775 (m, Cu–N str.).

Preparation $[LCu(Br)(\mu-Br)]_2Br, 2$

This compound was produced using the same method described for complex 1 except that 1.268 g of CuBr₂·2H₂O (5.68 mmol) and 1.018 g (5.68 mmol) ligand L were used. Yielded 1.067 g, 44% as dark blue crystals (Scheme 1). Anal. Calcd. for $C_{18}H_{26}Br_4Cu_2N_6O_2$ (MW = 805.15 g mol⁻¹): C,

Empirical formula	$C_{27}H_{41}Cu_4N_9O_4Cl_8$, 1	$C_{18}H_{26}Cu_2Br_4N_6O_2, 2$
Formula weight	1093.45	805.16
Temperature (K)	99.97(2)	99.91
Wavelength	0.71073	0.71073
Crystal size/mm ³	$0.25 \times 0.2 \times 0.2$	$0.5 \times 0.4 \times 0.3$
Crystal system, space group	Triclinic, P-1	Monoclinic, P2 ₁ /n
Color	Block, clear dark green	Blue
Unit cell dimensions		
<i>a</i> (Å)	8.3038(5)	7.4550(3)
b (Å)	14.2243(8)	23.5164(9)
<i>c</i> (Å)	16.9195(10)	7.4813(3)
α (°)	96.025(2)	90
β (°)	94.990(2)	110.1140(10)
γ (°)	92.992(2)	90
Volume ($Å^3$)	1976.1(2)	1231.59(8)
Z, Calculated density (Mg/m ³)	2, 1.838	4, 2.171
Absorption coefficient	2.711 mm^{-1}	8.244
F(000)	1100.0	780.0
Theta range for data collection	2.431–26.44 °	3.026
Index ranges	$-10 \le h \le 10, -17 \le k \le 17, -21 \le l \le 21$	$-9 \le h \le 9, -30 \le k \le 30, -9 \le l \le 9$
Reflections collected / unique	50,084 / 8129 [<i>R</i> (int)=0.1686]	23,896, 2837 [<i>R</i> (int)=0.0905]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8129/2/477	2837/0/145
Goodness-of-fit on F^2	1.041	1.094
Final R indices $[I > 2Sigma(I)]$	R1 = 0.0371, w $R2 = 0.0918$	$R_1 = 0.0406$, w $R_2 = 0.0960$
R indices (all data)	R1 = 0.0458, wR2 = 0.0974	$R_1 = 0.0440, wR_2 = 0.0978$
Largest diff. peak and hole	$0.54 \text{ and} - 0.82 \text{ e.} \text{\AA}^{-3}$	1.36 and – 1.32

 $P = (F_o^2 + 2F_c^2)/3; S = \sum [w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]^{1/2}$

 $w = 1/[\sigma^2(F_0^2) + (0.0001P)^2 + 15.8676P]$

Scheme 1. Reaction of synthesis of complexes 1 and 2



26.85; H, 3.26; N, 10.44; Cu, 15.78; found C, 26.93; H, 3.33; N, 10.50. Select IR data ($\bar{\nu}$ /cm⁻¹ using KBr disk) 3454 (br, OH str.), 3374 (m,, NH₂ str.), 3123(s, N–H str.), 3054 (s, C–H str. aromatic), 2895 (m, C–H str. aliphatic), 1642 (s, C=O str.), 1585 (s, C–N str.), 1456 (s, NH bend.), 1590 (s, C–N str.), 1297 (w), 1043 (w), 783(m), 696 (m, Cu–N str.), 674 (m, Cu–O Str.).

Results and discussion

Synthesis and characterization

The preparation of the compounds was performed by combining CuX₂·2H₂O and the ligand L in the solvent of methanol. The IR spectra of compounds 1 and 2 show (Fig. S1) a sharp band at 1651 and 1649 cm⁻¹, respectively which are attributed to ν (C=O) vibration that appeared in the free ligand at higher energy (1670 cm^{-1}). The band shifts in the complexes are associated with the coordination of the amide moiety of the ligand. The absorption band with medium intensity at 3382 and 3379 cm^{-1} in 1 and 2, respectively is associated with the NH₂ stretching vibration of the amide group. The presence of a narrow band at around 3150 cm^{-1} in both complexes can be attributed to the NH stretching vibration of the amide group, which was observed to be broader in the free ligand and at the higher frequency. As the lone pair of the electrons of the donor nitrogen atoms become involved in the metal-ligand bond, the transfer of the electron density of the donor nitrogen atoms to the metal atoms in the complexes and the subsequent polarization of the ligand involves electron depopulation of the N–H bond, which culminates in a shift to lower frequencies (Golchoubian et al. 2011). The stretching band of C–N of the pyridyl groups appeared at around 1585 cm⁻¹ in the studied complexes, which observed at a similar region in the related complexes (Golchoubian and Rezaee 2009).

X-ray structure

Crystallographic analysis of compound 1 indicates that there are two structurally different dinuclear complexes in the unit cell designated as units 1a and 1b. A perspective view of the crystal structure of [LCu(Cl)(µ-Cl)CuCl₃][LCu(Cl)(µ-Cl) $CuL(H_2O)$]Cl, 1 and the atom labelling scheme are shown in Fig. 2. The selected bond distances and angles are given in Table 2. In both structural units, the tridentate ligand L is coordinated to the copper(II) in a meridional type and the copper atoms are linked by a chloro ligand. The geometry around the copper(II) ions in unit 1a is different, Cu(1) is considered as a square pyramidal environment, with two nitrogen atoms of the pyridyl and amine, an oxygen atoms of the amide group and a chloro ligand in equatorial plane, CuN₂OCl, and another chloro ligand in axial position that is linked to Cu(2) ion that is tetra-coordinated. The distortion factor τ_5 value for the penta-coordinated copper ion is 0.15 that reveals a distorted square-pyramidal shape of the coordination polyhedron (the ideal τ_5 value for a square-pyramidal



Fig. 2 ORTEP views of units 1a (top) and 1b (bottom)

situation is 0 and for a trigonal bipyramidal situation is 1.0) (Addison et al. 1984). The apical Cu(1)–Cl(2) bond distance, 2.7617(9)Å, is normal as the Jahn–Teller elongated bond. The basal atoms are nearly coplanar; the deviations from the least-squares plane through the CuN_2OCl atoms are N(1) 0.122, N(2) - 0.131, O(1) 0.115, Cl(1) - 0.106 and Cu(1) 0.157 Å. The bite angles of the five-membered chelate rings, $80.88(10)^{\circ}$ is almost the same as those found for a chelate ring of 2-(methylamino)pyridine complexes (Shirvan et al. 2019). The bite angle of the six-membered chelate ring, $92.84(9)^{\circ}$, is almost the same as those found for a chelate ring of amide complexes (Chao et al. 2008 and 2011). Cu(2) atom adopts a four-coordinated CuCl₄ environment, giving a tetrahedral geometry that one of the chloride, Cl(2) bridges to Cu(1). The geometry index for four-coordinate copper ion, τ_4 is 0.63 (τ_4 index is the sum of angles α and β , the two largest angles in four-coordinate species, subtracted from 360°, all divided by 141°). The τ_4 values are zero for a perfect square planar geometry and unity for a regular tetrahedral one (Yang et al. 2007). As a result, the coordination environment about the Cu(2) is seesaw. The Cu–Cl–Cu bridging angle is 124.15(3)° and the non-bonding Cu-Cu distance within the complexes in the unit **a** is 4.443(15)Å.

Unit **1b** consists of a dinuclear penta-coordinated, in which the copper atoms are linked by a chloro ligand. The

Table 2 Selected bond lengths and bond angles of complex 1						
Bond Length (Å)						
Cu(1)-O(1)	1.973(2)	Cu(2)-Cl(2)	2.2595(8)			
Cu(1)-Cl(1)	2.2342(8)	Cu(2)-Cl(3)	2.2741(8)			
Cu(1)-N(1)	2.003(2)	Cu(2)-Cl(4)	2.2615(8)			
Cu(1)-N(2)	2.013(3)	Cu(2)-Cl(5)	2.2111(8)			
Cu(1)-Cl(2)	2.7617(9)	Cu(2)-O(8)				
Cu(3)-O(2)	2.011(2)	Cu(4)-O(3)	1.996(2)			
Cu(3)-Cl(6)	2.2533(8)	Cu(4)-O(4)	2.381(2)			
Cu(3)-N(4)	1.999(2)	Cu(4)-N(7)	2.017(2)			
Cu(3)-N(5)	1.987(2)	Cu(4)-N(8)	1.995(3)			
Cu(3)-Cl(7)	2.7203(8)	Cu(4)-Cl(7)	2.2663(8)			
Bond angles (°)						
O(1)-Cu(1)-N(1)	173.59(10)	Cl(6)-Cu(3)-Cl(7)	95.50(3)			
O(1)-Cu(1)-Cl(1)	90.21(6)	O(2)-Cu(3)-Cl(6)	89.05(6)			
O(1)-Cu(1)-Cl(2)	90.89(7)	O(2)-Cu(3)-Cl(7)	95.91(6)			
N(1)-Cu(1)-N(2)	92.84(9)	N(5)-Cu(3)-Cl(6)	173.87(8)			
O(3)-Cu(1)-Cl(1)	95.51(8)	N(4)-Cu(3)-Cl(7)	87.31(7)			
N(1)-Cu(1)-Cl(2)	90.89(7)	N(5)-Cu(3)-O(2)	92.43(9)			
Cl(1)-Cu(1)-Cl(2)	100.62(3)	N(4)-Cu(3)-O(2)	173.85(9)			
N(1)-Cu(1)-N(2)	80.88(10)	N(5)-Cu(3)-N(4)	82.29(10)			
N(2)-Cu(1)-Cl(1)	164.64(8)	N(5)-Cu(3)-Cl(7)	90.27(8)			
N(2)-Cu(1)-Cl(2)	94.39(8)	N(5)-Cu(3)-Cl(6)	95.88(7)			
O(4)-Cu(4)-Cl(7)	86.34(6)	Cl(2)-Cu(2)-Cl(3)	96.96(3)			
O(3)-Cu(4)-Cl(7)	90.55(6)	Cl(2)-Cu(2)-Cl(4)	135.84(3)			
O(3)-Cu(4)-O(4)	93.00(9)	Cl(3)-Cu(2)-Cl(5)	135.38(3)			
O(3)-Cu(4)-N(7)	173.44(10)	Cl(4)-Cu(2)-Cl(5)	100.92(3)			
N(7)-Cu(4)-Cl(7)	95.65(8)	Cl(2)-Cu(2)-Cl(5)	98.49(3)			
N(7)-Cu(4)-O(4)	85.26(9)	Cl(3)-Cu(2)-Cl(4)	96.37(3)			
N(8)-Cu(4)-Cl(7)	172.21(8)	Cu(1)-Cl(2)-Cu(2)	124.15(3)			
N(8)-Cu(4)-O(3)	93.40(9)	Cu(3)-Cl(7)-Cu(4)	92.78(3)			
N(8)-Cu(4)-O(4)	100.14(10)					
N(8)-Cu(4)-N(7)	80.71(10)					

geometry around each copper(II) ions is considered as a square pyramidal environment, with two nitrogen atoms of the secondary amine and pyridyl group, an oxygen atom of the amide moiety of the ligand L and a chloro ligand in the equatorial plane, and a Cl atom. The apical site of Cu(3) is occupied by a bridging chloride, which is in the equatorial plane of the neighboring copper(II) complex (Fig. 3). The axial position of Cu(4) is occupied by the oxygen atom of a water molecule. Each copper(II) in the dinuclear complex is in an ideal square-pyramid polyhedron reflected by the τ_5 values of zero and 0.02 for Cu(3) and Cu(4), respectively. The deviation of Cu(3) from the basal plane defined by N(4)-N(5)-O(2)-Cl(6) is only 0.085 A towards the apical Cl(7). The deviation of Cu(4) from the basal plane defined by N(7)-N(8)-O(3)-Cl(7) is only 0.041 Å towards the apical O(4). The axial Cu(3)-Cl(7) bond length is significantly longer than that of Cu-Cl bonds in the basal planes (Table 2). The



Fig. 3 The square pyramid arrangement of the coordinated atoms around the copper(II) center in units 1a (top) and 1b (below)

Cu–Cl–Cu bridging angle is 92.78(3) and the intramolecular Cu—Cu separation is 3.624(3) Å in the unit **1b**. The equatorial least-squares planes of the two copper atoms are not parallel and form an angle of $174.93(7)^{\circ}$.

There are multiple inter- and intra-molecular hydrogen bonds in the compound **1** so that an extensive hydrogenbonded three dimensional network is formed due to the participation of oxygen atoms of the amide group with hydrogen atoms of the amide groups of adjacent molecules and chloride atoms of the tetra coordination site with its own amide hydrogen (Table S1). A portion of such a hydrogen bonding network is shown in Fig. S2.

The molecular structure of **2** is displayed in Fig. 4. The selected interatomic distances and angles are listed in Table 2. The structure consists of centrosymmetric dimeric $[LCu(\mu-Br)]_2Br_2$ units that two bromine atoms bridge the copper atoms forming a four-membered ring. The Cu(1)-Br-Cu(1A) bridging angle is 90.238(19)^O, and the Br(1)-Cu-Br(1A) angle is 89.762(19)^O. The bridging is to an appreciable extent unsymmetrical in nature with different Cu–Br bond distances [Cu(1)–Br(1) 2.4538(6)Å, Cu(1)–Br(1A) 2.7800(6)Å] (Table 3). The structure of the complex demonstrates penta-coordinated Cu(II) ions forming a square



Fig. 4 ORTEP views of 2

pyramidal geometry. The two nitrogen atoms and an oxygen atom of the ligand L and bromine one defines a distorted square plane while the apical position of the pyramid is occupied by a second bromine atom belonging to the other half of the dimer. The coordination polyhedron around the copper(II) ion could be best described as near-ideal square pyramid, with $\tau = 0.08$. As it was pointed out, the two Cu(II) centers are bridged by two bromine atoms in such a fashion that the two square pyramids share one base-to-apex edge while having their basal planes parallel (Fig. 5). the Cu(1)···Cu(1A) intra-dimeric distance is 3.716(4) Å. the axial Cu–Br bond 2.7800(6) Å is considerably longer than the corresponding basal Cu-Br bonds 2.4538(6) Å due to the Jahn-Teller effect. The angle of the five-membered chelate ring, $82.22(13)^{\circ}$ is nearly the same as those found for the chelate rings of 2-(methylamino)pyridine complexes

Table 3 Selected bond lengths (Å) and angles (°) for complex 2

Bond distances (Å)			
Cu(1)-O(1)	1.961(3)	Cu(1A)-Br(1) ^a	2.7800(6)
Cu(1)-Br(1)	2.4538(6)	Cu(2)-N(2)	2.012(3)
Cu(1)-N(1)	1.988(3)	Cu(1)-Cu(1A)	3.716(4)
Bond angles (°)			
Cu(1)- Br(1)-Cu(1A) ^a	90.238(19)	N(1)-Cu(1)-Br(1) ^a	94.17(10)
$Br(1)$ - $Cu(1)$ - $Br(1)^a$	89.762(19)	N(1)-Cu(1)-Br(1)	95.68(10)
O(1)-Cu(1)-Br(1) ^a	93.19(9)	N(1)-Cu(1)-N(2)	82.22(13)
O(1)-Cu(1)-Br(1)	88.76(8)	N(2)-Cu(1)-Br(1) ^a	103.46(10)
O1(1)-Cu(1)-N(1)	171.42(13)	N(2)-Cu(1)-Br(1)	166.71(10)
O(1)-Cu(1)-N(2)	91.77(12)		

^a1-X,1-Y,1-Z



Fig. 5 Two square pyramidal coordination environments of the copper(II) centers 2 sharing one base-to-apex edge

(Shirvan et al. 2019). The bond angles of the six-membered chelate ring are $91.77(12)^{\circ}$ that is very similar to those found for the chelate rings of the amide complexes (Chao et al. 2011). The five-membered chelate ring in the complex is puckered so that the torsion angles of N(1)-C(5)-C(6)-N(2) is $21.92(10)^{\circ}$.

The crystal structure is stabilized by a two-dimensional hydrogen-bonding network with intramolecular interactions of hydrogen bonds between the N–H groups of the amine moieties and the non-bridging bromine and intermolecular interactions between the bridging bromine neighboring dinuclear units, respectively (Fig. S3 and Table S2).

Thermal analyses of compounds 1 and 2

The thermograms of the compounds including simultaneous TG and DTA curves are shown in Fig. 6. TGA-DTA of both compounds was investigated in an argon atmosphere from 25–600 °C at a heating rate of 10 $^{\circ}$ C/min. DTA curve compound **1** shows an endothermic process without any weight loss from 135 to 175 $^{\circ}$ C due to the breakage of weak Cu–Cl bonds. Next, the compound loses weight equal to 30.2% in the temperature range of 200–330 °C. This could correspond to the loss of 3Py-CH₂-NH and a coordinated water molecule (calc. 29.9%). The next endothermic process occurs at 330–00 $^{\circ}$ C associated with fragmentation and thermal degradation of the organic moiety and formation of four molecules of CuCl₂ with a mass loss of 49.3% (calc. 49.2%).

Compound **2** exhibits decomposition behavior nearly like compound **1** except the temperature ranges. DTA curve of compound **2** shows an endothermic process devoid of weight loss from 175 to 205 $^{\circ}$ C owing to breakage of weak Cu-Br in [LCu(µ-Br)]₂Br₂ and formation of 2[LCuBr]Br. Then, the endothermic process occurs up to 600 $^{\circ}$ C associated with fragmentation and thermal degradation of the ligand. The final remnant of decomposition is equal to 55.4% that



Fig. 6 TGA and DTA curves for 1 (top) and 2 (below)

corresponds to the presence of two molecules $CuBr_2$ (calc. 55.5%).

Chromotropism study

Both compounds are chromotropic in solution and display well-defined color change. The color variations are because of a change in absorption maxima of the d-d transition of copper(II) with d⁹ electron configuration. It should be noted that in the aqueous solution, both compounds seem to be single-core complexes with approximately similar cationic complexes due to dissociation of the halide bridges and consequently substitution with water molecules. These structural changes are confirmed by an increase in molar conductance of compounds and the similarity of their UV–Vis spectra as shown in Fig. S4 in the supplementary contents.

Halochromism

Both compounds are halochromic in aqueous solution so that, they show color change with respect to pH. This phenomenon is totally reversible. The visible electronic spectra of the solution were studied in pH ranges of 1.3-12.0. It seems that in aqueous solution the weaken Cu-halide bonds located in the bridge in the dinuclear complexes are broken and substituted by water molecules as shown in Schemes 2 and 3. This was further confirmed by an increase in the molar conductance of compound **2** to the standard value of 2:2 electrolytes. Upon raising the pH of solutions by



NaOH (0.1 M), the d–d band in both complexes shifts to higher energy with the appearance of two isosbestic points. In compound **1** the first isosbestic point appears at 657 nm at a pH range of 5.14–8.84 and the second at 621 nm at a pH range of 8.14–11.3 (Fig. 7). The first and the second isosbestic points in compound **2** appear at 649 nm (at pH

range 5.84–8.86) and 604 nm (at pH range 8.86–11.2), respectively. As it was illustrated in schemes 2 and 3 the first isosbestic point is due to ionization of the coordinated water molecules with pK_a values of 5.41 and 8.40 in 1 and 5.68 and 8.57 in 2 and the second isosbestic is associated with deprotonation of the secondary amine moiety with pK_a

Fig. 7 pH titration of compound **1** (6 mM in H_2O) with NaOH (0.10 M). The inset graphs (left and middle) show isosbestic points and the right shows the increase of 500 nm absorbance on titration of NaOH (0.1 M)



values of 10.74 in **1** and 11.14 in **2** that is assisted with copper(II) ion. These values are similar to the pK_a values 5.5 for $[LCu(H_2O)_2]^{2+}$ (L=2,9-Diamino-*o*-phenanthroline) (Wall et al. 1999) and $[Cu(Me_6tren)(H_2O)]^{2+}$ (Thaler et al. 1998). Spectrophotometric titration of the complexes with NaOH (0.1 M) exhibited the release of three protons for the compounds (Insert Figs. 7 and S5). The compounds are practically stable in aqueous acidic solution, so that their absorption maxima (at $\lambda_{max} = 680$ nm in **1** and $\lambda_{max} = 678$ nm in **2**) are almost unchanged upon addition of perchloric acid (0.1 M). (Fig. S6).

Ionochromism

The ionochropism of compound **1** was not taken into consideration due to the presence of $[CuCl_4]^{2-}$ species that react with pseudo-halides and interferes with the d-d band of $[LCu(Cl)(H_2O)_2]^+$ and makes complicated visible spectrum in aqueous solution and problematic to be resolved. As a result, complex **2** was taken into account in ionochromism study. The interaction of the complex with some pseudo-halide anions (CN⁻, NO₂⁻, SCN⁻ and N₃⁻) was explored by the visible absorption spectroscopy in buffer solution (pH=5.47). The solution of the complex was at a concentration of 5.0×10^{-3} M. Upon addition of sodium cyanide and sodium azide, the absorption spectra show the evidently ionochromic behavior, so that the original blue color of the

solutions changed to colorless and green respectively, but with the addition of the other anions, the wavelength of the maximum absorbance was unchanged as shown in Fig. 8. However, upon addition of SCN⁻ the initial intensity of the d-d band (ε = 69 Lit.cm⁻¹.mol⁻¹) increases (ε = 234 Lit.cm⁻¹.mol⁻¹) and show hyperchromicity. Although the identity of the compound was not identified, it seems there is an interaction between the cationic complex and SCN⁻. The dependence of absorption spectra of complex **2** in buffer solution on the concentration of CN⁻ was investigated by the absorption spectroscopy titration method. The color variations of complex **2** upon the addition of CN⁻ salt in



Fig. 8 The absorption spectra of compound 2 (5 mM) upon addition of NaCN, NaSCN, NaN₃ and NaNO₂ in buffer solution



Fig. 9 The absorbance spectra compound 2 upon addition of 4.0, 5.0, 6.0 equiv NaCN

the buffer solution is shown in Fig. 9. With the addition of CN^- , the absorption wavelength at 680 nm shifted to higher energy (blue shift) along with a decline in absorbance intensity. When the molar proportion of the complex and CN^- is arrived at 1:5 ratios, the absorbance intensity of complex at 680 nm approached almost to zero and the solution turns colorless. This is because of the strong coordination power of the cyanide anion that destroys the original complex by formation of copper(II) cyanide complex that decomposes

rapidly into copper(I) cyanide and cyanogen (Brotherton and Lynn 1959). These results indicated that complex has high-sensitive and selective toward CN⁻. Upon the addition of N_3^{-} , the absorption band of the complex at UV region tailed to the visible region while the d-d band was almost no evidently changed. Furthermore, an anion competition was also carried out by mixing anions NaX ($X = CN^{-}$, NO_{2}^{--} , SCN⁻ and N_3^{-}) (5 equivalents) in buffer solution (pH = 5.47) of the complex at room temperature. The color of the mixture became colorless indicating that none of the anions are capable to compete effectively with CN⁻ ion. In another experiment, the same competition reaction was carried out by excluding cyanide ion. It was found that the color of the original blue solution turned to green within a few seconds. These results indicate that complex 2 is high-sensitive and selective towards CN⁻ and N₃⁻ anions.

Solvatochromism

The compounds are soluble in a polar solvent and solvatochromic. Their solvatochromism was investigated in methanol, water, dimethylformamide, and dimethyl sulfoxide. Their visible spectra in the aforementioned solvents are shown in Fig. 10 and their shift in wavelength maxima



Fig. 10 Absorption spectra of the compounds 1 and 2 in some solvents

Table 4 The solvent parameter values and electronic spectra of compounds 1 and 2 in selected solvents $\lambda_{max}/nm (e/lit cm^{-1} mol^{-1})$

DN	Compound 1	Compound 2	
29.8	742 (101)	712 (107)	
26.6	756 (121)	732 (138)	
19.0	718 (128)	706 (96)	
18.0	680 (73)	680 (70)	
	78	52	
	DN 29.8 26.6 19.0 18.0	DN Compound 1 29.8 742 (101) 26.6 756 (121) 19.0 718 (128) 18.0 680 (73) 78	

are gathered in Table 4. As it is clear compound 1 is more solvatochromic than 2. Their solvatochromism properties are possibly due to structural changes in different solvents and donor/acceptor interaction of solute and solvent.

Conclusions

Dinuclear chloro- and dibromo-bridged copper(II) complexes containing tridentate ligand were prepared and characterized. The structures about copper(II) ions in both compounds are distorted square pyramidal. The compounds are chromotropic with distinct color changes. The visible absorption spectrum of the compounds changed in pH range 1.3-12.0 due to ionization of the coordinated water molecules and deprotonation of the secondary amine moiety. As a result, they have potential utility as a chemical sensor for probing pH changes of biological and environmental samples. The compound 2 display sensitivity towards cyanide and azide anions with the obvious color changes in aqueous solution in the presence of other pseudohalide anions (NO₂⁻, SCN⁻ and N₃⁻). So, these anions can be detected with the naked eyes. In other words, a signal can be simply read by the naked eye without help to any spectroscopic equipment. The solvatochromism properties of the compounds are due to dissociation of weakly bounded halides and the presence of the vacant coordination site on the top and below of the copper centers that allow the solvent molecules with different coordination power coordinate to the copper(II) ion. This phenomenon changes the ligand field around the copper(II) center that causes the shift in the absorption wavelength of the compounds. In addition, compound 2 is thermochromic in solid-state and shows reversible color change from blue to green. However, the lack of the appropriate instrument hinders to track record this phenomenon.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest

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