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Synthesis, spectroscopy, magnetic and redox behaviors of copper(II) complexes with *tert*-butylated salen type ligands bearing bis(4-aminophenyl)ethane and bis(4-aminophenyl)amide backbones

Veli T. Kasumov^{a,*}, Yusuf Yerli^b, Aysegul Kutluay^a, Mehmet Aslanoglu^a

^a Department of Chemistry, Harran University, Osmanbey, 63300 Şanlıurfa, Turkey ^b Department of Physics, Gebze Institute of Technology, Gebze-Kocaeli, Turkey

HIGHLIGHTS

- New N,N-bis(X,3-tbutylsalicylidene) separated by bis(4-aniline)ethane/amide ligands Cu(II) complexes.
- Spectroscopic characteristics of all compounds.
- ► Effect of linkers on the magnetic moments of Cu(II) complexes.
- Chemical oxidation of synthesized compounds.

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Introduction

GRAPHICAL ABSTRACT



ABSTRACT

New salen type ligands, *N*,*N*'-bis(X-3-tert-butylsalicylidene)-4,4'-ethylenedianiline [(X = H (1), 5-tertbutyl (2)] and *N*,*N*'-bis(X-3-tert-butylsalicylidene)-4,4'-amidedianiline [X = H (3), 5-tert (4)] and their copper(II) complexes **5–8**, have been synthesized. Their spectroscopic (IR, ¹H NMR, UV/vis, ESR) properties, as well as magnetic and redox-reactivity behavior are reported. IR spectra of **7** and **8** indicate the coordination of amide oxygen atoms of **3** and **4** ligands to Cu(II). The solid state ESR spectra of **5–8** exhibits less informative exchange narrowed isotropic or anisotropic signals with weak unresolved low field patterns. The magnetic moments of **5** (2.92 $\mu_{\rm B}$ per Cu^{II}) and **6** (2.79 $\mu_{\rm B}$ per Cu^{II}) are unusual for copper(II) complexes and considerably higher than those for complexes **7** and **8**. Cryogenic measurements (300– 10 K) show weak antiferromagnetic exchange interactions between the copper(II) centers in complexes **6** and **8**. The results of electrochemical and chemical redox-reactivity studies are discussed.

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The coordination chemistry of transition metal complexes with salen-type ligands has achieved a considerable attention in the last decades, because of their oxygen carrying reactivity, redox-chemistry, unusual magnetic and structural properties, as well as their usage as models for metalloproteinase [1–5], as catalysts for the oxidation and polymerization reactions [1,4–7]. Particularly, the

steric and electronic effects of substituents of salicylic and aniline rings are the key factors in various reactions such as symmetrical or asymmetrical salen catalysts, the epoxidation, polymerization catalysts and the electron transfer reactivity of the metal complexes with ligands bearing bulky *tert*-butyl for instance, in symmetrical or asymmetrical salen catalysts, in the epoxidation and polymerization catalysts and in the electron transfer reactivity of the metal complexes with ligands bearing bulky *tert*-butylphenol moieties [4–6]. The oxidative chemistry of transition metal complexes with proradical ligands, and the correlation of reactivity with electronic structure have been an area of considerable

^{*} Corresponding author. Tel.: +90 414 318 3588; fax: +90 414 3440051. *E-mail address:* vkasumov@harran.edu.tr (V.T. Kasumov).

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research interest [1,2]. One of the unique properties of complexes bearing tert-butylphenol is that they easily generate relatively stable M(II)/M(III)-phenoxyl radical complexes upon chemical or electrochemical oxidation [5–7]. Especially, the discovery of protein radicals such as copper-containing enzymes (galactose and glyoxal oxidases) and others [8] has stimulated the development of simple model transition metal complexes bearing phenolic pendant arms, which are capable of to generating M(II)/M(III)-phenoxyl radical complexes upon oxidation [5-7]. In addition, recent studies have revealed that the complexes of group 4 metals [6d,e,9] as well as p-block metals [10-12] with bulky tert-butylated bi-, tri- and tetradentate phenoxyimine type ligands are one of the highly active catalysts for olefin polymerization or a variety of asymmetric oxidation, epoxidation and other reactions. Yoshida and co-workers and others [10,11] have designed several new salen-type ligands and their transition metal complexes in which two N.O-bidentate chelating moieties are separated *via* aromatic backbones having a central $-CH_2$, -O-, -S-, $-SO_2$, $-C_6H_4$, $-O-C_6H_4$ and other spacer groups. X-ray structural studies performed on M(II) complexes of above salen type ligands revealed that the formed chelates, in general, possess a binuclear or tetranuclear doublehelical structure which is mainly controlled by the intramolecular π - π stacking and CH- π interactions between the spacer groups [10-12].

In the course of our interest in the structure, spectroscopic behavior and redox reactivity of transition metal complexes with redox-active ligands bearing *tert*-butylated phenol fragments [13], we have interested in the coordination chemistry of *tert*-butylated salen type ligands, in which salicylaldene moieties are separated by backbones bearing bis(phenyl)ethane and bis(phenyl)amide groups. In this paper, we describe the synthesis, spectroscopic characterization, magnetic and redox reactivity behaviors of the new salen type ligands **1–4** and their copper(II) complexes abbreviated as **5**, **6**, **7** and **8** (Scheme 1).

Experimental

Methods

The elemental analyses (C, H, N) were performed at the Scientific and Technological Research Center, Inönü University of Turkey. UV-vis spectra were measured on a Perkin–Elmer Lambda 25 spectrometer operating between 200 and 1100 nm. IR spectra were recorded as KBr pellets on a Perkin–Elmer FTIR spectrometer in the 450–4000 cm⁻¹ region. ¹H NMR spectra were measured on a Bruker Spectro spin Avance DPX-300 Ultra Shield Model NMR with Me₄Si as an internal standard in CDCl₃ solutions. The room temperature (r.t.) magnetic susceptibility was measured by using a Sherwood Scientific magnetic balance. Variable temperature (10–



Scheme 1. Chemical structures of ligands (1-4) and their complexes (5-8).

300 K) magnetic susceptibility measurements were carried out with a Quantum Design PPMS SQUID magnetometer operating at a magnetic field of 10 kOe. The measured magnetic susceptibilities were corrected for temperature-independent paramagnetisim and ligand diamagnetism using Pascal's constants. EPR spectra were recorded with a Bruker EMX X-band spectrometer (9.8 GHz) with about 20 mW microwave power and 100 kHz magnetic field modulation. An EcoChemie Autolab-12 potentiostat with the electrochemical software package GPES 4.9 (Utrecht, The Netherlands) was used for voltammetric measurements. A platinum disk (2 mm o.d.) was employed as a working electrode, a platinum coil as a counter electrode, and an Ag/AgCl as reference electrode, respectively. All measurements were performed in CH_2Cl_2 containing 0.05 M n-Bu₄NClO₄ as a supporting electrolyte at room temperature (r.t.) and under nitrogen atmosphere.

Materials

All other chemicals were commercially available *N*,*N*-dimethylformamide (DMF), dimethylulfoxide (DMSO), acetonitrile (MeCN), chloroform, ethanol, methanol, 2,4-di-*tert*-butylphenol, copper(II) acetate monohydrate, (NH₄)₂Ce(NO₃)₆, acetic acid, 4,4'-diaminodiphenylethane, 4,4'-diaminodiphenylamide, 3-*tert*-butyl-salicylaldehyde and n-Bu₄NClO₄ obtained from Aldrich Chemical Co, Inc., and were used without further purification. The 3,5-di-*tert*butylsalicylaldehyde was synthesized according to a published procedure [14].

Synthesis of ligands

General method for the synthesis of ligands. To a hot solution of X-tert-butylsalicylaldehyde (8 mmol) in 50 ml absolute ethanol was added the corresponding amine (4 mmol) in 30 ml ethanol and then a few drops of formic acid as a catalyst. The yellow solution was further heated at reflux with stirring for about 8–10 h and that a yellow precipitate was appeared. The volume of the reaction mixture was reduced to ca. 30 ml and allowed to cool to r.t. The resulting light yellow precipitate was filtered, washed with ethanol and air-dried. The crude product was recrystallized from dichloromethane/methanol (1:1) solvent mixture.

Bis(N-3-tert-butylsalicylidene-4-aminophenyl)ethane (1)

Yield 88%. M.p. 219 °C. Anal. calcd. for $C_{36}H_{42}N_2O_2$ (532.76): C, 81.17; H, 7.57; N, 5.26%. Found: C, 81.05; H, 7.34; N, 5.17%. IR [KBr pellet, $v(cm^{-1})$]: 2865, 2913, 2957 (C–H, ^tBu), 2650 (OH, intramolecularly OH···N), 1618 (C=N), 1595, 1506 (C=C). ¹H NMR (300 MHz, CDCl₃): δ = 13.73 (br shoulder, 2 H; OH), 8.68 (s, 2 H; CH=N), 7.36 (d, 2 H; *J* = 1.6 Hz, meta-coupled doublet in salicylic ring), 7.22 (*t*, *J* = 4. 45 Hz, 2 H in salicylic ring), 7.26–7.43 (m. 8 H; Ph), 2.96 (t, *J* = 13.6 Hz, 4 H, -CH₂-CH₂-), 1.4372 (s, 18H, C(CH₃)₃).

Bis(N-3,5-di-tert-butylsalicylidene)-4-aminophenyl)ethane (2)

Yield: 94%. M.p. 244. Anal. calcd. for $C_{44}H_{56}N_2O_2$ (644.93): C, 81.95; H, 8.75; N, 4.34%. Found: C, 81.05; H, 8.54, 4.45%. IR [KBr pellet, *v*(cm⁻¹)]: 2867, 2909, 2951 (C—H, ¹Bu), 2560–2780 (intramolecularly H-bonding OH), 1619 (C=N), 1585, 1506 (C=C). ¹H NMR (300 MHz, CDCl₃): δ = 13.81 (br shoulder, 2 H; OH), 8.68 (s, 2 H; CH=N), 7.36 (d, 2 H; *J* = 1.0 Hz, meta-coupled doublet in salicylic ring), 7.088 (d, 2 H; *J* = 1.2 Hz, meta-coupled doublet in salicylic ring), 7.36–7,53 (m. 8 H; Ph), 2.95 (t, *J* = 13.6 Hz, 4 H, -CH₂--CH₂--), 1.437 (s, 18H, C(CH₃)₃), 1.298 (s, 18H, C(CH₃)₃).

Bis(N-3-tert-butylsalicylidene)-4-aminophenyl)amide (3)

Yield: 82%. M.p. 224–225 °C. Anal. calcd. for C₃₅H₃₇N₃O₃ (547.68): C, 78.27; H, 8.09; N, 6.36%. Found: C, 77.42; H, 7.97; N, 6.84%. ¹H NMR (300 MHz, CDCl₃): *δ* = 13.58 (br shoulder, 2 H; OH···N), and 13.51 (br, 1 H; −HN−C=O), 8.70 (s, 1 H; CH=N), 8.71 (s, 1 H; CH=N), 7.9 (d, 2 H; *J* = 8.4 Hz, meta-coupled doublet in salicylic ring), 7.8 (d, 2 H; *J* = 15.9 Hz, meta-coupled doublet in salicylic ring), 7.25 (m, (eight doublets), 8 H; phenyl rings), 1.436 (s, 18H, C(CH₃)₃), IR [KBr pellet, *v*(cm⁻¹)]: 3378 (N−H), 2872, 2909, 2952 (C−H, ^tBu), 2740 (OH, OH···N), 1659(C=O), 1616 (C=N), 1594, 1509 (C=C).

Bus(*N*-3,5-*di*-*tert*-*buty*|*salicy*|*idene*)-4-*aminopheny*|*)amide* (4)

Yield: 87%. M.p. 270 °C. Anal. calcd. for $C_{43}H_{53}N_3O_3$ (659.89): C, 78.27; H, 8.09; N, 6.36%. Found: C, 77.42; H, 7.97; N, 6.84%. ¹H NMR (300 MHz, CDCl₃): δ = 13.48 (br shoulder, 2 H; OH…N), and 13.64 (br, 1 H; —HN—C=O), 8.70 (s, 1 H; CH=N), 8.71 (s, 1 H; CH=N), 7.9 (d, 2 H; *J* = 8.4 Hz, meta-coupled doublet in salicylic ring), 7.8 (d, 2 H; *J* = 15.9 Hz, meta-coupled doublet in salicylic ring), 7.25 (m, (eight doublets), 8 H; phenyl rings), 1.437 (s, 18H, C(CH₃)₃), 1.298 (s, 18H, C(CH₃)₃), IR [KBr pellet, ν (cm⁻¹)]: 3452 (N—H), 2868, 2907, 2954 (C—H, ^tBu), 2560–2780 (OH, OH…N), 1682(C=O), 1619 (C=N), 1585, 1506 (C=C).

Synthesis of complexes

General method for the synthesis of copper(II) complexes (5-8)

A solution of copper(II) acetate monohydrate (0.055 g, 0.275 mmol) in methanol (5 ml) was added, under constant stirring, to a hot suspension of ligand (0.275 mmol) in EtOH/CHCl₃ (50/20 ml). After heating (70–80 °C) the solution for a 30–40 min, the solution volume was reduced to ca. 20 ml and then allowed to cool to r.t. A green precipitate has been formed immediately for the complexes 5, 6 and 7 upon the addition of Cu(II) acetate to the corresponding ligand solution. The resulting green precipitate was collected by vacuum filtration and washed with methanol and ethanol and dried at 45-50 °C. 5: yield: 0.3 g, 91%. M.p. (decomp) > 260 °C. Anal. calcd. for C₃₆H₃₈N₂O₂Cu (594.24): C, 72.76; H, 6.45; N, 4.71%. Found: C, 72.81; H, 6.32; N, 4.63%. IR [KBr pellet, v(cm⁻¹)]: 2868, 2907, 2954 (C–H, ^tBu), 1613 (C=N), 1588, 1506 (C=C), 1536 (C-O), 562, 533, 507 (Cu-O and Cu-N). Magnetic moment per Cu^{II} (μ_{eff}): 2.92 μ_{B} 295 K. **6**: yield: 0.3 g, 91%. Mr. (decamp.) > 300 °C. Anal. calcd. for C₄₄H₅₄N₂O₂Cu (706.46): C, 74.81; H, 7.71; N, 3.96%. Found: C, 72.91; H, 7.50; N, 4.26%. IR [KBr pellet, v(cm⁻¹)]: 2867, 2905, 2953 (C–H, ^tBu), 1614 (C=N), 1588, 1506 (C=C), 1529 (C-O), 631, 538, 512 (Cu-O and Cu-N). Magnetic moment per Cu^{II} (μ_{eff}): 2.79 μ_{B} . **7**: yield: 73%. M.p. (decomp) > 300 °C. Anal. calcd. for C₃₅H₃₅N₃O₃Cu (609.22): C, 69.00; H, 5.79; N, 6.89%. Found: C, 69.07; H, 5.87; N, 6.97%. IR [KBr pellet, *v*(cm⁻¹)]: 3314 (N–H), 2867, 2907, 2952 (C–H, ^tBu), 1647 (C=O), 1610 (C=N), 1589, 1507 (C=C), 1533 (C-O), 553, 530 (Cu-O and Cu–N). Magnetic moment per Cu^{II} (μ_{eff}): 1.85 μ_B at 292 K. **8**: Yield: 73%. M.p. (decomp) > 300 °C. Anal. calcd. for $C_{43}H_{51}N_3O_3Cu$ (721.43): C, 71.59; H, 7.13; N, 5.82%. Found: C, 69.87; H, 6.87; N, 5.97%. IR [KBr pellet, v(cm⁻¹)]: 3316 (N–H), 2867, 2904, 2953 (C-H, ^tBu), 1669 (C=O), 1615 (C=N), 1585, 1507 (C=C), 1528 (C–O), 553, 530 (Cu–O and Cu–N). Magnetic moment per Cu^{II} (μ_{eff}): 1.79 μ_{B} at 298 K.

Results and discussion

The bis(X-*tert*-butylsalicylidene)-4,4'-(diaminophenyl)ethylene/amide ligands **1–4** were synthesized in good yields by simple Schiff base condensation of one equivalent of the respective diamines and two equivalents of *tert*-butylated salicylaldehydes in ethanol under reflux. These ligands (Scheme 1) contain bis(Xtert-butylsalicylidene) chelating sites in which the imine groups are linked via bis(4-aminophenyl)ethane (1 and 2) and bis(4aminophenyl)amide (3 and 4) spacers. As predicted by quantum chemical semi-empirical AM1 calculations the above ligands predominantly adopt anti-opened conformer structure (Figs. 1 and 2). Complexes 5, 7 and 8 are satisfactory soluble in the strong solvents such as DMF, CH₂Cl₂ and CHCl₃ but the solubility of complex 6 is very poor in the above solvents probably due to its polymeric nature. The coordination ability of **3** and **4** ligands having CONH amide linkage group is quiet interesting with respect that they are potentially pentadentate, and could be to form an O₂N₃ or O_3N_2 type donor trigonal-bipyramidal or square-pyramidal Cu(II) complexes. The structures of all the synthesized compounds (1-8) are confirmed by UV/vis, IR, ¹H NMR spectral studies and elemental analysis. Despite numerous attempts, single crystals of 5, 7 and 8 complexes suitable for X-ray crystallography could not be obtained.

IR and ¹H NMR spectra **1–4** ligands

Selected characteristic IR absorption frequencies of ligands (1–4) are given in the Experimental section. The vC=N and vO-H stretching's of the 1–4 free ligands appeared within 1616–1619 and 2600–2800 cm⁻¹ ranges as strong and medium intensity bands, respectively. Narrow bands at 3378 and 3452 cm⁻¹ observed in the IR spectra of the amide linkage **3** and **4** ligands, respectively, are assigned to amide vN-H stretching vibrations. A broad strong bands at 1659 and 1682 cm⁻¹ detected in the spectra of **3** and **4** can be attributed to vC=O frequencies, respectively. The ¹H NMR spectral results obtained for **1–4** ligands in CDCl₃ with their assignments is given in 'Synthesis of ligands'. ¹H NMR signals were assigned on the basis of their integral intensity, spin–spin coupling patterns and chemical shift values.

AM1 optimization for 2 and 4

In order to identify the most stable conformers for **2** and **4** ligands, the Semiempirical calculations on ligands **2** and **4** were carried out using the AM1 method. The geometry optimization revealed that the most stable minimum energy geometry for both



Anti-closed conformer Anti-ope



Fig. 2. Electronic spectra of 1 and 2 ligands in EtOH.

compounds is non-planar anti-opened conformer (Fig. 3). The lowest total energy (E_{tot}) and the heats formation energy (ΔH_f) for both conformers are calculated by using AM1 method. The AM1 optimized energies for conformer **2** ($E_{tot} = -10800 \text{ kcal/mol}$, $\Delta H_f = -18.2884 \text{ kcal/mol}$) and conformer **4** ($E_{tot} = -10660.41 \text{ kcal/mol}$, $\Delta H_f = -33.55$ kcal/mol) have been predicted. The dihedral angles between neighboring benzene rings, which are labeled as **a-d** (Fig. 3), in both conformers also have been evaluated by AM1 calculations. The dihedral angles between benzene rings, $\varphi_{\mathbf{a}/\mathbf{b}}$, $\varphi_{\mathbf{b}/\mathbf{c}}$ and $\varphi_{c/d}$ are 51.028°, 28.102° and 50.173°, respectively, for conformer of 2. Similarly, the dihedral angles between the four benzene rings were as following: $\varphi_{a/b} = 44.432^\circ$, $\varphi_{b/c} = 62.66^\circ$ and $\varphi_{c/}$ $_{d}$ = 45.009° for conformer **4**. While the total energy for **2** and **4** stable conformer is close to each other, the heats of formation energy for 4 is significantly higher than that for 2. Thus, in both stable conformers the aromatic rings are not coplanar. The AM1 optimized conformations for 2 and 4 are in good agreement with those observed for theoretically optimized geometry of similar salen type ligands [10,12d].

IR spectra of 5-8 complexes

The IR spectra of the complexes **5–8** show that the v(C=N)stretching is blue shifted to $1600-1615 \text{ cm}^{-1}$, while vO-H (2600–2800 cm⁻¹ due to intramolecularly H bonded OH…N in **1**– 4) disappears in all complexes, indicating the coordination of the imine nitrogen and deprotonated phenolic oxygen atoms to copper. The coordination mode of **5–8** was further supported by the appearance of new strong band at 1525-1536 cm⁻¹ attributable to vC-O [15,16] and medium intensity absorptions in the region 450–600 cm⁻¹ assignable to vCu–O and vCu–N stretching modes [16]. The comparison of the free ligands amide linkage vN-H bands of **3** (3378 cm⁻¹) and **4** (3452 cm⁻¹) with those for their **7** and 8 complexes show low frequency shift to 3314 and 3316 cm⁻¹, respectively. Similarly, strong broad bands of the free ligands **3** (1659 cm⁻¹) and **4** (1682 cm⁻¹) are shifted to 1646 and 1664 cm^{-1} in the spectra of complex **7** and **8**, accordingly. The observed blue shifts in vC=O and vN-H, indicate the coordination of the amide linkage to Cu(II) ion occur via carbonyl oxygen atom [17]. These observations indicate that amide linkage ligands act as pentadentate N₂O₃ chelators. Thus, comparison of the free ligands IR spectra with those for their complexes suggests pentacoordinate geometry (trigonal bipyramidal or square pyramidal) with CuN₂O₃ coordination chromophore for the **7** and **8** complexes.

Electronic spectra of 1-4 ligands

Electronic absorption spectral data of **1–4** in ethanol and DMF are given in Table 1 and Fig. 3. The strong absorption bands observed below 300 nm are assigned to intraligand $\pi \rightarrow \pi^*$ transitions in the aromatic rings $({}^{1}A_{1g} \rightarrow {}^{1}E_{1u}, {}^{1}A_{1g} \rightarrow {}^{1}B_{1u}, {}^{1}A_{1g} \rightarrow {}^{1}B_{2u})$ and the C=N chromophores [3b,18,19a]. The absorption band observed in ligands spectra within the range of 327–340 nm is most probably due to the transition of $n \rightarrow \pi^*$ of imine group [18]. The intense bands appeared in the 357–370 nm region, according to their higher extinction coefficients (log $\varepsilon = 4.34-4.88 \text{ M}^{-1} \text{ cm}^{-1})$



Fig. 3. The AM1-optimized conformers of 2 and 4 ligands. The C, O, N and H are represented by green, red, blue and white color spheres, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Electronic spectral data of 1-8 and their oxidized species under ambient conditions.

Compound	Solvent	Electronic spectra, λ (nm), (log ε , M ⁻¹ cm ⁻¹)		
1	EtOH	209, 225, 239 ^a , 275, 311, 324, 350		
	DMF	277(4.6), 313(4.7), 326(4.73), 350(4.73), 430 ^a		
	DMF + Ox.	269, 325, 347, 500 ^a		
2	EtOH	207(4.6), 228(4.4), 278(4.4), 313(4.5), 327(4.5),		
		357(4.4), 430		
	DMF	280(4.42), 314(4.42), 328(4.48), 357(4.47)		
	DMF + Ox.	278, 314, 326, 355, 530 ^a		
3	EtOH	214(4.6), 236(4.4), 281(4.6), 338(4.2), 363(4.2),		
		460 ^a (2.2)		
	DMF	282(4.7), 322 ^a , 335 ^a , 366(4.8), 460 ^a		
	DMF + Ox.	280, 363, 530 ^a		
4	EtOH	207, 220ª, 238ª, 288ª, 340, 369, 480ª		
	DMF	286(4.6), 345(4.79), 369(4.83), 480 ^a (2.11)		
	DMF + Ox.	268, 310, 340 ^a , 365 ^a , 530 ^a		
5	CH_2Cl_2	296(4.57), 412(4.26), 670(268)		
	DMF	300(4.5), 406(4.3), 667(2.32)		
	DMF + Ox.	277, 311, 324, 350, 550°		
6	CH_2Cl_2	245, 299, 363ª, 423		
	DMF	300, 327 ^a , 357, 420 ^a , 460 ^a		
7	CH_2Cl_2	240 ^d (4.44) 298(4.39), 408(4.03), 672(2.28)		
	DMF	316(4.4), 414(4.1), 520 ^b , 686(2.45)		
_	DMF + Ox.	282, 338 ^ª , 365, 390 ^ª , 430 ^ª , 470 ^ª , 560 ^ª		
8	CH_2Cl_2	$245^{a}(4.53), 316(4.62), 431(4.32), 665^{a}(2.48)$		
	DMF	316(4.6), 426(4.3), 530 ^v , 700 ^a (2.4)		
	DMF + Ox.	266, 311, 362ª, 490 ª, 636, 750 [®] , 840 [®]		

 $Ox. = (NH_4)_2 Ce(NO_3)_6.$

^a Shoulder.

^b Very weak shoulder.

can be assigned to the charge transfer transitions within the delocalized π^* system in the molecular structure [18,19]. The weak shoulder appeared at around 430 nm which is assignable to $n \rightarrow \pi^*$ transition in their keto-amine tautomeric forms, indicates that only minor amounts of keto tautomer are present in these ligands [19].

Electronic spectra of 5-8

Because of poor solubility of 6 in CH₂Cl₂, CHCl₃, DMSO and DMF solvents, we could obtain its electronic spectra only within 245-460 nm region (Table 1). All 5, 7 and 8 complexes in CH₂Cl₂, CHCl₃ and DMF solutions exhibit very similar intense bands in the 300-433 nm region (Table 1 and Figs. 4 and 5). The intense broad band within 406–431 nm can be assigned to Cu(II) (d_{π}) -to-phenolate (p_z) MLCT transition [20]. The electronic spectra of all complexes in the above solvents exhibit two similar doublets within 300-432 nm region assignable to overlapped $n \rightarrow \pi^*$ and LMCT transitions [3,19,20]. In visible region, 5, 7 and 8 exhibit a broad absorption about 660-700 nm (Table 1). The band appeared at 667 nm $(\varepsilon = 211 \text{ M}^{-1} \text{ cm}^{-1})$ in the spectrum of **5** is assigned to d-d transitions in the tetrahedrally distorted square-planar geometry. The band observed at 686 and 700 nm in the visible spectrum of 7 and **8**, respectively, can be assigned to the d-d transitions in the square-based pyramidal geometry since CuN₂O₃ chromophore is proposed for the complex 7 and 8 according to their IR and UV/ vis spectra [20-22]. A square-based pyramidal geometry with an approximate C_{4v} symmetry is proposed for these complexes since the absorptions in the 650-700 nm region in the visible spectra of **7** and **8** complexes lie within range typical for tetrahedrally distorted square-planar and square-based pyramidal geometries [21] and on the basis of their solid state ESR spectra $(g_{//} > g_{\perp})$ results.

ESR characterization of 5-8 complexes

The polycrystalline ESR spectra of all **5–8** were obtained at 300 K (Fig. 6). No half-field Δ Ms = ±2 lines typical for binuclear

triplet-state species [14b,21] were observed. Powdered ESR spectrum of **5** shows poorly resolved axial spectrum with g_{ll} of ca. 2.243 and nearly isotropic singlet at $g_{iso} = 2.074$ with an exchange narrowed line width (ΔH_{pp}) of 68.5 G [Fig. 6A (5)]. The powder spectrum of **6** along with intense isotropic singlet at $g_{iso} = 2.108$ $(\Delta H_{pp} = 115 \text{ G})$ also exhibits very weak and poorly distinguishable broad pattern approximately around g-factor of 2.5, as presented in Fig. 6A (6). It is interesting that when the ESR spectrum of this sample was scanned at 120 K, the intensity of the above broad feature is increased and a broad signal becomes clearly apparent at g = 2.566 [Fig. 7A (6a)]. In addition, an isotropic singlet at g_{iso} = 2.108 [Fig. 6A (6)] was converted to anisotropic broad pattern with $g_{//}$ around of 2.222, g_{\perp} = 2.069 and line width ΔH_{pp} of 120 G [Fig. 7A (6a)] at 120 K, suggesting a change in geometry around the copper atom. Fig. 7A (6b) shows the twofold increased left site part of the spectrum presented in Fig. 7A (6a). The significant increase in the intensity of signal at g = 2.566 upon cooling to ca.120 K suggests the existence of ferromagnetic interactions between adjacent Cu(II) centers in paramagnetic species which formed the above EPR signal. The r.t. ESR spectrum of powder sample of **7** is characterized by an axial g tensors with g_{II} $(2.248) > g_{\perp}(2.074) > g_e$ [Fig. 6B (7)]. The observed trend, $g_{||} > g_{\perp} > g_e$, suggests a $(d_{x^2-y^2})^1$ ground state in a copper centers for above complexes [21]. The exchange-coupling parameter, $G = (g_{1/2} - g_e)/(g_1 - g_e)$, reflects the exchange interaction between the copper(II) centers in polycrystalline solids [22]. According to Hathaway and Billing [22], if G > 4 the exchange interaction is negligible. The obtained value G = 3.62 for powder samples of 7, suggests the presence of an exchange coupling interaction between Cu(II) centers in the solid state [22]. On the other hand, in the powder spectrum of **8** along with a very weak intensity two g_{ll} components with A_{II} about of 150 G, the anisotropic splitting of g components with $g_{//}$ = 2.151 and g_{\perp} = 2.094 (g_{av} = 2.113) can be determined from Fig. 6B (8). The observed trend, $g_{//} > g_{\perp} > g_{e}$, suggests a $(d_{x^2-y^2})^1$ ground state in a copper centers for above complexes [21c]. It is necessary to note that, since IR spectra of 7 and **8** indicate the N_2O_3 donor site for these complexes, it is likely that the coordination mode around copper(II) center can adopt a square pyramidal or trigonal-bipyramidal geometry in above complexes. However, the ESR spectra of 7 and 8 having signals with g_{ll} > g_{\perp} > 2.03 and UV–vis spectral data are typical for square-pyramidal geometry [21].

Unfortunately, because of low solubility of the **5–8** complexes, the solution ESR spectra in dichloromethane could be obtained only for **5** and **8** compounds at room temperature. As can be seen from Fig. 8, the expected a four-line copper hyperfine spectrum, which is usually detected in the solution ESR spectra of Cu(II), has not been appeared in the spectra of **5** and **8** complexes. The solution ESR spectra of these complexes in CH₂Cl₂. display a broad component at g = 2.546 and narrow ones at $g_{iso} = 2.096$ ($\Delta H_{pp} = 109.8$ G) for **5** in Fig. 7B (**5**) and the same parameters with g = 2.551 and $g_{iso} = 2.113$ ($\Delta H_{pp} = 117.4$ G) for **8** in Fig. 7B (**8**), which are not typical for mononuclear Cu(II) compounds. We suppose that the observed solution's spectral feature, most probably, is originated from polynuclear Cu(II) polyhedrons and without X-ray structural data, the accurate interpretation of the above spectral features is not easy.

Magnetic characterization of 5-8 complexes

All magnetic measurements were corrected for diamagnetism using Pascal's constants. The r.t. effective magnetic moments, μ_{eff} , for **5** (2.92 μ_B) and **6** (2.79 μ_B) per Cu(II) ions are considerably higher even the highest possible limit value (2.3 MB). Nevertheless, the absence of ferromagnetic interaction in these polycrystalline samples was supported by the field dependence measurements of the



Fig. 4. Electronic spectra of 6 and 8 complexes: (a) spectra of 6 and 8 in CHCl₃. Inset: (b) spectrum of 8 in DMF.



Fig. 5. Electronic spectrum of 5 (I, II and III) and its one-electron oxidized species [5 + 2 equiv Ce(IV)] in DMF and at r.t (IV–XII): (a) spectra IV–VIII scanned subsequently via 50 s; (b) spectra IX–XII monitored after 15, 25, 50 and 70 min, respectively; XIII-spectrum of diluted sample XII. The arrow indicates the direction of increasing absorbance.

magnetization M at 300 K. According to literature [10,11], bi-, trior tetranuclear helical structure can be predicted for complexes **5**, **7** and **8** and a polymer type structure might be proposed for complex **6** because of its practically non-solubility feature. On the other hand, the r.t. μ_{eff} for **7** (1.85 μ_{B}) and **8** (1.79 μ_{B}) per Cu(II) agrees well with the values reported for square-planar or five-coordinate Cu(II) compounds, i.e. 1.7–2.0 μ_{B} [23]. Magnetic susceptibility data for polycrystalline samples of complexes **6** and **8** were collected over temperature range 10–300 K at a magnetic field of 10 kOe. The obtained data for the samples of **6** and **8** complexes can be fitted by the relation $\chi_{\text{m}}(T) = C/(T - \theta) + N_{\alpha}$, where *C* is Curie constant, θ is Weiss constant and N_{α} is temperature-independent paramagnetisim. The fitting procedure leads to $C = 0.7192 \pm$

0.0005 emu K mol⁻¹, $N_{\alpha} = 0.000463$ emu K mol⁻¹ and $\theta = -0.2998 \pm 0.009$ for **6** and *C* = 0.1500 emu K mol⁻¹, $N_{\alpha} = 0.000785$ emu K mol⁻¹ and $\theta = -1.389$ K for **8** were determined. Negative Weiss temperatures suggest the presence of weak antiferromagnetic interactions between Cu(II) ions within the **6** and **8** complexes. The cryomagnetic behavior of **6** is shown in Fig. 8a, in terms of the molar magnetic susceptibility (χ_m) and $\chi_m T$ product versus *T*. The $\chi_m T$ value of 2.124 cm³ mol⁻¹ K ($\mu_{eff} = 4.124 \ \mu_B$) at 300 K of **6** decreased monotonously with lowering temperature to 0.766 cm³ mol⁻¹ K ($\mu_{eff} = 2.477 \ \mu_B$) at 10 K, due to temperature-independent paramagnetism (N_{α}) associated with the Cu^{II} ion [24]. The cryomagnetic property of complex **8** is shown in Fig. 8b in the form of χ_m and $\chi_m T$ vs. *T* plot. The $\chi_m T$ product of **8** was



Fig. 6. Powder ESR spectra of 5 and 6 (A) and spectra of 7 and 8 (B) at 300 K.



Fig. 7. (A) Powder ESR spectrum of 6 (6a) at 120 K. Inset: (6b) the twofold enhanced spectrum of the low field site part of spectrum 6a. (B) Solution ESR spectra of 5 and 8 in CH₂Cl₂ at 300 K.

determined to be $0.4155 \text{ cm}^3 \text{ mol}^{-1} \text{ K} (\mu_{\text{eff}} = 1.82 \ \mu_{\text{B}})$ at 300 K. Upon cooling $\chi_m T$ product also decreases monotonously with decreasing temperature from 0.4155 emu K mol⁻¹ (μ_{eff} = 1.79 μ_B) at 300 K to 0.1578 emu K mol⁻¹ (μ_{eff} = 1.124 μ_{B}) at 10 K. It follows that two hypotheses can be proposed to explain the decrease in $\chi_{\rm m}T$ when the temperature is lowered. The first one attributes this phenomenon to the thermally induced spin conversion in the complex, present as an impurity. The second one postulates the existence of a significant temperature-independent paramagnetism, which would be due to a relative closeness of thermally unpopular ted excited levels with respect to the ground state [25]. The second postulate is valid for our complexes. For comparison magnetic behavior, we also prepared non tert-butylated analogs of 5 and 6 and found that its effective magnetic moment per Cu(II) was 2.22 $\mu_{\rm B}$ 290 K, which also suggests the existence of ferromagnetic interactions between Cu(II) centers. It should be noted that the ligands having $-C_6H_4$ -(CH₂)_n-, n = 1, 2 asymmetric spacer groups between 3,5-di-tert-butylsalicylidene moieties, which are very similar to our ligands, form a binuclear and a tetranuclear Cu(II) complexes and exhibits temperature-independent μ_{eff} in the range 5–295 K and, in addition, possesses normal magnetic moments expected for uncoupled Cu(II) centers [9c].

Chemical oxidation of 1-8 compounds

In previous studies of the electron transfer behavior of *N*-Alkyl (Aril)-3,5-di-*tert*-butylsalicylaldimine, 3,5-di-*tert*-butyl-salen type ligands and their transition metal complexes, it has been found that the generation of relatively stable uncoordinated phenoxyl or coordinated M(II)-phenoxyl radical complexes were detected upon one-electron oxidation of the above compounds [12b-d].

The oxidative behavior of **1–8** compounds was investigated by in situ UV/vis spectral measurements. The results of UV/vis spectral changes were observed during the chemical oxidation of **1–8** are given in Table 1 and Figs. 5, 9 and 10. Upon one-electron oxidation of ligand **1–4** ligands (\sim 0.005 M) with 1 equiv of Ce(IV) in



Fig. 8. Temperature dependence of the molar magnetic susceptibility χ_m for **6** (a) and **8**(b). Solid line represents a fit by Curie–Weiss law. Inset: the temperature dependence of $\chi_m T$ product.



Fig. 9. (a) Electronic spectra of **1** and its oxidation products ((**1** + 1 equiv Ce(IV)); (b) electronic spectra of **2** and its one-electron oxidation products (**2** + 1 eqv ox.); spectra presented as a-e in figure (b) are recorded with period 45 s after addition of Ce(IV) to a solution of ligand **2**. All spectra are scanned in DMF.



Fig. 10. UV/vis spectra of complex **8** (1–3) in DMF. The changes in the electronic absorption spectrum of **8** (2.3×10^{-3} M) during the chemical oxidation for **8** + 2 equiv Ce(IV) system in DMF solution and aerobic conditions. Each spectrum from 4 to 7 is scanned with 50 s period, 7, 8 and 9 monitored via 5, 10 and 15 min, respectively. The spectra 10, 11 and 12 obtained with 20 min period. Spectra 13 and 14 scanned by dilution of 12.



Fig. 11. (Left) A cyclic voltammogram of complex 5 in dichloromethane and 0.05 M n-Bu₄NClO₄ as supporting electrolyte. Scan rate 100 mV/s. (Right) Cyclic voltammo-grams of complex 5 in dichloromethane at increasing scan rates: 100, 200, 300 and 400 mV/s.

DMF, a color of ligand solution simultaneously turns from yellow to red along with the disappearance of the original ligand band at ca 430 and the blue shifts in the bands with $\lambda < 366$ nm, the appearance of a new shoulder in the range 500–530 nm were observed (Table 1 and Fig. 9). Upon successive scanning of **2** + 1 equiv Ce(IV) system, the increase of the intensity of a shoulder appeared around 530 nm (Fig. 9b) indicates that the generated oxidized species are relatively stable under above conditions. The appearance of new bands in the spectra of the oxidized ligands is assigned to phenoxyl radical species.

Upon chemical oxidation of 5 and 7 with 2 equiv of Ce(IV) in DMF, along with simultaneously disappearance of the d-d band at 667 and 686 nm, the appearance of a new weak shoulder at around 550 and new maxima bands in UV region were detected (Table 1, Fig. 5). Under above conditions chemical oxidation of complex 8 with 2 equiv of Ce(IV) in DMF, along with immediate disappearance of the bands at 426 and 700 nm, the appearance of new absorptions at 286, 324 and 368 nm were detected (Fig. 11). Upon successive scanning of 8 + 2 equiv Ce(IV) system along with the appearance of new weak shoulders at around 750 and 840 nm, as well as the appearance of another new shoulder around 650 nm were observed. Upon further scanning the transformation of a shoulder at 650 nm to maximum at 636 nm can be clearly seen from Fig. 10. The disappearance of the d-d transitions is indicative to reduction of Cu(II) to Cu(I) or one-electron oxidation of Cu(II) to Cu(III) with concomitant generation of the coordinated phenoxyl radical to copper(II) center. The reappearance of new bands in the visible region around 750 and 840 nm, and then disappearance with the following appearance of a new band at 636 nm can be interpreted by the conversion of one intermediate Cu(II) complex, probably, with trigonal bipyramidal symmetry to another Cu(II) complex with square-pyramidal geometry.

Electrochemistry

Electrochemical properties of copper complexes were studied on a Pt disc electrode in dichloromethane containing 0.05 M n-Bu₄₋

Table 2

Voltammetric data for 5-8 copper(II) complexes.

Complex	Epa (V)	Epc (V)	$\Delta Ep (mV)$	Epc (V)
5	0.948	0.865	83	-0.794
6	1.068	0.846	222	-0.450
7	0.968	0.863	105	-0.870
8	1.117	0.436	681	-1.000

Supporting electrolyte = 0.05 M n-Bu₄ClO₄, scan rate = 50 mV/s.

NClO₄ as the supporting electrolyte. The results of cyclic voltammetry (CV) measurements are given in Table 2. Representative voltammograms are shown in Fig. 11. The CV of copper complex 5-8 exhibit quasi-reversible waves at of versus Ag/AgCl which can be ascribed to Cu(III)/Cu(II) couples. As shown in Fig. 11a. complex 5 displays an oxidation peak at Epa = 0.948 V with a corresponding reduction peak at Epa = 0.865 V. The peak separation for this couple (ΔEp) is 83 mV. The most significant feature of this redox couple is the one-electron transfer electrochemical process of the formation of Cu(III)/Cu(II). 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 electrochemical behavior of **5** can be explained by having the presence of noninteracting copper ion centers where the redox process for each occurs at about the same potential. The appearance of only one wave has been previously reported for a number of multicopper systems [26–29]. Generally, one wave is seen if ΔEp between two or more separate processes such as Cu^{III}-Cu^{III}+ $e^- \rightarrow Cu^{II}-Cu^{II} + e^- \rightarrow Cu^{II}-Cu^{II}$ is <-100-200 mV. The analysis of cyclic voltammetric responses with the scan rate varying 100-400 mV/s gives the evidence for a quasi-reversible one electron oxidation (Fig. 11b). 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 $Ip/v^{1/2}$ value is almost constant for all scan rates. This establishes the electrode process as diffusion controlled [30]. The separation in peak potentials increases at higher scan rates. These characteristic features are consistent with the quasi-reversibility of Cu(III)/Cu(II) couple. The other reduction peaks are listed in the Table 2 and are probably due to the ligand moiety of complex. The electrode potentials of the rest of the copper complexes are given in Table 2.

Conclusion

A new flexible Schiff base ligands [bis-(*N*,*N'*-X-*tert*-butylsalicylidene)-4-amino-phenyl]ethylene (**1** and **2**) and bis-[(*N*,*N'*-3,5-di*tert*-butylsalicylidene)-4-aminophenyl] amide (**3** and **4**) ligands and their copper(II) complexes (**5–8**) have been synthesized. Their spectroscopic (IR, ¹H NMR, UV/vis, ESR), magnetic behaviors and redox reactivity were studied. On the basis of IR, UV/vis and solid state ESR spectroscopic results for amide linkage **7** and **8** complexes a square based pyramidal geometry is proposed. The r.t. effective magnetic moments, μ_{eff} , for **5** (2.92 μ_B) and **6** (2.79 μ_B) per Cu(II) ions are considerably higher even the highest possible limit value (2.3 μ_B) for Cu(II) compounds. Variable temperature (10–300 K) study of **6** and **8** shows that their magnetic moments linearly decreased from 4.12 to 1.79 $\mu_{\rm B}$ at 300 K to 2.48 and 1.13 $\mu_{\rm B}$ at 10 K, respectively. Chemical oxidation of ligands lead to the formation of a new band in the 500-530 nm region assignable to phenoxyl radicals. Also, except 8, along with the disapperance of the d-d and LMCT bands, a weak shoulder around 500-560 nm was observed for the oxidized complexes. The electrochemical behavior of copper complexes also exhibit the presence of noninteracting copper(II) centers where the redox processes occur. Thus, according to electrochemical and chemical study results, metal centered oxidation can be proposed for these complexes.

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