Preparation, characterisation and redox properties of four new tetradentate salicylaldimines with their Cu(II) complexes

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Some new tetradentate salicylaldimine ligands of Schiff bases were synthesised by treating 3,5-di-tert-butyl-2-hydroxybenzaldehyde with 1,2-bis-(*o*-aminophenoxy)ethane, 1,4-bis-(*o*-aminophenoxy)butane, 1,4-bis-(*m*-aminophenoxy)buthane and 1,4-bis-(*p*-aminophenoxy)butane. The compounds were characterised by IR, UV-vis, ^{1}H NMR, ^{13}C NMR, magnetic susceptibility measurements, elemental analysis, molar conductance (Λ_M), thermogravimetric analysis (TGA) and cyclic voltammetry. The metal to ligand ratios of the Cu(II) complexes were found to be 1:1. The coordination of the novel tetradentate salicylaldimines appears to occur through the two azomethine nitrogens and two *o*-OH groups. Cyclic voltammetric studies showed that all of the Cu(II) complexes undergo quasi reversible one-electron transfer redox processes attributed the Cu(II)/Cu(I) couples in dimethylsufoxide. The electron donor affinity of copper(II) complexes increases in order Cu(L$_4$)>Cu(L$_3$)>Cu(L$_2$)>Cu(L$_1$).

Keywords: salicylaldimine, Schiff bases, complexes, Cu(II)

Schiff bases and relevant transition metal complexes are of interest in inorganic chemistry and have been studied extensively.[1-3] The design, synthesis and structural characterisation of salicylaldimine complexes is a subject of current interest due to their interesting structural, magnetic, spectral, catalytic, redox properties, use as models for enzymes and various theoretical interest.[4-7] It has also been reported that transition metal complexes of Schiff bases containing tetradentate ligands have anti-microbial activity.[8] Transition metal complexes with redox active ligands bearing sterically hindered salicylaldimines are also reported to undergo one- or two-electron transfer.[9] Sterically hindered ligands bearing salicylaldimines are known to be effective antioxidants and are widely used in rancidification of fats and oils.[9] Copper(II) ions play a central role in biological redox metalbenzymes such as plastocyanin, hemocyanin, azurin, and galactose oxidase.[10]

We now report the synthesis, spectral and electrochemical characterisation of Cu(II) complexes with Schiff bases derived from condensation of 1,2-bis-(*o*-aminophenoxy)ethane, 1,4-bis-(*o*-aminophenoxy)butane, 1,4-bis-(*m*-aminophenoxy) butane and 1,4-bis-(*p*-aminophenoxy)butane with 3,5-di-*tert*-butyl-2- hydroxybenzaldehyde.

Experimental

Data contained in supplementary Tables and Figs are available from the corresponding author on request.

Material and methods

Unless otherwise stated, all chemicals were of analytical-reagent grade and purchased from Sigma or Merck. 3,5-Di-tert–butyl-2-hydroxybenzalde-hyde (3,5-DTB) was synthesised according to the literature procedure.[11] 1,2-bis-(*o*-aminophenoxy)ethane, 1,4-bis-(*o*-aminophenoxy)butane, 1,4-bis-(*m*-aminophenoxy)butane and 1,4-bis-(*p*-aminophenoxy)buthane were synthesised by the method described in the literature.[12,13] N-N'-Bis(3,5-di-*t*-butylsalicylaldimine)-1,2-bis-(*o*-aminophenoxy)ethane (L$_1$H$_2$), N-N'-Bis(3,5-di-*t*-butylsalicylaldimine)-1,4-bis-(*o*-aminophenoxy)butane (L$_2$H$_2$), N-N'-Bis(3,5-di-*t*-butylsalicylaldimine)-1,4-bis-(*m*-aminophenoxy) butane (L$_3$H$_2$) and N-N'-Bis(3,5-di-*t*-butylsalicylaldimine)-1,4-bis-(*p*-aminophenoxy)buthane (L$_4$H$_2$) were prepared here for the first time. Tetrabuthylamoniumperchlorate [*n*-Bu$_4$N]ClO$_4$ was used as supporting electrolyte in voltammetric experiments.

The elemental analyses and ^{1}H NMR spectra were carried out in the laboratory of Tubitak (Scientific and Technical Research Council of Turkey), IR spectra were recorded on a Perkin Elmer Spectrum RXI FT-IR spectrometer as KBr pellets, magnetic susceptibilities were determined on a Sherwood Scientific Magnetic Susceptibility Balance (Model MK1) at room temperature (20 °C) using Hg[Co(SCN)$_4$] as a calibrant; diamagnetic corrections were calculated from Pascal's constants.[11] UV spectra were recorded on a Schimadzu 1601 PC. Voltammetric experiments were performed using an EcoChemie Autolab potentiostat-12 with an electrochemical software GPES 4.9. A three electrode system was used: a 2 mm sized Pt disc working electrode, an Ag/AgCl reference electrode and a Pt wire counter electrode. The working electrode was polished with 0.05 µm alumina prior to each experiment. Throughout the experiment oxygen-free dinitrogen was bubbled through the solution for 10 min. Voltammetric experiments were performed at room temperature.

Synthesis of the ligands L$_1$H$_2$, L$_2$H$_2$, L$_3$H$_2$ and L$_4$H$_2$

L$_1$H$_2$, L$_2$H$_2$, L$_3$H$_2$ and L$_4$H$_2$ ligands were synthesised by the reaction of 10 mmol 3,5-D7B in 20 ml absolute ethanol and 5 mmol of appropriate phenoxide in 10 ml ethanol, respectively. Also 3–4 drops of acetic acid were added. The mixture was refluxed for 3 h, followed by cooling to room temperature. The crystals were filtered, then the products were recrystallised from ethanol/DMF (1:2). The products are soluble in common solvents such as CHCl$_3$, DMF and DMSO.

Synthesis of Cu(II) complexes

1 mmol L$_1$H$_2$, L$_2$H$_2$, L$_3$H$_2$ or L$_4$H$_2$ ligand was dissolved in absolute DMF (40 ml) and mixed with 1 mmol Cu(Ac)$_2$.H$_2$O in DMF (20 ml). The stirred mixture was refluxed for 24 h. The mixture was evaporated to a volume of 15–20 ml in vacuum and left to cool to room temperature. The compounds precipitated after adding 5 ml ethanol. The products were filtered in vacuum and washed with a small amount of methanol and water, then recrystallised from DMF. The products are soluble in solvents such as CHCl$_3$, DMF and DMSO.

Results and discussion

The reaction steps for the synthesis of ligands are given in Schemes 1 and 2. The first step is the synthesis of 1,2-bis-(*o*-nitrophenoxy)ethane, 1,4-bis-(*o*-nitrophenoxy)butane, 1,4-bis-(*m*-nitrophenoxy)butane and 1,4-bis-(*p*-nitrophenoxy) butane from the reaction of sodium *o*-nitrophenolate, sodium *m*-nitrophenolate or sodium *p*-nitrophenolate with 1,2-dibromoethane or 1,4-dibromobuthane (Scheme 1). In the second step, 1,2-bis-(*o*-nitrophenoxy)ethane, 1,4-bis-(*o*-nitrophenoxy)butane, 1,4-bis-(*m*-nitrophenoxy)butane or 1,4-bis-(*p*-nitrophenoxy)butane and Pd/C as catalyst were reacted to obtain 1,2-bis-(*o*-aminophenoxy)ethane, 1,4-bis-(*o*-aminophenoxy)butane, 1,4-bis-(*m*-aminophenoxy)butane and 1,4-bis-(*p*-aminophenoxy)butane (Scheme 1).

Additional analytical data are given in supplementary Tables 2–5 and Figs 3–5 (obtainable from the authors). The ligands L$_x$H$_2$, on interaction with Cu(II) salts yielded complexes corresponding to the general formula [Cu(L$_x$)].

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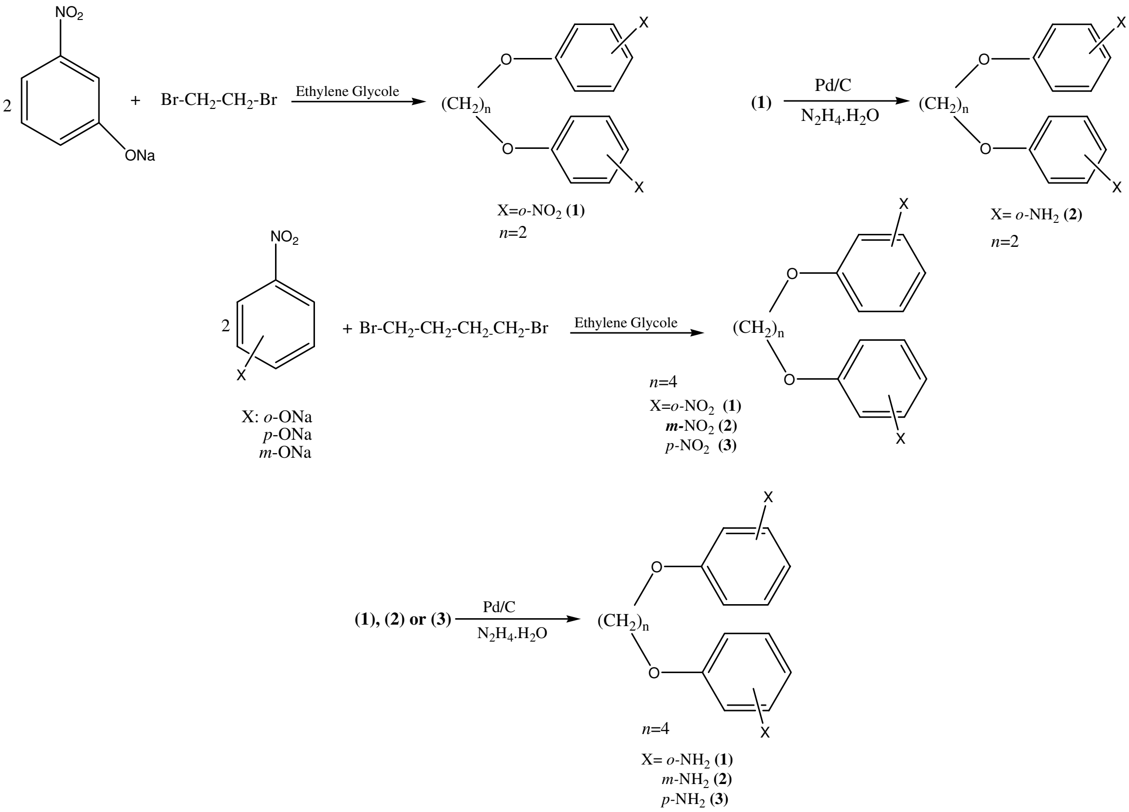
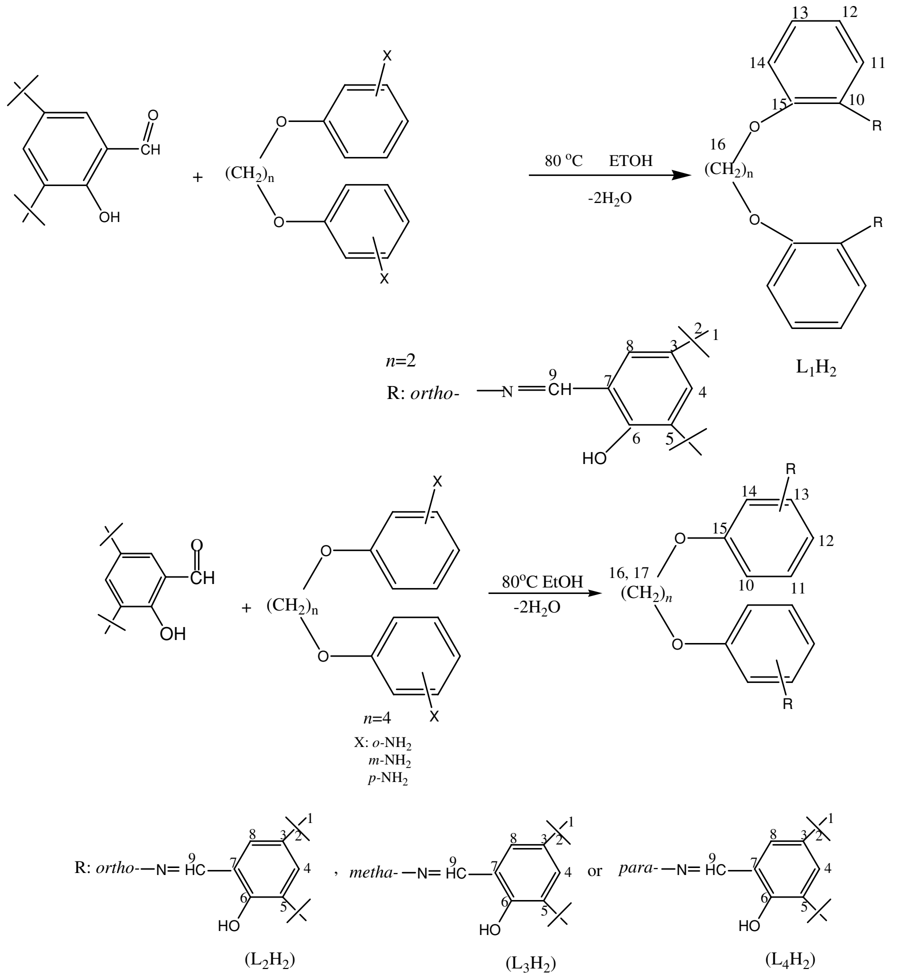


Scheme 1 Synthesis scheme for the preparation of the amine compounds.



Scheme 2. Synthesis route to the ligands.

NMR spectra

On the basis of ^{1}H NMR spectra for L_xH, the deuterium exchangeable proton of Ar–OH/NH shows a singlet at $\delta = 14.15$ ppm for L_1H_2, $\delta = 14.44$ ppm for L_2H_2 $\delta = 13.62$ ppm for L_3H_2 and $\delta = 13.76$ ppm for L_4H_2, respectively.

In the ^{1}H NMR spectra of ligands (L_1H_2, L_2H_2, L_3H_2 and L_4H_2), the chemical shifts observed at $\delta = 8.76$ ppm, $\delta = 8.73$ ppm, $\delta = 8.64$ ppm and $\delta = 8.62$ ppm are assigned to the protons of azomethine.[14] Also, the protons of the *tert*-butyl groups of the ligands exhibit two sharp singlets peaks $\delta = 1.28$–1.52 ppm, indicating that the the *tert*-butyl protons of these compounds are magnetically nonequivalent.[3] The ^{1}H NMR data of the other ligands are given in supplementary Table 4. Since Cu(II) complexes are paramagnetic,[15] their ^{1}H NMR spectra could not be obtained.

FT-IR spectra

The important characteristic IR bands of Schiff base ligands and their copper(II) complexes are given in supplementary Table 2. The IR spectra of the ligands are characterised by the appearance of a broad band in the region 2400–3600 cm^{-1} due to the υ(O-H) groups.[16] The lower frequency shifts of υ(C = N) in the IR spectra of the Cu(II) complexes, suggest chelating of L_xH_2 via a deprotonated –OH groups and the azomethine N atoms.

In the IR spectra of ligands; characteristic bands were observed at 1618 cm^{-1} for L_1H_2, at 1619 cm^{-1} for L_2H_2, at 1619 cm^{-1} for L_3H_2 and at 1619 cm^{-1} for L_4H_2 respectively. These strong bands, attributed to the υ(C = N) stretch, showed a negative shift to *ca* 1604–1614 cm^{-1} in the spectra of all the complexes. The bands in the region 1273–1288 cm^{-1} in the IR spectra of the synthesised ligands are ascribed to the phenolic υ(C–O) stretching vibrations.[3] These bands shifted to lower frequencies due to O–metal coordination.[17] Conclusive evidence of the bonding is also shown by the observation that new band in the spectra of the metal complexes at 530–537 cm^{-1} assigned to υ(M–N) stretching vibrations which are not observed in the spectra of ligands.[18]

Electronic spectra

Electronic spectra of the four new ligands were measured in $CHCl_3$ solution and three or four absorption bands are observed, along with bands in the 244–360 nm region which are due to $\pi \rightarrow \pi^*$and $n \rightarrow \pi^*$ transitions of the benzene ring and the C = N group.[3]

The electronic spectra of Cu(II) complexes were recorded in DMF at room temperature (supplementary Table 3). The electronic spectra of all Cu(L_x) complexes show a group of identical absorption bands at 291–870 nm in DMF. The bands below 419 nm have very high extinction coefficients and are almost certainly associated with intraligand $\pi \rightarrow \pi^*$and $n \rightarrow \pi^*$ or charge-transfer transitions. The copper(II) complexes also show absorption bands in the range 660–870 nm, presumably due to d–d transitions. The Cu(II) complexes show an absorption band at 419–870 nm attributed to the $^2T_2g \rightarrow {}^2Eg$ (G) transition, which is compatible with these complexes having a square-planar structure.[19]

Magnetic susceptibility

The room temperature magnetic moments of Cu(L_xH) complexes are in the range 1.66–1.95 B.M, which are typical for mononuclear Cu(II) compounds with a $S = ½$ spin state and did not indicate antiferromagnetic coupling of spin at this temperature.[20]

Molar conductivity

The Cu(II) complexes are non-electrolytes as shown by their molar conductivity (Λ_M) in DMF, which is in the range 2.8–6.4 Ω^{-1} cm^2 mol^{-1}.[21]

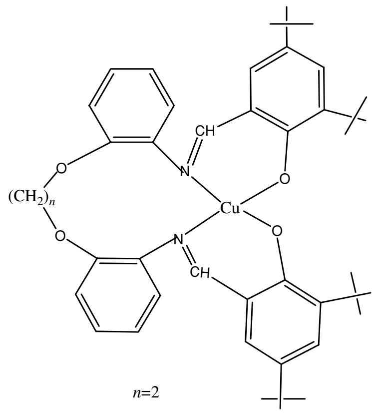


Fig. 1 Mononuclear Cu(II) complexes of L_1H_2.

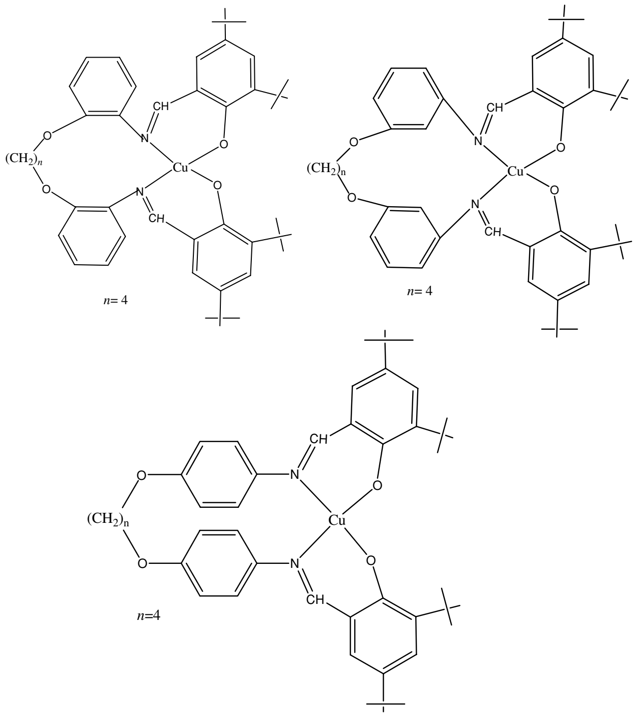


Fig. 2 Mononuclear Cu(II) complexes of L_2H_2, L_3H_2 and L_4H_2.

Thermal study

The compounds were investigated by TGA. The TGA curves, which were obtained under dinitrogen at 20–900 °C, show that ligands L_1H_2, L_2H_2, L_3H_2 and L_4H_2 are thermally stable up to 254, 230, 326 and 144 °C, respectively. Thus L_3H_2 has the highest thermal stability of the ligands and L_4H_2 the lowest. Also, [Cu(L_2)] has the highest thermal stability of the complexes and [Cu(L_4)] the lowest.

Electrochemistry

The electrochemical behaviours of copper(II) complexes were studied by means of cyclic voltammetry using a Pt disc electrode in dimethylsulfoxide containing 0.05 M n-Bu_4NClO_4 as supporting electrolyte. A cyclic voltammogram of Cu(L_1) is presented in Fig. 3. Cu(L_1) displays a reduction peak at $E_{pc} = 0.173$ V with a corresponding oxidation peak at $E_{pa} = 0.281$ V. This redox couple is assigned to Cu(II)/Cu(I) process. The peak separation of this couple (ΔE_p) is 0.108 V at 0.1 V and increases with scan rate. This behaviour shows that the heterogeneous electron transfer rate is relatively slow. This process is consistent with a quasi

Table 1 The colours, formulae, formula weights, melting points, magnetic susceptibilities, yields and elemental analyses results of the ligands and the complexes

Compounds	F.W. (g/mol)	Colour	M.p. /°C(dec.)	Yield/%	μ_{eff} [B.M]	Elemental analyses		
						% Calculated (found)		
						C	H	N
L_1H_2	676	Pale yellow	168	78	-	78.1 (77.7)	8.3 (8.4)	4.1 (4.2)
$Cu(L_1)$	737.5	Green	260	72	1.66	71.6 (71.0)	7.6 (7.1)	3.8 (4.0)
L_2H_2	704	Orange	197	75	-	78.4 (77.9)	8.5 (8.4)	4.0 (4.1)
$Cu(L_2)$	765.5	Green	290	70	1.71	72.1 (72.0)	7.6 (7.7)	3.7 (3.5)
L_3H_2	704	Pale yellow	135	80	-	78.4 (78.1)	8.5 (8.2)	4.0 (4.1)
$Cu(L_3)$	765.5	Dark green	165	76	1.95	72.1 (71.9)	7.6 (7.6)	3.7 (3.5)
L_4H_2	704	Yellow	195	72	-	78.4 (78.0)	8.5 (8.6)	4.0 (4.1)
$Cu(L_4)$	765.5	Dark green	250	65	1.77	72.1 (71.8)	7.6 (7.6)	3.7 (3.5)

reversible one electron transfer redox reaction.[22] The results for all copper(II) complexes are summarised in supplementary Table 5. All the mononuclear copper(II) complexes show a single quasi reversible one-electron transfer reduction process. Each voltammogram shows one quasi reversible wave at positive potential in the range 0.173 to 0.104 V. The reduction potential of the mononuclear copper(II) complexes of ligands L_1H to L_4H displays a shift towards the cathodic region. The reduction of $[Cu(L_4)]$ proceeds at a less positive potential than the others, indicating greater electron donor properties of L_4. The electron donor affinity of copper(II) complexes increases in order $Cu(L_4)>Cu(L_3)>Cu(L_2)>Cu(L_1)$. The formal potential of copper(II) complexes depends upon both electronic and structural factors.

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