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# Assemblies of substituted salicylidene-2-ethanolamine copper(II) complexes: From square planar monomeric to octahedral polymeric halogen analogues

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#### ABSTRACT

A series of copper(II) complexes with tridentate salicylidene-2-ethanolamine type ligands is described. The complexes were isolated and characterized by single crystal X-ray diffraction, elemental analysis, IR and UV–Vis spectroscopy as well as cyclic voltammetry and magnetic susceptibility measurements. Single-crystal X-ray structure measurements for complexes with unsubstituted as well as 5-chloro and 5-bromo substituted salicylidene-2-ethanolamines demonstrate interesting differences in copper coordination geometry as well as topology of the crystal lattices. It was found, that the nature of the substituent in *meta* position affects supramolecular assembly in solid state and physicochemical properties such as magnetic features by lowering the expected magnetic moments for  $d^9$  electronic configuration of copper(II). Cyclic voltammetry measurements show several irreversible reduction and oxidation processes attributed to coordinated ligands and metal centre. The resemblance of the solid state UV–Vis reflectance spectra of octahedral and square planar copper complexes makes them indistinguishable.

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#### 1. Introduction

Coordination chemistry of Schiff bases is an object of interest for many inorganic chemists mainly due to a possibility to project and synthesize ligands possessing a desirable chemical nature. Knowledge about the crystal structure of solid material helps to understand and somehow predict its potential applications as a functional material. Hereby, we present the synthesis and characterization of copper(II) complexes with salicylidene-2-ethanolamine and its substituted derivatives.

The first infrared spectrum analysis of salicylidene-2-ethanolamine was reported by Hanninen et al. in 1950 [1]. Since then, ligands of this type were investigated in context of inhibition of corrosion of steel [2] and as antimicrobial agents [3]. Transition metal complexes of Cu(II), Ni(II) and Mn(IV) with potentially tridentate salicylidene-2-ethanolamine type ligands have intriguing magnetic properties, being a consequence of magnetic interactions in polynuclear cubane like clusters [4], or mixed metal complexes [5]. The hydroxylic group in ligands of this type can coordinate in bridging mode affording formation of multinuclear clusters possessing spectacular magnetic features, for instance,  $Mn_4$  core tetranuclear complexes display slow relaxation of magnetization in susceptibility measurements [6]. The features of hanging hydroxylic groups, in case of square planar salicylaldimine complexes of copper and nickel, favor formation of conducting polymers in processes of electro polymerization and as a result the modified electrodes can be applied as sensors [7]. In addition, mononuclear Ni(II) and Cu(II) square planar complexes have been investigated in context of non-linear optical properties [8] and liquid crystalline phases [9]. On the other hand, in catalysis, copper(II), oxovanadium(IV) and dioxomolybdenum(IV) complexes with salicylidene-2-ethanolamines were found effective in applications in reactions of epoxidation of olefins [10] and degradation of lignin [11]. Finally, studies of polynuclear complexes of iron with this type of ligand provided information helpful in understanding of biological systems [12].

X-ray structures of mononuclear complexes with halogen substituted salicylidene-2-ethanolamine Schiff bases were reported previously for several transition metals including Ni(II), [13] Mn(III), [14] Cd(II) [15] and Co(III) [16]. Salicylidene-2-ethanolamine copper(II) complex was synthesized earlier and structurally analyzed by Paulus et al. [17] and was tested for catalytic applications in reactions of mild oxidation of alcohols by Midões and co-workers [18]. The mixed ligand copper(II) complexes with dibromo- and hydroxo- substituted salicylidene-2-ethanolamines were synthesized earlier by Chumakov et al. [19]. It is worth to note, that mononuclear complexes of copper(II) with halogen meta-substituted salicylidene-2-ethanolamines have not been neither synthesized nor characterized structurally. In this work we present synthesis of four mononuclear complexes of copper(II), their characterization including IR and electronic spectroscopy and cyclic voltammetry. For three complexes single-crystal X-ray structural studies are also included.



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Scheme 1. Synthesis of copper complexes 1, 2, 3 and 4.

#### Table 1

Summary of crystallographic data for  $[Cu(heimp)_2]$  (1),  $[Cu(cheimp)_2]$  (2) and  $[Cu(bheimp)_2]$  (3). Standard deviations are included in parentheses.

Compound	1	2	3
Chemical formula	C18H20CuN2O4	C18H18Cl2CuN2O4	C <sub>18</sub> H <sub>18</sub> Br <sub>2</sub> CuN <sub>2</sub> O <sub>4</sub>
$M_r$	391.90	460.78	549.70
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Temperature (K)	293	293	110
a (Å)	18.317(5)	4.9393(1)	13.1588(3)
b (Å)	4.822(5)	16.7975(4)	4.4005(1)
<i>c</i> (Å)	19.765(5)	10.7076(2)	16.4511(3)
α (°)	90	90	90
β(°)	98.792(5)	94.593(2)	90.174(2)
γ (°)	90	90	90
V (Å <sup>3</sup> )	1725.22(2)	885.53(3)	952.60(4)
Ζ	4	2	2
Radiation type	Μο Κα	Μο Κα	Μο Κα
$\mu$ (mm <sup>-1</sup> )	1.29	1.56	5.37
Measured reflections	6402	3983	4375
Independent reflections	3813	1960	2059
Observed $[I > 2\sigma(I)]$ reflections	2481	1681	1806
R <sub>int</sub>	0.020	0.025	0.025
$R_1[F^2 > 2\sigma(F^2)]^a$	0.038	0.031	0.030
$wR_2(F^2)^a$	0.103	0.070	0.068
S	1.04	1.04	1.04
Number of parameters	237	125	125
$\Delta ho_{ m max}$ (e Å $^{-3}$ )	0.26	0.40	0.62
$\Delta  ho_{ m min}$ (e Å <sup>-3</sup> )	-0.35	-0.37	-0.53

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.0712P]$  where  $P = (F_o^2 + 2F_c^2)/3$ ,  $R_1 = \Sigma(|F_0| - |F_c|)/\Sigma(|F_0|)$  and  $wR_2 = \{\Sigma[w(F_0 - F_c^2)^2\}^{1/2}$ .

#### 2. Experimental

#### 2.1. Materials and methods

All reagents were purchased from Sigma-Aldrich and used as supplied. Microanalyses on carbon, hydrogen and nitrogen were performed using the Vario Micro Cube elemental analyzer. Solid samples for IR spectroscopy were compressed as KBr pellets and the IR spectra were recorded on a Bruker EQUINOX 55 FT-IR spectrophotometer. Electronic absorption spectra were measured with a Shimadzu UV-Vis-NIR UV-3600 spectrophotometer. Cyclic voltammetry measurements were carried out in dimethyl sulfoxide (DMSO) with [Bu<sub>4</sub>N]PF<sub>6</sub> (tetrabuthyloammonium hexafluorophospate) (0.10 M) as the supporting electrolyte using Pt working and counter and Ag<sup>+</sup>/AgCl reference electrodes on an AUTOLAB/PGSTAT 128 N Potentiostat/Galvanostat.  $E_{1/2}$  values were calculated from the average anodic and cathodic peak potentials,  $E_{1/2} = 0.5(E_a + E_c)$ . The redox potentials were calibrated versus ferrocene, which was used as an internal potential standard for measurements in organic solvents to avoid the influence of liquid junction potential; the final values are reported versus standard hydrogen electrode (SHE).

#### 2.2. Synthesis

General synthetic approach is depicted in Scheme 1. Complex **1** was synthesized previously [17] and characterized structurally (see Section 1) while complexes **2**, **3** and **4** were not. The synthesis method of **1** was different from that previously reported – it is less time consuming and gives comparable yield, as well.

## 2.2.1. Synthesis of bis{2-[(2-hydroxyethyl)iminomethyl]phenolato} copper(II), [Cu(heimp)<sub>2</sub>], (**1**)

Thirty millilitre of ethanolic solution of 2 mmol (0.122 ml) of aminoethanol and 2 mmol (0.213 ml) of salicylaldehyde was refluxed for 30 min, then 1 mmol (182 mg) of copper(II) diacetate was added. The solution colour changed from slightly yellow to dark brown during 30 min of heating under reflux. The solvent was removed (~15 ml) under reduced pressure on a rotary evaporator and the bright green crystalline precipitate was filtered off, washed with cold ethanol and dried in air. The single crystals suitable for X-ray analysis were grown in the filtrate solution, employing a slow evaporation of solvent at 298 K. Yield: 225 mg (57%); *Anal.* Calc. for C<sub>18</sub>H<sub>20</sub>CuN<sub>2</sub>O<sub>4</sub>: C, 55.16; H, 5.14; N, 7.15. Found: C, 55.26; H, 5.14; N, 7.06%. IR (KBr, cm<sup>-1</sup>): 458w, 579w,

Table 2a	
The selected bond lengths (Å) and angles (°) for complexes <b>1</b> , <b>2</b> and <b>3</b> . Standard deviations are included in pa	arentheses.

1		2		3	
Selected bond lengths					
Cu2-N21	1.994(2)	Cu-N1	1.991(2)	Cu–N1	2.005(2)
Cu2-013	1.881(2)	Cu-01	1.956(1)	Cu-01	1.894(2)
N21-C22	1.465(3)	N1-C08	1.477(3)	N1-C8	1.475(3)
C20-N21	1.291(4)	C07-N1	1.283(3)	C7-N1	1.285(3)
013-C14	1.304(4)	01-C01	1.314(3)	01-C1	1.309(3)
C11-012	1.429(4)	O2-C09	1.421(3)	C9-02	1.430(3)
N09-C10	1.477(3)	Cl1-C04	1.754(2)	Br1-C4	1.906(3)
O01-C02	1.312(3)	Cu-02′	2.503(2)		
Cu1-001	1.871(2)				
Cu1-N09	1.999(2)				
C23-O24	1.419(4)				
C08-N09	1.289(3)				
Selected angles					
001-Cu1-N09	92.06(8)	O1-Cu-N1	91.14(7)	01-Cu-N1	91.70(8)
001-Cu1-N09	87.94(8)	O1-Cu-N1	88.86(7)	01-Cu-N1	88.30(8)
001-Cu1-001	180.00(8)	01-Cu-01	180.00(6)	01-Cu-01	180.00(8)
N09-Cu1-N09	180.00(8)	N1-Cu-N1	180.00(7)	N1-Cu-N1	180.00(8)
Cu1-001-C02	130.6(2)	Cu-01-C01	120.8(1)	Cu-01-C1	129.8(2)
Cu1-N09-C08	123.6(2)	Cu-N1-C07	122.2(1)	Cu-N1-C7	124.5(2)
Cu1-N09-C10	120.4(2)	Cu-N1-C08	121.1(1)	Cu-N1-C8	119.8(2)
C07-C08-N09	127.7(2)	C06-C07-N1	125.5(2)	C6-C7vN1	126.7(2)
C08-N09-C10	115.9(2)	C07-N1-C08	116.6(2)	C7-N1-C8	115.7(2)
C20-N21-C22	116.2(2)	Cl1-C04-C03	119.9(2)	Br1-C4-C3	118.9(2)
N21-C22-C23	111.2(2)	Cl1-C04-C05	119.3(2)	Br1-C4-C5	120.4(2)
O01-C02-C03	118.5(2)	O1-C01-C02	120.7(2)	01-C1-C2	118.9(2)
001-C02-C07	123.3(2)	O1-C01-C06	122.1(2)	01-C1-C6	123.6(2)
N09-C10-C11	112.2(2)	N1-C08-C09	113.1(2)	N1-C8-C9	111.1(2)
013-Cu2-013	180.00(9)	N1-Cu-O2′	89.24(6)	C8-C9-O2	111.8(2)
C19-C20-N21	127.4(3)	01-Cu-02"	84.70(6)		
Cu2-N21-C20	124.0(2)	01-Cu-02′	95.30(6)		
Cu2-N21-C22	119.8(2)	02'-Cu-O2"	180.00(5)		
Cu2-013-C14	130.3(2)	C09-02-Cu	118.6(1)		
N21-Cu2-N21	180.00(9)				
N21-Cu2-O13	88.55(9)				
013-Cu2-N21	91.45(9)				
Selected torsion angles					
Cu1-001-C02-C03	172.71	Cu-O1-C01-C02	145.19	Cu-01-C1-C2	171.40
Cu1-001-C01-C07	7.04	Cu-O1-C01-C06	36.20	Cu-01-C1-C6	8.79
Cu1-N09-C08-C07	1.27	Cu-N1-C07-C06	7.58	Cu-N1-C7-C6	0.44

741w ( $\nu_{\text{O}-\text{H}}$ ), 761s ( $\nu_{\text{O}-\text{H}}$ )., 869w, 891w, 1043m, 1060m ( $\nu_{\text{C}-\text{O}}$ ), 1128w, 1149m ( $\nu_{\text{C}-\text{O}}$ ), 1208m, 1327s ( $\nu_{\text{C}-\text{O}}$ ), 1350m, 1396m, 1434m ( $\nu_{\text{C}=\text{C}}$ ), 1452s ( $\nu_{\text{C}-\text{N}}$ ), 1471s ( $\nu_{\text{C}-\text{N}}$ ), 1540s ( $\nu_{\text{C}-\text{N}}$ ), 1624vs ( $\nu_{\text{C}=\text{N}}$ ), 2911w ( $\nu_{\text{C}-\text{H}}$ ), 2972w ( $\nu_{\text{C}-\text{H}}$ ), 3024w ( $\nu_{\text{C}-\text{H}}$ ), 3050w ( $\nu_{\text{C}-\text{H}}$ ), 3226w ( $\nu_{\text{O}-\text{H}}$ ).

#### 2.2.2. Synthesis of bis{4-chloro-2-[(2-hydroxyethyl)iminomethyl]phenolato}-copper(II), [Cu(cheimp)<sub>2</sub>], (**2**)

The preparation method of complex **2** was similar to that of complex **1** with one exception; instead of salicylaldehyde 5-chloro-salicylaldehyde was used (30 ml of ethanol; 0.122 ml, 2 mmol of aminoethanol; 313 mg, 2 mmol of 5-chlorosalicylaldehyde; 182 mg, 1 mmol of Cu(CH<sub>3</sub>COO)<sub>2</sub>). Green single crystals of complex **2**, suitable for X-ray analysis, were grown in the filtrate by slow solvent evaporation at 298 K. Yield 400 mg (87%); *Anal.* Calc. for C<sub>18</sub>H<sub>18</sub>Cl<sub>2</sub> CuN<sub>2</sub>O<sub>4</sub>: C, 46.92; H, 3.94; N, 6.08. Found: C, 47.09; H, 3.98; N, 6.10%; IR (KBr, cm<sup>-1</sup>): 429w, 462w, 486w, 587w, 660w, 707s ( $v_{O-H}$ ), 808m ( $v_{O-H}$ ), 825s ( $v_{O-H}$ ), 873w, 940w, 973w, 1041s ( $v_{C-O}$ ), 1056s ( $v_{C-O}$ ), 1079w, 1129w, 1178m, 1199m, 1215w, 1243w ( $v_{C-O}$ ), 1323s ( $v_{C-O}$ ), 1339w, 1359w, 1388s ( $v_{C-N}$ ), 1434m ( $v_{C=C}$ ), 1467vs ( $v_{C-H}$ ), 3048w ( $v_{C-H}$ ), 3252m ( $v_{O-H}$ ), 3335m ( $v_{O-H}$ ).

#### 2.2.3. Synthesis of bis{4-bromo-2-[(2-hydroxyethyl)iminomethyl]phenolato}copper(II), [Cu(bheimp)<sub>2</sub>], (**3**)

The preparation method of complex **3** was similar to that of complex **1** with one exception; instead of salicylaldehyde

5-bromosalicylaldehyde was used (30 ml of ethanol; 0.122 ml, 2 mmol of aminoethanol; 402 mg, 2 mmol of 5-bromosalicylaldehyde; 182 mg, 1 mmol of Cu(CH<sub>3</sub>COO)<sub>2</sub>). The green single crystals of **3** were grown in ethanol using a slow evaporation method in temperature of 298 K. Yield: 480 mg (87%); *Anal.* Calc. for C<sub>18</sub>H<sub>18</sub> Br<sub>2</sub>CuN<sub>2</sub>O<sub>4</sub>: C, 39.33; H, 3.30; N, 5.10. Found: C, 39.37; H, 3.25; N, 5.08%. IR (KBr, cm<sup>-1</sup>): 461w, 479w, 555w, 650w, 684s ( $v_{O-H}$ ), 711w, 824s ( $v_{O-H}$ ), 874w, 903w, 973w, 1040m ( $v_{C-O}$ ), 1055s ( $v_{C-O}$ ), 1132w, 1176m, 1197m, 1216w, 1243w ( $v_{C-O}$ ), 1322s ( $v_{C-O}$ ), 1340w, 1361w, 1385s ( $v_{C-N}$ ), 1432m ( $v_{C-C}$ ), 1466vs ( $v_{C-N}$ ), 1528m, 1589m, 1625vs ( $v_{C=N}$ ), 2872w ( $v_{C-H}$ ), 2914w ( $v_{C-H}$ ), 2975w ( $v_{C-H}$ ), 3041w ( $v_{C-H}$ ), 3258m ( $v_{O-H}$ ), 3338m ( $v_{O-H}$ ).

#### 2.2.4. Synthesis of bis{4-bromo-6-methoxy-2-[(2-hydroxyethyl)iminomethyl]phenolato}copper(II), [Cu(mbheimp)<sub>2</sub>], (**4**)

Forty millilitre of ethanolic solution of 2 mmol (0.122 ml) of aminoethanol and 2 mmol of 5-bromo-3-methoxy-salicylaldehyde (464 mg) was refluxed for 30 min, then 1 mmol of copper(II) diacetate (182 mg) was added. The solution colour changed from orange to yellowish green. In the first five minutes of heating under reflux the product precipitated and the small yellowish green needle like crystals were filtered off, washed with cold ethanol and dried in air. Yield: 517 mg (85%); *Anal.* Calc. for C<sub>19</sub>H<sub>20</sub>-BrCuN<sub>2</sub>O<sub>5</sub>: C, 39.40; H, 3.64; N, 4.59. Found: C, 39.41; H, 3.64; N, 4.81%. IR (KBr, cm<sup>-1</sup>): 475vw, 521vw, 684vw ( $v_{O-H}$ ), 765vw, 798w ( $v_{O-H}$ ), 875vw, 913vw, 982vw, 1066w ( $v_{C-O}$ ), 1087vw, 1123vw, 1187vw, 1243s ( $v_{C-O}$ ), 1326m ( $v_{C-O}$ ), 1357w, 1397vw,

**Table 2b**The hydrogen bonds parameters.

Complex	D-A	<i>d</i> (DA) [Å]	DHA [°]
1	024-012	2.726	170.64
	012-024	2.748	171.04
	C05-O12	3.712	167.48
	C04-024	3.512	135.06
	C22-012	3.607	125.25
2	C09-Cl1	3.876	147.00
	C09-Cl1	3.761	121.22
	C07-Cl1	3.804	165.17
	C08-Cl1	3.431	118.69
	02-01	2.656	171.30
3	02-02	2.705	162.92
	C7–Br1	3.979	162.52
	C3-C2	3.670	147.16

1416vw, 1436w ( $\nu_{C=C}$ ), 1477s ( $\nu_{C-N}$ ), 1543w, 1588vw, 1622vs ( $\nu_{C=N}$ ), 2927vw ( $\nu_{C-H}$ ), 3005vw ( $\nu_{C-H}$ ), 3054vw ( $\nu_{C-H}$ ), 3427vw ( $\nu_{O-H}$ ).

#### 2.3. Crystallographic data collection and structure refinement

The crystals of **1**, **2** and **3** suitable for X-ray analysis were selected from the materials prepared as described in Section 2. Intensity data were collected on a SuperNova diffractometer (*Agilent Technologies*) at 293 and 110 K equipped with Atlas detector and microfocus Mo–K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source operating at 50 kV and 1 mA for **1**, **2** and **3**, respectively. Data were processed using *CRYSALIS<sup>Pro</sup>*.[20] The crystal data and details of data collection and structure refinement parameters are summarized in Table 1. The positions of most atoms were determined by direct methods (SIR92) [21], other non-hydrogen atoms were located on difference Fourier maps. All hydrogen atoms bonded to carbon were included



Fig. 1. The molecular structure (a) and crystal packing (b) of 1; ellipsoids represent 50% displacement probability; hydrogen atoms in (b) were omitted for clarity.



Fig. 2. The molecular structure (a) and crystal packing (b) of 2 with hydrogen bonds presented as dotted lines; ellipsoids represent 50% displacement probability; hydrogen atoms in (b) were omitted for clarity.



Fig. 3. The molecular structure (a) and crystal packing (b) of 3 with hydrogen bonds presented as dotted lines; ellipsoids represent 50% displacement probability; hydrogen atoms in (b) were omitted for clarity.



**Fig. 4.** The distances from square planes (gray colour) defined by positions of the  $N_2O_2$  donor aoms; molecular structures of complexes **1**(a), **2**(b) and **3**(c). Ellipsoids represent 50% of displacement probability. Given numbers are distances in Å.



**Fig. 5.** The layers along plane *ab* in crystal lattice of **1**. Ellipsoids represent 50% of displacement probability.



**Fig. 6.** Chains parallel to *ac* plane in crystal lattice of **2**. Ellipsoids represent 50% of displacement probability.

in the structure factor calculations at idealized positions. The structures were refined by SHELXL program [22]. Structural description graphics were performed with program ORTEP III for Windows [23] and MERCURY 2.3.

#### 3. Results and discussion

#### 3.1. Crystal structures

Crystal structure of **1** has been reported previously [17], but the current experimental and unit cell parameters are more accurate, thus we decided to include them in this work. The selected bond lengths and angles for complexes **1**, **2** and **3** are presented in Tables 2a and 2b. All of the complexes crystallize in monoclinic crystal system in  $P2_1/c$  and  $P2_1/n$  space groups.

#### 3.1.1. Cu(heimp)<sub>2</sub>, (**1**)

The molecular structure of neutral centrosymmetric square planar copper(II) complex **1** is presented in Fig. 1. The unit cell of **1** contains 4 molecules and two symmetrically inequivalent copper centers. The both central copper(II) atoms are in N<sub>2</sub>O<sub>2</sub> coordination environment of two chelating ligands with slightly different angles and bond lengths. The bite angles for different copper centers are  $O01-Cu1-N09 \ 92.06(8)^\circ$ ,  $O13-Cu2-N21 \ 91.45(9)^\circ$  and are faintly distorted from ideal  $90.0^\circ$ . The Cu–N and Cu–O bond lengths are 1.999(2) and 1.871(2) Å for Cu1, respectively. The equatorial NO distances are 2.688(3), 2.787(3) Å for Cu1 and 2.706(3) Å and 2.776(3) Å for Cu2. In both cases, coordinating atoms lay on the same plane as centre atom with N–Cu–N and O–Cu–O angles equal to  $180^\circ$ , within standard deviation.



Fig. 7. Layers along bc plane in crystal lattice of 3. Ellipsoids represent 50% of displacement probability.



**Fig. 8**. π–π Stacking interactions in crystal lattice of **1**: (a) a parallel assembly of molecules; (b) a perpendicular view to aromatic rings plane. Ellipsoids represent 50% of displacement probability.



Fig. 9.  $\pi$ - $\pi$  Stacking interactions in crystal lattice of 2: (a) a parallel assembly of molecules; (b) a view perpendicular to aromatic rings. Ellipsoids represent 50% of displacement probability.

#### 3.1.2. Cu(cheimp)<sub>2</sub>, (**2**)

The crystal structure of **2** consists of chains along axis *a*, built up from *bis* chelated copper centers tied axially by hanging hydroxyl groups of other monomers. The molecular structure as well as crystal packing of **2** is depicted in Fig. 2. Compared to **1**, complex **2** contains only one symmetrically inequivalent metal centre in the asymmetric unit and two molecules per unit cell. The bite angle is equal to  $88.86(7)^\circ$  and is smaller than for **1**. The Cu–N09, Cu–O1 (equatorial) and Cu–O2' (axial) bond lengths are 1.991(2), 1.956(1) and 2.503(2)Å respectively, indicating very weak bonding of the hydroxylic group. The O1–Cu–O2' angle is  $95.30(6)^\circ$ , which gives

the measure of angular distortion from ideal value of 90.0°, which should be maintained between square plane and the axial oxygen atom. The non-bonding NO distances of equatorially coordinating donor atoms are 2.819(2) and 2.763(2)Å. The N09'-Cu-N09 and O2'-Cu-O2" angles are equal to  $180^{\circ}$  within standard deviation.

#### 3.1.3. Cu(bheimp)<sub>2</sub>, (3)

Compound **3** is neutral centrosymmetric square planar chelate of copper(II) and strongly resembles complex **1**. The molecular structure and crystal packing of **3** are presented in Fig. 3. Central atom is in  $N_2O_2$  coordination environment, the bite angle of the



Fig. 10.  $\pi$ - $\pi$  Stacking interactions in crystal lattice of 3: (a) a parallel assembly of molecules; (b) a view perpendicular to aromatic rings. Ellipsoids represent 50% of displacement probability.



**Fig. 11.** The cyclic voltammograms of 1(a), 2(b), 3(c) and 4(d) registered in three electrode system with platinum working, auxiliary and Ag<sup>+</sup>/AgCl reference electrodes in DMSO with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte and *Fc/Fc*<sup>+</sup> as an internal standard; room temperature; 100 mV/s sweep rate.

ligand is  $91.70(8)^\circ$ , which is similar value to that for **1**. The Cu–N and Cu–O bond lengths are also close to that of **1**, with values 2.005(2) and 1.894(2) Å, respectively. The equatorial contacts between coordinating imine nitrogen and phenolic oxygen are also demonstrating values similar to these for complex **1**, 2.779(3) and 2.717(3) Å, respectively.

#### 3.1.4. Supramolecular assemblies

There are significant differences among described complexes. The shortest Cu  $\cdots$ Cu non-bonding distance in crystal lattice of **1** is 4.822(5) Å while in **2** this distance is 4.939(1) Å. The shortest Cu  $\cdots$ Cu non-bonding distance among characterized complexes occurs in crystal lattice of **3** with the value of 4.401(1) Å. The two symmetrically different molecules in the unit cell of complex **1** are located spatially in planes defined by positions of square plane atoms under angle of 71.94°. The deviations of the complex molecules from planarity are presented in Fig. 4. The angular deviations of the aromatic ring planes to the square planes are different for each Cu1 and Cu2 copper centers with values of 5.33° (Cu1) and 10.59° (Cu2). The same angles in crystal lattices of complexes **2** and **3** are 39.09° and 10.01°, respectively. These values indicate

the strongest deviation from planarity in case of complex **2** and similarities between complexes **1** and **3**.

Taking into consideration flexibility of the described molecules, particularly in fragments consisting of the oxygen and nitrogen donor atoms, the deviation from co-planarity with square plane in each case is mediated by the strength of hydrogen bonds involving the substituents. Bromine atom is larger than chlorine, therefore it is soft Lewis base and this explains the less pronounced affinity to forming hydrogen bonds in case of **3**. The shortest halogen-halogen distance is equal to that of Cu ··· Cu in **2**, whereas in crystal lattice of **3** this value is smaller. Another deviations which can be considered, are distances of hydroxylic oxygen and halogen atoms to the square planes (Fig. 4). The former value is the biggest for complex **1** and **3**. The latter value is connected with the angular distortion between square and aromatic ring planes due to the fact that the *meta* substituent lies on the aromatic ring plane to which it is bonded.

Several types of hydrogen bonds are responsible for observed crystal packing of synthesized complexes. The hydrogen bond parameters are presented in Table 2. In case of **1**, the O12 oxygen is not only a donor of hydrogen bond with O24 but also is an acceptor of hydrogen bond from O24 atom of the nearest molecule. Thus,



**Fig. 12.** The cyclic voltammograms of 1(a), 2(b) and 3(c) registered in a three electrode system with platinum working, auxiliary and Ag<sup>+</sup>/AgCl reference electrodes in DMSO with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte and *Fc/Fc<sup>+</sup>* as an internal standard; room temperature; 100 mV/s sweep rate.

molecules are forming layers parallel to *ab* plane (Fig. 5). Additionally, the same hydroxylic oxygen (O12) forms very weak hydrogen bonds with aliphatic C22 and aromatic C05 carbon atoms (Fig. 1, Table 2). Therefore, we observe three-dimensional topology of hydrogen bonds in this case. In contrast, in the described family of complexes only in **2** the hydroxylic group forms intramolecular hydrogen bonds, what contributes to formation on chains parallel to *ac* plane (Fig. 6). The chlorine atom takes part in three intermolecular hydrogen bonds as an acceptor from two C09 and C07 carbon atoms from another three molecules. These weak interactions can be classified as hydrogen bonds, according to Kovacs et al. and contribute to formation of three dimensional net of hydrogen bonds [24].

The hydroxylic group in complex **3** is also involved in hydrogen bonding (Fig. 7), being a donor as well as an acceptor of intermolecular hydrogen bonds from the nearest two hydroxyl groups. Further, the bromine atom forms very weak hydrogen bonds with aliphatic C07 carbon atom. Assuming the weak hydrogen bonds involving bromine atoms, the topology of hydrogen bonding net is also three dimensional in crystal structure of **3**, as it is in case of complex **1** and **2**.

The  $\pi$ - $\pi$  stacking intermolecular interactions are present in the crystal structures of all described complexes. In complex **1** (Fig. 8) the distance between parallel aromatic rings planes is equal to 3.250 Å. In complex **2** (Fig. 9) this distance is 3.228 Å while in complex **3** (Fig. 10) 3.382 Å, – the longest among all three complexes.

The IR data is consistent with the presented structures (spectra are included in supplementary information). The characteristic strong band at *ca*. 1620 cm<sup>-1</sup>, associated with imine C=N stretching vibration is present in IR spectra of each compound. Moreover, the strong and medium bands at *ca*. 1320 cm<sup>-1</sup> indicate deprotonation as well as coordination of the phenolic group (stretching C–O vibrations). Strong and medium bands in the range 680–830 cm<sup>-1</sup> can be assigned to out of plane bending vibrations of the alcoholic –OH group.

#### 3.2. Magnetic susceptibility measurements

Magnetic susceptibility measurements show typical values for  $d^9$  system in case of **1** and **2** with values 1.67 and 1.71 BM, respectively (without diamagnetic corrections). Complexes **3** and **4** are showing lower than expected values of magnetic moment 1.36 and 1.50 BM, respectively (without diamagnetic corrections). Significant difference between these magnetic moments can be attributed to short copper–copper distance [in **3** 4.401 Å) compared to **1** (4.822 Å) and **2** (4.939 Å)] enabling antiferromagnetic coupling.

#### 3.3. Cyclic voltammetry

The cyclic volatammetry measurements were carried out in dimethyl sulfoxide and acetonitryle. The initial scans registered in DMSO and MeCN are depicted in Fig. 11 and in Fig. 12, respectively. The peak positions are presented in Table 3. Measurements in DMSO reveal the presence of several reduction and oxidation peaks of irreversible nature. In acetonitrile, a quasi reversible system is observed (Fig. 12a) for **1**, whereas in cases of the rest of the complexes the potential-current response contains only irreversible redox waves. Complex **4** is poorly soluble in acetonitrile, thus the cyclic voltammetry measurements were not possible to perform.

The first reduction peak in DMSO,  $I_{red}$ , located at the most negative potential, occurs in voltammograms of all four compounds and can be assigned to the reduction of imine. This process requires source of protons and probably occurs with intramolecular proton transfer [25]. The redox potentials of this peak are similar in case of complexes 1, 2 and 4 while the complex 3 shows significant difference in this potential. In case of 3 the potential is shifted to higher values by 145 mV in comparison to the most negative value for complex 2. The reason for such difference can be explained by the individual influence of the substituent in the -5 and -3 positions on the electronic structure of the molecule. In comparison to the

Table 3 Cyclic voltammetry peak positions vs. SHE [V] in DMSO and acetonitrile at 100 mV/s scan rate, 298 K.

Complex	I <sub>red</sub>		II <sub>red</sub>	II <sub>red</sub>		I <sub>ox</sub>		II <sub>ox</sub>		III <sub>ox</sub>	
	DMSO	MeCN	DMSO	MeCN	DMSO	MeCN	DMSO	MeCN	DMSO	MeCN	
1	-1.536	-	-0.672	-0.602	-0.628	-0.388	0.241	0.072	0.708	0.949	
2	-1.569	-	-0.721	-0.598	-1.043	-0.301	-0.065	-0.028	0.612	0.978	
3	-1.424	-	-0.649	-0.608	-0.757	-	0.295	-0.107	-	0.940	
4	-1.556	-	-0.719	-	-	-	-0.131	-	0.628	-	



Fig. 13. The UV-Vis spectra of 1, 2, 3 and 4 in MeCN (black solid line) and DMSO (black dashed line) at the room temperature.



**Fig. 14.** The reflectance spectra of **1**, **2**, **3** and **4** after Kubelka–Munk transformation, in the right upper corner of the picture are presented the *d*–*d* bands.

Table 4
UV-vis spectral data in DMSO and MeCN at room temperature after deconvolution to
Gaussian functions. Spectroscopic data; $\lambda$ [nm] ( $\varepsilon \times 10^3$ [M <sup>-1</sup> cm <sup>-1</sup> ]).

Complex	Complex										
1		2		3	3						
DMSO	MeCN	DMSO MeCN		DMSO MeCN		DMSO	MeCN				
-	-	-	-	-	-	-	204				
-	222	-	223	-	228	-	233				
-	243	-	243	-	247	245(34)	248				
269(32)	267	264(18)	267	264(50)	266	282(21)	277				
304(16)	306	301(9.6)	303	304(26)	299	293(17)	307				
363(17)	367	365(9.5)	373	369(23)	372	375(8.1)	377				
622(0.2)	609	630(0.1)	610	626(0.3)	610	646(0.2)	-				

rest of the peaks there is no simple correlation between peak potential and substituent withdrawing effect.

able 5			
olid state diffuse	reflectance UV–Vis spect	troscopic data	(λ [nm]).

Co	mple	ĸ												
1 2 3	212 213 223	230 - 233	247 245 250	272 265 274	- 290 -	305 301 303	- 318 -	- 353 -	374 380 375	396 405 404	447 429 444	614 615 615	694 691 686	-
4	214	228	246	278	-	303	318	335	387	414	472	630	706	

The second reduction peak  $\mathrm{II}_{\mathrm{red}}$  can be attributed to the one electronic reduction to copper(I) [26]. In acetonitrile complex 1 exhibit quasi reversible behaviour with peak to peak separation 0.214 V and peak current ratio *ca*. 1.0. indicating a very slow electron transfer kinetics. The process is diffusion controlled and the dependence of peak current from the square root of the potential sweep rate is characteristic for a quasi-reversible system. The values of peak potentials of the II<sub>red</sub> peak are shifted towards positive potentials in MeCN in comparison to DMSO. It is worth to note that the II<sub>red</sub> potentials in MeCN are very similar while in DMSO these potentials are shifted to lower values. This difference is probably caused by significant change in polarity of the solvents. The differences between voltammetric curves of the corresponding compounds in the shape of the II<sub>ox</sub> oxidation peak are significant in DMSO and acetonitrile. Taking into consideration its characteristic stripping shape, it can be attributed to reoxidation of the metallic copper electrodeposited as a result of previous reduction reactions occuring in acetonitrile. The positions of this peak differ among characterized complexes. On the basis of current data the difference could not be explained. Factors which can influence the potential and shape of the stripping-like copper reoxidation peak were previously investigated by Grujicic et al. [27]. It is worth to note that measurements in the multiscan mode in DMSO revealed peak current increase of some peaks during subsequent scans, which can indicate electro polymerisation process on the surface of the working electrode (see supporting information). The oxidation peaks III<sub>ox</sub> can be attributed to oxidation processes occurring at the phenolic groups coordinated to metal center.[28] The peak positions of III<sub>ox</sub> in acetonitrile are shifted towards positive

potentials, in comparison to DMSO, indicating strong influence of the electron donating solvent properties.

Copper(II) complexes with Schiff bases synthesized from salicylaldehyde and different amine half units were previously studied by means of cyclic voltammetry and various spectroelectrochemical methods [26c,29]. Similar redox processes have been reported for these systems likewise in case of the title compounds.

#### 3.4. UV-VIS spectra

The UV–VIS spectra were recorded in MeCN and DMSO (Fig. 13) in the room temperature as well as in solid state (Fig. 14). The peak positions and absorption coefficients are presented in Tables 4 and 5. The strongest bands in solution occurring in the UV range can be attributed to the electronic transition in the aromatic  $\pi$  system ( $\pi$ – >  $\pi^*$ , n– >  $\pi^*$  transitions) [30]. The bands around 370 nm can be attributed to LMCT transitions, and in case of **2**, the position of this band in DMSO (373 nm) is shifted considerably in MeCN, towards lower energies (365 nm) [29b]. The solvatochromic shift of the LMCT band is highest in case of complex **2** and lowest for **3**, which correlates with the shifts of the peak II<sub>red</sub> in cyclic voltammograms of the complexes.

In solid state the complexes exhibit numerous bands in the UV range. These can be attributed to transitions in the ligand part. The charge transfer bands are shifted toward visible range in comparison to the solution spectra of the corresponding compounds. Two d-d bands can be assigned to square planar or distorted octahedral geometry of the metal centre. There is no significant difference between reflectance spectra of **4** and **1–3** complexes. Therefore, the coordination geometry of the copper center in **4** cannot be distinguished.

#### 4. Conclusions

Employing the same synthetic conditions a family of complexes with ligands differing only in type of one substituent in aromatic ring was obtained. These compounds were supposed to exhibit very similar structural as well as physicochemical properties due to the similarity of electronegativity and withdrawing electron effects of the substituents. However, the X-ray structural studies showed substantial differences between synthesized compounds. Moreover, the physicochemical differences are strongly manifested in redox as well as magnetic properties. The most probable cause explaining the differences is the effective size and basicity of substituents, which influence the ability to form hydrogen bonds. The wider investigations of the electro-polymerization processes of the complexes are planned in the future research.

#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.09.029.

CCDC 888232, CCDC 888233 and CCDC 888234 contains the supplementary crystallographic data for **1**, **2** and **3**, respectively. These data can be obtained free of charge *via* http://www.ccdc.ca-m.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. The additional data concerning cyclic voltammetry of studied systems as well as IR spectra are also available free of charge as supporting information on the journal website.

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