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Polyhedron 25 (2006) 1133-1141



# Synthesis, structure, spectroscopic and redox properties of copper(II)-*N*-3, 5-Bu<sup>t</sup><sub>2</sub>phenylsalicylaldinine complexes: Crystal and molecular structure of bis(N-3, 5-Bu<sup>t</sup><sub>2</sub>-phenylsalicylaldininato)copper(II)

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> Received 22 June 2005; accepted 15 August 2005 Available online 18 October 2005

# Abstract

New bulky bis(N-3, 5-Bu<sup>1</sup><sub>2</sub>phenyl-R-salicyaldiminato)copper(II) complexes **X** were synthesized and characterized by analytical, spectroscopic (IR, UV/Vis, EPR), electrochemical methods, and their chemical redox reactivity were studied. X-ray structural analysis of **1** revealed that the CuN<sub>2</sub>O<sub>2</sub> coordination core forms a distorted square-planar geometry with a *cis*-N<sub>2</sub>O<sub>2</sub> donor set which is not expected for analogous complexes. The UV/Vis and EPR results indicate that **X** complexes have a tetrahedrally distorted square-planar structure in the solid state and in solution. In the chemical oxidation of **X** by (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> along with disappearance of their EPR spectra, the appearance of new Cu(II) patterns at g = 2.169-2.189 for all **X** and radical signals in the cases of **5** and **6** were detected. The chemical reduction of some **X** complexes was accompanied by the disappearance of their EPR signals. The separation in peak potentials ( $\Delta E_p$ ) for complexes **X** are in order 4 < 3 < 2 < 1 < 6. The electrochemical results suggested that the complex **4** has the highest electrochemical rate assuming both the Cu(II) and Cu(I) forms appear in a similar geometrical configuration, so the electron transfer does not require larger reorganization of the complex in complex **4**.

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Keywords: Bulky salicylaldiminato-Cu(II) complexes; X-ray crystal structure; Spectroscopy; Electrochemistry; Chemical redox behaviors

# 1. Introduction

The design, synthesis and structural characterization of salicylaldimine (sal) complexes are a subject of current interest due to their interesting structural, magnetic, spectral, catalytic and redox properties, use as models for enzymes and various theoretical interests [1–3]. During our systematic studies on these systems, we have established that introduction of two bulky *tert*-butyl substituents into phenoloate groups on the *ortho*- and *para*-positions, enable

them to produce peripherally bounded stable phenoxyl radical complexes and in some cases affords dramatically changing in the chemical properties of some  $bis(N-Bu'_2 phenyl-X-sal)M(II)$  complexes [4,5]. For example, we have found that in the complexations of Cu(II) with N-2,  $6-Bu'_2$ -1-hydroxyphenyl-R-sal (I) in polar solvents instead of the expected  $bis(N-2, 6-Bu'_2-1-hydroxyphenyl-R-sal)Cu(II)$ , as founded by X-ray structural analysis, the formation of copper(II) complexes having oxidative C–C coupled tetradentate-sal ligand were observed [4b]. In addition,  $bis(2-oxy-3, 5-Bu'_2phenyl-arylazo)Cu^{II}$  [5c] and some  $bis(N-Bu'_2phenyl-R-sal)Cu^{II}$  chelates depending on the positions of *tert*-butyl groups on the phenyl rings possesses

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<sup>0277-5387/</sup>\$ - see front matter © 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.poly.2005.08.048

strikingly different reactivity behaviors towards triarylphosphines [5]. In order to further examination of the effect of *tert*-butyl groups on the structural properties and redox reactivity of the Cu(II) salicylaldiminates we have carried out the synthesis of bis(N-3, 5-Bu<sup>t</sup><sub>2</sub>-phenyl-R-sal)copper(II) complexes, where  $\mathbf{R} = \mathbf{H}$ , OH, OCH<sub>3</sub>, *t*-Bu, and their spectroscopic, structural and redox reactivity properties were studied.

In the present work, the preparation, spectroscopy, electrochemical and chemical redox properties of  $bis(N-3, 5-Bu_2^t)$  phenyl-R-sal)copper(II) complexes, (**X**), derived from  $3, 5-Bu_2^t$  aniline and salicylaldehyde derivatives, i.e.:  $bis(N-3, 5-Bu_2^t)$  phenylsal)copper(II) (**1**),  $bis(N-3, 5-Bu_2^t)$  phenyl-3-methoxy-sal)copper(II) (**2**),  $bis(N-3, 5-Bu_2^t)$  phenyl-4-methoxy-sal)copper(II) (**3**),  $bis(N-3, 5-Bu_2^t)$  phenyl-3-hydroxy-sal)copper(II) (**3**),  $bis(N-3, 5-Bu_2^t)$  phenyl-3-hydroxy-sal)copper(II) (**4**),  $bis(N-3, 5-Bu_2^t)$  phenyl-4-hydroxy-sal)copper(II) (**5**),  $bis(N-3, 5-Bu_2^t)$  phenyl-3,  $5-Bu_2^t$  ph

#### 2. Experimental

#### 2.1. Chemicals

All solvents,  $Cu(ac)_2 \cdot H_2O$ ,  $(NH_4)_2Ce(NO_3)_6$ , *n*-Bu<sub>4</sub>N-ClO<sub>4</sub>, PPh<sub>3</sub>, 3,5-di-*tert*-butylaniline, salicylaldehyde and its 3-HO, 4-HO, 3-OCH<sub>3</sub>, 4-OCH<sub>3</sub> derivatives were purchased from Aldrich Chemical Co. and were used without further purification. 3,5-di-*tert*-butylsalicylaldehyde was prepared according to the procedure described by Jacobsen and his co-workers [3d].

#### 2.2. Ligands

N-3,5-di-tert-butylphenyl-R-sal ( $L_yH$ ) were prepared in good yields by the condensation of 3,5-di-tert-butylaniline and appropriate salicylaldehydes in refluxing methanol. The yellow imines were recrystallized from methanol. Yields of the  $L_xH$  are in the range 75–88%. Compound  $L_1H$ : yield % 78; m.p. 114 °C; selected IR (cm<sup>-1</sup>, KBr): 1618 (CH=N), 2902–2964 (C–H, Bu<sup>t</sup>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 13.47 (s, 1H, OH), 8.64 (s, 1H, CH=N), 7.44-7.34 (m, 3H, ArH), 7.13-6.91 (m, 4H ArH), 1.37 (s, 18 H, t-Bu); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 162.1 (CH=N), 152.2, 132.9, 132.2, 121.1, 118.9, 117.3, 115.4, 35.1, 31.5; UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$  1 cm<sup>-1</sup> M<sup>-1</sup>): 210(sh), 230(4.40), 268(4.25), 341(4.26), 438(2.36) nm; Anal. Calc. for C21H27NO: C, 77.50; H, 8.36; N, 4.30. Found: C, 7.71; H, 8.24; N, 4.48%. Compound L<sub>2</sub>H: yield % 82; m.p. 144 °C; selected IR (cm<sup>-1</sup>, KBr): 1624 (CH=N), 2902–2960 (C–H, Bu<sup>t</sup>); UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$  $cm^{-1} M^{-1}$ ): 214(3.95), 239(4.56), 290\*, 341(4.51), 416(3.88)1620. Anal. Calc. for C22H29NO2: C, 77.84; H, 8.61; N, 4.12. Found: C, 77.68; H, 8.37; N, 4.23%. Compound  $L_3H$ : Yield % 85; m.p. 102 °C; Selected IR (cm<sup>-1</sup>, KBr): 1626 (CH=N), 3452, 2902–2964 (C-H, Bu<sup>t</sup>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 14.04 (s, OH), 8.5 (s, 1H, CH=N), 7.39 (s, 1H, ArH), 7.06-6.95 (m, 4H, ArH), 6.82

(d, J = 8.0 Hz., 1H ArH), 1.37 (s, 18H, t-Bu); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 161.3 (CH=N), 152.4, 146.3, 145.5, 122.8, 121.4, 118.5, 117.2, 115.2, 35.1, 31.5; UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$ , cm<sup>-1</sup> M<sup>-1</sup>) = 222(4.45), 280(4.22), 318(4.19), 461(2.60) nm  $1 \text{ cm}^{-1} \text{ M}^{-1}$ ; Anal. Calc. for C<sub>22</sub>H<sub>29</sub>NO<sub>2</sub>: C, 77.84; H, 8.61; N, 4.12. Found: C, 78.58; H, 9.09; N, 4.26%. Compound L<sub>4</sub>H: Yield % 75; m.p. 163 °C; Selected IR (cm<sup>-1</sup>, KBr): 1620 (CH=N), 3452 (OH), 2902–2964 (C–H, Bu<sup>t</sup>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  13,46 (s, 1H), 8.6 (s, 1H, CH=N), 7.39 (s, 1H, ArH), 7.06–6.95 (m, 4H, ArH), 6.82 (d, J = 8.0 Hz., 1H, ArH), 1.37 (s, 18 H, t-Bu); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 161.3 (CH=N), 152.4, 146.3, 145.5, 122.8, 121.4, 118.5, 117.2, 115.2, 35.1, 31.5; UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$ ,  $1 \text{ cm}^{-1} \text{ M}^{-1}$ ) = 222(4.45), 280(4.22), 318(4.19), 461(2.60) nm cm<sup>-1</sup> M<sup>-1</sup>; Anal. Calc. for C<sub>21</sub>H<sub>27</sub>NO<sub>2</sub>: C, 77.50; H, 8.36; N, 4.30. Found: C, 78.12; H, 8.43; N, 4.37%. Compound L<sub>5</sub>H: yield % 81; m.p. 192 °C; Selected IR (cm<sup>-1</sup>), KBr): 1622(CH=N), 3259 (bs, OH), 2902-2964 (C-H, Bu<sup>t</sup>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  13,75 (s, 1H), 8.4 (s, 1H, CH=N), 7.35 (t, 1H, Ar), 7.19 (d, J = 8.8 Hz, 1H Ar), 7.1 (d, J = 1.6 Hz, 3H, Ar), 6.9 (bs, 1H, Ar), 6.5 (s, 1H, OH), 6.4 (d, J = 8.4 Hz, 2H, CH)); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 159.1 (CH=N), 152.9, 134.8, 120.9, 114.6, 113.9, 110.3, 108.6, 104.1, 31.9 (d, J = 1.2 Hz, C-Bu<sup>t</sup>); UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$  cm<sup>-1</sup> M<sup>-1</sup>): 214(3.95), 239(4.56), 290(sh), 341(4.51), 416(3.88); Anal. Calc. for C22H29NO2: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.68; H, 8.17; N, 4.43%. Compound L<sub>6</sub>H: yield % 85; m.p. 119 °C; Selected IR (cm<sup>-1</sup>, KBr): 1619 (CH=N), 2902-2964 (C–H, Bu<sup>t</sup>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ 13.97 (s, 1H, OH), 8.60 (d, J = 6.0 Hz, 1H, CH=N), 7.49–7.15 (m, 4H, ArH), 1.54–1.37 (m, 36 H, t-Bu); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ 163.2 (CH=N), 158.3, 152.1, 148.2, 140.5, 136.9, 127.8, 126.7, 120.8, 118.5, 115.5, 35.1, 34.2, 31.6, 29.5; UV/Vis (EtOH):  $\lambda$  (log  $\varepsilon$  1 cm<sup>-1</sup> M<sup>-1</sup>): 210(sh), 230(4.40), 268(4.25), 341(4.26), 438(2.36) nm; Anal. Calc. for C<sub>29</sub>H<sub>43</sub>NO: C, 82.61; H, 10.28; N, 3.32. Found: C, 82.42; H, 9.87; N, 3.42%.

#### 2.3. Complexes

The complexes **X** were prepared by refluxing methanolic solutions of Cu(ac)<sub>2</sub> · H<sub>2</sub>O (0.25 mmol) and L<sub>x</sub>H (0.5 mmol) in a 1:2 molar ratio for 1.0–1.5 h. The volume of the resulting solution was reduced to one half and left at room temperature without stirring. The precipitate microcrystals were collected by filtration, washed with a small amount of cold methanol and dried on air (yields 68–85%). Recrystallization of **1** from methanol afforded X-ray suitable crystals. Yield: 76%. M.p. 196 °C.  $\mu_{\text{eff}} = 1.76\mu_{\text{B}}$ ; UV/Vis (CHCl<sub>3</sub>):  $\lambda$  (log $\varepsilon$ ) = 294(4.79), 400(4.41), 500(sh), 670-(2.43); IR (KBr, cm<sup>-1</sup>):  $\nu = 1608$  (CH=N), 2864–2956 (C–H in Bu<sup>t</sup>). C<sub>42</sub>H<sub>52</sub>N<sub>2</sub>O<sub>2</sub>Cu: Calc.: C, 74.2; H, 7.7; N, 4.1. Found: C, 74.3; H, 7.6; N, 4.2%. Elemental analysis, physico-chemical, electronic spectral and IR data of **X** complexes are summarized in Table 1.

Table 1	
Elemental analysis, physico-chemical, electronic sr	pectral and IR data of X compounds

Compound	M.p. (°C)	Yield (%)	Electronic spectra, $\lambda/nm (\log \epsilon, cm^{-1} M^{-1})$	IR spec cm <sup>-1</sup>	$\xi$ spectra, Found (C $n^{-1}$		ulc.) (%)		
				v <sub>C=N</sub>	v <sub>OH</sub>	С	Н	Ν	
1	196	76	294(4.8), 400(4.4), 500 <sup>a</sup> , 660(2.2)	1608		74.3(74.2)	7.6(7.7)	4.2(4.1)	
2	262	78	$306(4.6), 408(4.4), 500^{a}$ (3.2), $700^{a}$	1603	3488	71.2(71.4)	7.7(7.6)	3.9(3.8)	
3	196	82	255, 305, 379, 480 <sup>a</sup> , 673(2.25)	1612	3438	71.2(71.4)	7.8(7.6)	3.7(3.8)	
4	245	68	293, 387, 500 <sup>a</sup> , 700 <sup>a</sup> (2.28)	1616	3432 <sup>b</sup>	71.7(70.8)	7.5(7.4)	4.1(3.9)	
5	236	75	308, 376, 450 <sup>a</sup> , 500 <sup>a</sup> , 700 <sup>a</sup>	1603	3286 <sup>b</sup>	70.6(70.8)	7.2(7.4)	3.7(3.9)	
6	>275	85	295, 416, 500, 710 <sup>a</sup> (2.36)	1598		86.3(86.5)	9.5(9.5)	3.2(3.1)	

<sup>a</sup> Shoulder.

<sup>b</sup> Strong narrow band.

# 2.4. Physical measurements

Elemental analyses were carried out using a LECO CHNS 932 elemental analyzer. The magnetic susceptibilities of powdered samples were measured in a Sherwood Scientific Magnetic Susceptibility Balance (Model MK 1) magnetometer at r.t. Electronic spectra were measured on a Shimadzu 1601 UV-Vis spectrophotometer in various solvents. The IR spectra were recorded on a Perkin-Elmer FTIR spectrometer using KBr discs. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Spectro spin Avance DPX-400 Ultra Shield Model NMR or on a BRUKER AC 200 using TMS as an internal standard in CDCl<sub>3</sub>. The ESR spectra were recorded on a Varian E-109 C model X-band spectrometer with 100 kHz modulations. The Xband EPR spectra at 300 and 113-133 K were recorded on a Varian E109 C model EPR spectrometer with 100 kHz frequency modulation using DPPH (g = 2.0036) as standard. Errors in  $g_{iso}$ ,  $g_{\parallel}$  and  $g_{\perp}$  are  $\pm 0.0005$ ; errors in  $A_{iso}$ ,  $A_{\parallel}$  and  $A_{\perp}$  are 0.5, 1.0 and 1.0 G, respectively.

An EcoChemie Autolab-12 potentiostat with the electrochemical software package GPES 4.9 (Utrecht, The Netherlands) was used for voltammetric measurements. A three electrode system was used: a Pt counter electrode, an Ag/AgCl reference electrode and a 2-mm sized Pt disc as working electrode. The potentiostat/galvanostat has an IR-compensation option. Therefore, the resistance due to the electrode surface was compensated throughout the measurements. Oxygen-free nitrogen was bubbled through the solution before each experiment. All experiments were carried out at room temperature.

#### 2.5. X-ray crystallography

A suitable single crystal was mounted on a glass fiber and data collections were performed on a STOE IPDSII image plate detector using Mo K $\alpha$  radiation ( $\lambda = 0.710690$  Å). Intensity data were collected in the  $\theta$ range 1.93–29.38° at 298 (2) K. Crystallographic data are listed in Table 2. Data collection: Stoe X-AREA [7]. Cell refinement: Stoe X-AREA [7]. Data reduction: Stoe X-RED [7]. The structure was solved by direct-methods using SIR97 [8] and anisotropic displacement parameters were ap-

Table 2	
Crystallographic data for the compound 1	

Formula	$C_{42}H_{52}CuN_2O_2$
Molecular weight	680.40
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	13.943(5)
b (Å)	16.413(5)
<i>c</i> (Å)	16.781(5)
β (°)	99.602
Volume	3786(2)
Ζ	4
Calculated density (Mg m <sup>-3</sup> )	1.194
$\mu (\mathrm{mm}^{-1})$	0.613
<i>F</i> (000)	1452
Crystal size (mm)	$0.42 \times 0.28 \times 0.19$
$\theta$ Range	1.93-29.38
Index ranges	$-19 \leq h \leq 19, -22 \leq k$
	$\leq 22, -21 \leq l \leq 23$
Reflections collected	35857
Independent reflections	5183
Reflections observed (> $2\sigma$ )	3111
Absorption correction	integration
Maximum and minimum	0.7065-0.8637
transmission	
Refinement method	full-matrix least-squares on $\vec{F}$
Data/restrains/parameters	3111/0/224
Goodness-of-fit on $F^2$	0.945
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0462, wR_2 = 0.1213$
R indices (all data)	$R_1 = 0.0772, wR_2 = 0.1331$
Largest difference in peak and hole $(Å^{-3})$	0.62 and -0.54

plied to non-hydrogen atoms in a full-matrix least-squares refinement based on  $F^2$  using SHELXL-97 [9]. All hydrogen atoms were positioned geometrically and refined by a riding model with  $U_{\rm iso}$  1.2 times that of attached atoms. Molecular drawings were obtained using ORTEP-III [10].

#### 3. Results and discussion

Except 5 (R = 4-OH) all X complexes are soluble in chloroform, dichloromethane, but less soluble in solvents such as alcohols, tetrahydrofuran and DMSO. The elemen-

tal analyses were satisfactory, indicating that the complexes have a ligand-to-metal ratio of 2:1.

It is well known that tetra coordinated copper(II)-Schiff base complexes derived from bidentate *N*-aryl(alkyl)-R-sal ligands with CuN<sub>2</sub>O<sub>2</sub> coordination sphere usually display *trans* square planar, distorted square planar or tetrahedral arrangement [2–4c,11]. At the same time, recently reported X-ray structural studies of the solvated Cu(*N*-Ph-5-Clsal)<sub>2</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub> [3a] and Cu(*N*-p-CH<sub>3</sub>Ph-sal)<sub>2</sub> · DMF [12] revealed that in these complexes the ligands are coordinated in a *cis*-N<sub>2</sub>O<sub>2</sub> planar configuration. Interestingly, in the present unsolvated complex **1** the copper atom has a tetrahedrally distorted square planar geometry with two 3, 5-di-Bu<sup>1</sup><sub>2</sub>phenyl-sal ligands in a *cis*-N<sub>2</sub>O<sub>2</sub> arrangement.

#### 3.1. Description of the structure of 1

The molecular structure of complex 1 is illustrated in Fig. 1. Details of the crystal and data collection are outlined in Table 2. The selected bond lengths and bond angles are listed in Table 3. The X-ray diffraction analysis of 1 show that the copper ion is bonded to the oxygen and nitrogen donor atoms of the two bidentate ligand molecules in the unusual a *cis*-N<sub>2</sub>O<sub>2</sub> arrangement. The geometry of 1 is distorted square planar where the dihedral angle between the two coordination planes defined by O1'Cu1N1' and O1CuN1 is  $36.91(6)^{\circ}$  (Fig. 1). The compound has crystallographic  $C_2$  2-fold axes passing through the copper

Table 3 Selected bond lengths  $(\text{\AA})$  and angles (°) for complex 1

Bond lengths	
Cu1–O1	1.8850(16)
Cu1–N1	1.9706(16)
N1-C1	1.293(3)
N1–C8	1.437(2)
O1–C7	1.293(3)
C2–C3	1.409(3)
C2–C7	1.411(3)
C3–C4	1.364(3)
C4–C5	1.388(4)
C5–C6	1.350(4)
Bond angles	
O1Cu1N1	93.73(7)
O1Cu1O1′	87.70(10)
N1Cu1N1′	97.13(9)
O1′Cu1N1′	93.73(10)
O1Cu1N1′	152.81(8)
N1C8C9	118.56(16)
N1C1C2	127.40(19)
C1N1C8	117.7(2)
C1C2C7	122.5(3)
C2C7O1	123.81(18)
Cu1N1C1	122.20(13)
Cu1O1C7	127.93(13)
Cu1N1C8	120.00(13)

atom. The crystal structure of **1** is built from pairs of molecules orientated in the *trans* position respect to each other and the two salicylidene groups of the neighboring mole-



Fig. 1. An ORTER diagram of 1. Displacement ellipsoids are drawn at the 40% probability level. H atoms are omitted for clarity.



Fig. 2. View of the packing in 1 along the *a*-axis showing the possible  $\pi \cdots \pi$  and C-H $\cdots \pi$  contacts at 10% probability displacement ellipsoids.

cules are oriented nearly parallel to each other as shown in Fig. 2. Although the centroids of the two di-tertbutylphenyl rings are indeed too far apart for any  $\pi$ - $\pi$  interactions [the distances between the centroids of the aromatic rings of the neighboring SA molecules are 4.791(2) and 4.568(2) Å, a distances that are longer than the sum of the van der Vaals radii of two carbon atoms (3.4-3.6 Å)], the rings are not parallel, and  $C8 \cdots C9'$  and  $C9 \cdots C8'$  are only 3.413(3) Å, indicating quite strong interactions between these two carbons in both rings [11]. The Cu-Cu distance between the neighboring complexes units is so large (8.392 Å) that intermolecular interaction can be excluded. The copper center in 1 is in a distorted square planar environment with O1-Cu1-N1<sup>i</sup>, N1-Cu1-N1<sup>i</sup>, and O1-Cu1-O1<sup>i</sup> (symmetry code: (i) x, y, -z + 0.5), angles of 152.81(8)°, 97.13(9)° and 87.70(10)°, respectively. The dihedral angles between two phenyl rings and between the two salicylidene benzene rings are 27.40(9)° and 28.49(8)°, respectively. The Cu1-N1 and Cu1-O1 bond distances of 1.9706(16) and 1.8850(16) Å, respectively, agree well with the corresponding distances founded in bis(N-phenyl-SA)copper(II) [Cu1–N1 (1.99) and Cu1–O1 (1.88) Å [6a], bis(*N*-*p*-methylphenyl-SA)copper(II) [Cu1–N1 1.965 (3) and Cu1–O1 1.895(2) Å] [13b] and bis[N-p-(CH<sub>3</sub>)<sub>2</sub>N-phenyl-SA]copper(II) [Cu-N 1.996 (6) and Cu-O 1.885(5) Å] [6b] and in many N-alkyl substituted bis-SA and bis-naphthaldimine-Cu<sup>II</sup> complexes [13,15,16]. Surprisingly, although, the present complex 1 differs from  $bis(N-3, 5-Bu_2^t-4 OCH_3$ -phenyl-SA)Cu<sup>II</sup> (II) complexes [4c] only with the absence of a OCH<sub>3</sub> group in the 4-position of aniline ring of 1, the latter complex has practically undistorted a trans-N<sub>2</sub>O<sub>2</sub> square-planar geometry around Cu(II) center with Cu1-N1 and Cu1-O1 distances of 2.029 and 1.900 Å, respectively [4c]. From a chemical point of view

the most significant aspect of the present structure is that it demonstrates the possibility coordination of the bidentate *N*-aryl-SA ligands to copper atom in the sterically unfavorable a *cis*- $N_2O_2$  arrangement configuration. The reasons that the *cis*-configuration is preferred for complex 1 are not clear.

# 3.2. IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra

In the IR spectra of the ligands along with characteristic bands in the 1619–1626 and 2550–2800 cm<sup>-1</sup> regions (Section 2.2) due to v(C=N) and intramolecularly H-bonded v(OH), respectively, a strong narrow peak at 3452 cm<sup>-1</sup> in L<sub>4</sub>H and a broad strong peak at 3259 cm<sup>-1</sup> in L<sub>5</sub>H attributed to v(OH) stretching of 3-OH group and intermolecularly H-bonded 4-OH, respectively, were observed.

In the spectra of **X** complexes the v(C=N) band of the ligands undergoes small shift to lower frequencies (1598–1616 cm<sup>-1</sup>), indicating that the ligands are coordinated through the imine nitrogen atoms. The disappearance of the broad band at 2600–2800 cm<sup>-1</sup> and the appearance of new medium intensity bands in the region 450–600 and a strong band centered at 1523–1552 cm<sup>-1</sup> which appeared only in the spectra of **X** can be assigned to  $v_{Cu-N}$ ,  $v_{Cu-O}$  and  $v_{C=C}$  (Table 1), respectively, as described in similar complexes [14]. The medium intensity bands detected at 3488 and 3438 cm<sup>-1</sup> in the spectra of **2** and **3**, respectively, assigned to  $v_{OH}$  of lattice water molecules.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectral results obtained for  $L_xH$  ligands in CDCl<sub>3</sub>, with their assignments are given in Section 2. <sup>1</sup>H NMR signals were assigned on the basis of their integral intensity, spin–spin coupling patterns and chemical shift values.

#### 3.3. Electronic spectra

Electronic spectral data of the  $L_xH$  ligands in EtOH solution are presented in the Experimental Section. The electronic spectra of **X** in CHCl<sub>3</sub> solutions (Table 1) along with intraligand absorptions originated from  $\pi \to \pi^*$  and  $n \to \pi^*$  transitions also exhibited three visible bands at 400–450, 500(sh) and 660–710 nm which are assigned to the following transitions in order of decreasing energy the MLCT transition (CT band from filled  $d_{\pi}$  orbitals of Cu<sup>II</sup> to the antibonding  $\pi^*$  orbitals of phenoate),  $d_{xy} \to d_{x^2-y^2}$ , and  $d_{z^2} \to d_{x^2-y^2}$ , respectively, in a distorted square planar geometry around copper(II) ion [17,18a].

# 3.4. EPR and magnetic properties

The room temperature effective magnetic moments of 1, 5, and 6 (1.73, 1.76 and  $1.70\mu_{\rm B}$ ) (Table 4) are close to the spin only value of  $1.73\mu_{\rm B}$  expected for  $3d^9$  systems. The similar magnetic behaviors are noticed in the magnetically dilute systems; therefore this indicates the absence of any coupling in the solid state [18a]. Indeed, our present Xray study revealed that the nearest Cu···Cu distance in 1 is 8.386 Å. The complexes 2, 4 and 3 exhibit magnetic moments (1.83 and  $1.97\mu_{\rm B}$ ) typical for square planar or pseudo-tetrahedral mononuclear copper(II) complexes with a S = 1/2 spin state [19,20].

The spin Hamiltonian parameters of X complexes is listed in Table 4. The EPR spectra of powder of all X at 300 and 113 K exhibit an axial signal with copper-hyperfine splitting with  $g_{\parallel} > g_{\perp} > g_e$  pattern typical for a slightly distorted square planar or square planar geometries with a  $d_{x^2-y^2}$  ground state [18]. Selected spectra are shown in Fig. 3. Spectral features for 1, 4, 5, were significantly different from those for 2, 3 and 6 for which in  $g_{\parallel}$  region two  $[(A_{\parallel} = 172 \text{ G} \text{ (for 2)}, 164 \text{ G} \text{ (for 3)}] \text{ and three components}]$  $(A_{\parallel} = 119 \text{ for } 6)$  of the four parallel copper hyperfine features were resolved (Fig. 3). When EPR spectra of 2, 3 and 5 were scanned from 293 to 113 K without any changes in the line widths and g-factors, the linearly increasing in intensity of the high field doublet spectrum which follows the Curie law (I = C/T) were detected. The similar behavior is consistent with  $J \ge 0$  (ferromagnetic coupling) or J = 0 [21].

pling to nuclei of <sup>65</sup> Cu ( $I = 3/2$ ) isotopes, without <sup>14</sup> N-shis
resolutions on the high-field $m_I = 3/2$ line component.
Complex 4 displays a five-line superhyperfine structure on
high field copper component with $A_{iso}^N = 8.8$ G due to cou-
pling with two <sup>14</sup> N ( $I = 1$ ) nuclei. The resonances show $m_I$
dependent line widths with the high field line being nar-
rower and more intense than the low field line. According
to spectral parameters obtained from frozen glass spectra
of X (Table 4) at 133 K the complexes exhibit axial symme-
try feature with $g_{\parallel} > g_{\perp} > 2.03$ indicating a $d_{x^2-v^2}$ or $d_{xv}$
ground state in a tetragonal copper centers [18b]. The quo-
tient $g_{\parallel}/A_{\parallel}$ value of 146–167 cm for X, lying between 140
and 250 cm again indicates a slightly distorted environment
for Cu(II) centers [22]. It is interesting that according to
$g_{\parallel}/A_{\parallel}$ value (Table 4) complex 1 prepared from unsubsti-
tuted salicylaldehyde exhibits significantly more tetrahedral
distortion than 6 prepared from sterically bulky 3,5-
Bu <sub>2</sub> salicylaldehyde. Another interesting feature consist of
significant difference between $g_{\parallel}/A_{\parallel}$ ratio for 6 determined
from its powdered spectrum (192 cm) and frozen glass
spectrum (146 cm), indicating changes its geometry from
strongly distorted tetrahedral to a slightly distorted planar

The solution EPR spectra except 5 of all X in  $CHCl_3$  at 300 K display the expected typical 4-line pattern from cou-

#### 3.5. Reduction of X complexes with $PPh_3$

in solution.

In our early works, it has been demonstrated that some copper(II) complexes with salicylaldimine, 2-hydroxybenzylamine and β-ketoamine ligands bearing sterically hindered 2,6-di-tert-butylphenyl fragment unlike their unhindered analogs, undergo one-electron transfer reactions in the interactions with triarylphosphines giving corresponding metal-stabilized radical intermediates [5a,5b,5c,5d,5e]. When some copper(II) bis-chelates with N-2, 5-di-Bu<sup>t</sup><sub>2</sub> pheny-R-sal, structural isomers of the present complexes, was treated with a 2-3-fold excess of PPh<sub>3</sub> in various solvents the decreasing of the intensity of copper EPR signals and immediate appearance of radical signals with g = 2.005-2.0082 for R = 3-OH,  $3-OCH_3$ , and 5-OHcomplexes were detected [23]. At the same time, no reduction process were observed for similar II complexes even in the interaction with 10-fold excess of PPh<sub>3</sub>. Similar treat-

Table 4					
EPR and	magnetic	moment	data	of X	complexes

Compound X	EPR parameters <sup>a</sup>											
	Solid			Solution (CHCl <sub>3</sub> )								
	$\mu_{\mathrm{eff}}\left(\mu_{\mathrm{B}} ight)$	$g_{\parallel}$	$g_\perp$	$g_{\rm iso}$	$g_{\parallel}$	$g_\perp$	$A_{\rm iso}$	$A_\parallel$	$A_{\perp}$	$g_{\parallel}/A_{\parallel}$ (cm)		
1	1.73	2.202	2.051	2.111	2.242	2.046	66	144	27	167		
2	1.83	2.186	2.063	2.129	2.245	2.071	68	156	24	155		
3	1.97	2.227	2.073	2.121	2.242	2.061	68	160	22	150		
4	1.83	2.142	2.046	2.127	2.217	2.082	80	192	24	124		
5	1.76	2.189	2.059									
6	1.70	2.236	2.047	2.118	2.232	2.063	63	164	11	146		

<sup>a</sup>  $A_{iso}$ ,  $A_{\parallel}$  and  $A_{\perp}$  values are given in units of G (Gauss).



Fig. 3. ESR spectra of some X complexes: microcrystalline solids (a) 1 and (b) 5 at r.t., (c) powdered solid 4 at 293 K and (d) at 113 K; (e) powdered 6 at 293 K; (f) solution spectrum 6 in CHCl<sub>3</sub> and (g) oxidized 6 at r.t. under identical scanning conditions.

ment of the present **X** complexes revealed that upon addition of 3–4-fold excess of PPh<sub>3</sub> to CHCl<sub>3</sub> solution of **1**, **2**, **4** and **6** complexes at r.t., during 3–6 h their black color changed to orange-yellow and their absorption peaks within the range of 450–700 nm were disappeared. Under similar conditions the dark brown color of **3**, during even 3 days has not changed practically [(340, 390(sh), 420(sh). 500(sh) and 670 nm(sh) (3 + PPh<sub>3</sub>)]. In the EPR monitoring of **X** + PPh<sub>3</sub> (**X** = **1**, **2**, **4**, **6**) systems during reaction process in air or in vacuum only slowly decreasing in the intensity of their spectra without appearance of any radical signals were detected.

#### 3.6. Chemical oxidation of the complexes

Our recent studies demonstrated that in the chemical oxidation of bis[*N*-alkyl(aryl)-3, 5-Bu<sup>t</sup><sub>2</sub>sal]copper(II) complexes with one-electron oxidant  $(NH_4)_2[Ce(NO_3)_6]$  (CAN) in CHCl<sub>3</sub>, along with decreasing of the Cu(II) signal intensity, the generation of directly coordinated phenoxyl radical complexes are also detected [23]. The present investigation of the oxidative behavior of **X** complexes at r.t. and in air conditions, revealed that when they are treated with of three to 5-fold excess amount of CAN along with color change from black or dark brown to light brown or light yellow, the disappearance of the EPR spectra of **X** and appearance new broad lines (peak-to-peak about  $\Delta H = 92$ -108 G) at g = 2.169-2.189 were detected. For complexes **5** and **6** besides broad singlets at 2.169 and 2.189 the strong radical signals at g = 2.0055 and

g = 2.0052 were observed (Figs. 3(f) and (g)). The decreasing of the signal intensity of **X** + CAN system suggest that one-electron oxidation results in the generation of a Cu<sup>II</sup>-phenoxyl radical complex and there is antiferromagnetic coupling between an S = 1/2Cu<sup>II</sup> and an S = 1/2 phenoxyl radical. We suggest that the detected radical signals more probably originate from Cu(L<sub>x</sub><sup>•</sup>)<sub>2</sub> type diradical species in which one radical center is fully antiferromagnetically coupled with Cu(II).

The spectral changes for  $\mathbf{X} + CAN$  systems were also monitored by UV–Vis spectroscopy during the progress of the oxidation of  $\mathbf{X}$  complexes with ACN in CHCl<sub>3</sub>. Since the oxidant is insoluble in CHCl<sub>3</sub> the reaction system was heterogeneous. However, the solution  $\mathbf{X} + CAN$  system was mixed using a spatula for 5–6 s prior to each scanning. When three to five excess of CAN was added to the solution of  $\mathbf{X}$  in CHCl<sub>3</sub> at r.t., the black solution turns to brown or light yellow with the disappearance of the original bands of visible bands at 450–700 nm.

#### 3.7. Electrochemistry

Electrochemical properties of the complexes X except 5 due to its poor solubility were studied on a Pt disc electrode in dimethylsulfoxide containing 0.05 M n-Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. Table 5 summarizes the electrode potentials for all complexes in dimethylsulfoxide. A cyclic voltammogram of 1 is given in Fig. 4. This complex displays a reduction peak at  $E_{pc}^1 = 0.14$  V with a corresponding oxidation peak at  $E_{pa}^1 = 0.26$  V. The peak separation of

Table 5				
Voltammetric	data	for	Cu(II)	complexes

X	$E_{\rm pa}^1$	$E_{\rm pc}^1$	$\Delta E_{\rm p}$	$E_{\rm pa}^2$	$E_{\rm pa}^3$	$E_{\rm pc}^2$	$\Delta E_{ m p}$	$E_{\rm pa}^4$	$E_{\rm pc}^3$	$\Delta E_{ m p}$	$E_{\rm pc}^4$
1	0.26	0.14	0.12	0.65	-0.45	-0.59	0.14		-0.28		-1.58
2	0.26	0.17	0.11	1.08	-0.11	-0.24	0.13	-0.44	-0.59	0.15	
3	0.24	0.14	0.10	1.04	-0.16	-0.22	0.06	-0.53	-0.67	0.14	
4	0.29	0.21	0.08	0.92	0.01	-0.09	0.10	-0.35	-0.48	0.13	
5	0.37	0.20	0.17		-0.47				-0.96		

Supporting electrolyte = 0.05 M n-Bu<sub>4</sub>NClO<sub>4</sub>, scan rate = 100 mV/s. Potentials are presented in volts.



Fig. 4. A cyclic voltammogram of 1 in dimethylsulfoxide containing 0.05 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. Scan rate = 100 mV/s.

this couple ( $\Delta E_p$ ) is 0.12 V at 0.1 V/s and increases with scan rate. The most significant feature of this redox couple is the 1e-transfer electrochemical process of the formation of Cu(II)/Cu(I). The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility of one electron transfer reaction. The analysis of cyclic voltammetric responses with the scan rate varying 50–300 mV/s gives the evidence for a quasireversible one electron oxidation. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with the increase of the square root of the scan rate. The  $I_{\rm p}/v^{1/2}$  value is almost constant for all scan rates. This establishes the electrode process as diffusion controlled [24]. The separation in peak potentials increases at higher scan rates. These characteristic features are consistent with the quasi-reversibility of Cu(II)/Cu(I) couple. The other oxidation or reduction peaks are listed in the Table 5 and are probably due to the ligand moiety of complex. The electrode potentials of the rest of the copper(II) complexes are given in Table 5.

A cyclic voltammogram of the complex **4** is given in Fig. 5. The complex **4** exhibits a reduction peak at  $E_{pc}^1 = 0.21$  V with a directly re-oxidation peak at  $E_{pa}^1 = 0.29$  V corresponding to the formation of Cu(II)/Cu(I) couple. The peak separation of this couple ( $\Delta E_p$ ) is 0.08 V. This redox couple also have quasi-reversible character as the separation in peak potentials are higher than 59 mV and the peak currents rises with increasing  $v^{1/2}$ . Diagnostic test for the complex **4** indicated that the elec-



Fig. 5. A cyclic voltammogram of **4** in dimethylsulfoxide containing 0.05 M *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. Scan rate = 100 mV/s.

trode process is controlled by diffusion. The separation in peak potentials ( $\Delta E_p$ ) for complexes are in order 4 < 3 < 2 < 1 < 6. The difference between forward and backward peak potentials can provide a rough evaluation of the degree of the reversibility. This shows that the electrochemical process of complex 4 is faster than that of the other complexes. This behavior may suggest that in complex 4, both the Cu(II) and Cu(I) forms appear in a similar geometrical configuration, so the electron transfer does not require larger reorganization of the complex coordination geometry.

In conclusion, the present work indicates that a small changes of the substituents on the ligands of the  $bis(N-3, 5-Bu'_2phenyl-R-sal)copper(II)$  type complexes results in striking changes both in the molecular structure of the complexes and their chemical redox reactivity. Surprisingly, in complex 1 with R = H unlike its structurally characterized bis(N-aryl(alkyl)-sal) analogs copper center exhibits a tetrahedrally distorted cis-N<sub>2</sub>O<sub>2</sub> square planar geometry. Chemical oxidation of some complexes leads to the formation of the coordinated Cu(II)-phenoxyl radical complexes. As supported by EPR and electronic spectral studies their reduction with PPh<sub>3</sub> proceeded slowly without generation any radical species. The electrochemical measurements have indicated that complexes showed quasireversible 1e-electron transfer reduction to Cu(I) along with the reduction and oxidation of the ligand moiety of the complexes. The results also indicated that 4 has the highest electrochemical rate assuming that the both couples have similar geometrical configuration, so the electron transfer does not require larger reorganization of the complex.

## 4. Supplementary data

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as the Supplementary Publication No. CCDC 253758. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk.

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