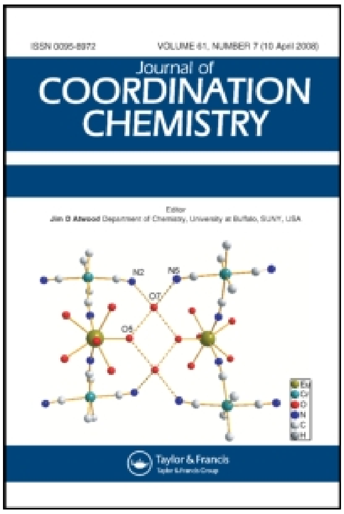

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, and electrochemical study of two new macroacyclic Schiff bases and their copper(II) and zinc(II) complexes

Hassan Keypour[a]; Maryam Shayesteh[a]; Davood Nematollahi[a]; Laura Valencia[b]; Hadi Amiri Rudbari[c]
[a] Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran [b] Departamento de Química Inorgánica, Facultad de Química, Universidade de Vigo, 36310 Vigo, Pontevedra, Spain [c] Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Universita' di Messina, 98166 Messina, Italy

To cite this Article Keypour, Hassan , Shayesteh, Maryam , Nematollahi, Davood , Valencia, Laura and Rudbari, Hadi Amiri(2010) 'Synthesis, characterization, and electrochemical study of two new macroacyclic Schiff bases and their copper(II) and zinc(II) complexes', Journal of Coordination Chemistry, 63: 23, 4165 — 4176

To link to this Article: DOI: 10.1080/00958972.2010.527963

URL: http://dx.doi.org/10.1080/00958972.2010.527963

Journal of Coordination Chemistry
Vol. 63, No. 23, 10 December 2010, 4165–4176

Synthesis, characterization, and electrochemical study of two new macroacyclic Schiff bases and their copper(II) and zinc(II) complexes

HASSAN KEYPOUR*†, MARYAM SHAYESTEH†,
DAVOOD NEMATOLLAHI†, LAURA VALENCIA‡ and
HADI AMIRI RUDBARI§

†Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran
‡Departamento de Química Inorgánica, Facultad de Química,
Universidade de Vigo, 36310 Vigo, Pontevedra, Spain
§Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica,
Universita' di Messina, 98166 Messina, Italy

(*Received 6 April 2010; in final form 30 August 2010*)

Two new potentially octadentate N_2O_6 Schiff-base ligands 2-((E)-(2-(2-(2-((E)-2-hydroxy-3-methoxybenzylideneamino)phenoxy)phenoxy)phenylimino)methyl)-6-methoxyphenol H_2L^1 and 2-((E)-(2-(2-(2-((E)-2-hydroxy-3-methoxybenzylideneamino)phenoxy)-4-tert-butylphenoxy)phenylimino)methyl)-6-methoxyphenol H_2L^2 were prepared from the reaction of O-Vaniline with 1,2-*bis*(2′-aminophenoxy)benzene or 1,2-*bis*(2′-aminophenoxy)-4-t-butylbenzene, respectively. Reactions of H_2L^1 and H_2L^2 with copper(II) and zinc(II) salts in methanol in the presence of $N(Et)_3$ gave neutral $[CuL^1]\cdot0.5CH_2Cl_2$, $[CuL^2]$, $[ZnL^1]\cdot0.5CH_2Cl_2$, and $[ZnL^2]$ complexes. The complexes were characterized by IR spectra, elemental analysis, magnetic susceptibility, ESI–MS spectra, molar conductance (Λ_m), UV-Vis spectra and, in the case of $[ZnL^1]\cdot0.5CH_2Cl_2$ and $[ZnL^2]$, with ^{1}H- and ^{13}C-NMR. The crystal structure of $[ZnL^1]\cdot0.5CH_2Cl_2$ has also been determined showing the metal ion in a highly distorted trigonal bipyramidal geometry. The electrochemical behavior of H_2L^2 and its Cu(II) complex, $[CuL^2]$, was studied and the formation constant of $[CuL^2]$ was evaluated using cyclic voltammetry. The logarithm value of formation constant of $[CuL^2]$ is 21.9.

Keywords: Schiff base; Copper(II) complexes; Zinc(II) complexes; O-Vaniline; X-ray crystal structure; Cyclic voltammetry

1. Introduction

Schiff bases have been extensively studied in coordination chemistry due to their facile syntheses, easily tunable steric and electronic properties, and good solubility in common solvents [1]. Azomethine compounds have wide applications in biology, for example, proteins [2], visual pigment [3], enzymic aldolization [4], decarboxylation reactions [5], in pyridoxal phosphate degradation [6], and in the field of color photography [7]. Transition metal complexes with oxygen and nitrogen donor Schiff bases are of

---

*Corresponding author. Email: haskey1@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.527963

particular interest [8–13] because of their ability to possess unusual configurations, be structurally labile, and their sensitivity to molecular environments [14]. Schiff-base complexes containing Ni, Co, Zn, and Cu have been studied in great detail for structures, structure–redox relationships, enzymatic reactions, mesogenic characteristics, and catalytic properties [15–17]. Zinc has a significant role in bioinorganic chemistry, involving a large number of enzymatic and catalytic functions [18, 19]. In this article, synthesis of potentially octadentate Schiff bases H_2L^1 and H_2L^2 and their Cu(II) and Zn(II) complexes are described. Analytical, structural, spectral, magnetic, molar conductivity measurements, and electrochemical studies were used to investigate the structures of these ligands and their complexes.

2. Experimental

2.1. *Starting materials*

1,2-*Bis*(2′-aminophenoxy)benzene and 1,2-*bis*(2′-aminophenoxy)-4-t-butylbenzene were synthesized according to the literature method [20–24]. o-Vaniline, solvents, metal salts, and other reagents were purchased from Merck and used without purification.

2.2. *Physical measurements*

Infrared (IR) spectra were collected using KBr pellets on a BIO-RAD FTS-40A spectrophotometer ($400–4000\,\mathrm{cm^{-1}}$). A Perkin-Elmer, Lambda 45 (UV-Vis) spectrophotometer was used to record electronic spectra. Electron impact (20 eV) mass spectra for ligands were recorded on a Shimadzu, QP1100EX spectrometer. ESI–MS spectra were recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Magnetic susceptibility measurements were performed at 25°C using a Johnson Matthey Alfa MSBMKI Gouy balance. CHN analyses were carried out using a Perkin-Elmer, CHNS/O elemental analyzer model 2400. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ^{1}H- and ^{13}C-NMR spectra were taken in $CDCl_3$ and DMSO on a Bruker Avance 300 and 500 MHz and a Jeol 90 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. Cyclic voltammetry was performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a Pt disc (1.8 mm diameter) and platinum wire was used as the counter electrode. Working electrode potentials were measured *versus* Ag wire (all electrodes from AZAR Electrodes). A stream of pure nitrogen was used to remove the dissolved oxygen in the solution before voltage scanning.

2.3. *X-ray crystallography*

Single crystals of $[ZnL^1]\cdot 0.5CH_2Cl_2$ complex were obtained from dichloromethane by *n*-hexane diffusion. The single crystal X-ray diffraction analysis was performed on a Bruker SMART APEX2 CCD area detector at 150(1) K using

Table 1. Crystal data and structure refinement for $[ZnL^1] \cdot 0.5CH_2Cl_2$.

Empirical formula	$C_{34.50}H_{27}ClN_2O_6Zn$
Formula weight	666.40
Temperature (K)	150(1)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C\,2/c$
Unit cell dimensions (Å, °)	
a	24.6500(11)
b	12.1260(4)
c	22.4350(11)
α	90
β	118.7811(17)
γ	90
Volume (Å^3), Z	5877.5(4), 8
Calculated density (g cm^{-3})	1.506
Absorption coefficient (mm^{-1})	0.978
F(000)	2744
Crystal size (mm^3)	$0.22 \times 0.20 \times 0.06$
θ range for data collection (°)	3.01–27.55
Index ranges	$-32 \le h \le 31$, $-15 \le k \le 15$, $-24 \le l \le 29$
Reflections collected	17807
Independent reflections	6629 [R(int) = 0.0652]
Completeness to $\theta = 25.24$ (%)	99.1
Absorption correction	Multi-scan
Max. and min. transmission	0.965 and 0.879
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6629/0/407
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0581$, $wR_2 = 0.1201$
R indices (all data)	$R_1 = 0.1311$, $wR_2 = 0.1472$
Largest difference peak and hole (e Å^{-3})	0.764 and −0.467

graphite-monochromated Mo-Kα X-ray radiation ($\lambda = 0.71073$ Å). Details of the X-ray experiments and crystal data are summarized in table 1.

2.4. *Synthesis*

2.4.1. H_2L^1. 1,2-*Bis*(2′-aminophenoxy)benzene (0.292 g, 1 mmol) in methanol (20 mL) was added dropwise with stirring to a solution of o-Vaniline (0.304 g, 2 mmol) in methanol (30 mL). The mixture was stirred and heated to reflux for 4 h. A red precipitate was obtained that was filtered off, washed with cold methanol, and dried *in vacuo*. Red crystals of H_2L^1 were obtained by liquid diffusion of *n*-hexane into a solution of the ligand in chloroform. Yield: 0.5 g (89%); m.p. 151°C. Anal. Calcd for $C_{34}H_{28}N_2O_6$: C, 72.8; H, 5.0; N, 5.0. Found: C, 72.4%; H, 5.2%; N, 5.4%. IR (cm^{-1}, KBr): 1615 (s, νC=N). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 271(123700), 287(sh), 345(29560). Mass spectral parent ion; m/z 560.

2.4.2. H_2L^2. In a manner similar to that for H_2L^1, a methanol solution (20 mL) of 1,2-*bis*(2′-aminophenoxy)-4-t-butylbenzene (0.348 g, 1 mmol) was added dropwise with stirring to a solution of o-Vaniline (0.304 g, 2 mmol) in methanol (30 mL). The mixture was stirred and heated to reflux for 4 h. A red solid product that formed was washed with cold methanol and dried *in vacuo*. Red crystals of H_2L^2 were obtained by liquid diffusion of *n*-hexane into a solution of the ligand in chloroform. Yield: 0.4 g (65%); m.p. 132°C. Anal. Calcd for $C_{38}H_{36}N_2O_6$: C, 74.0; H, 5.9; N, 4.5. Found: C, 73.7%; H, 5.9%; N, 4.9%. IR (cm^{-1}, KBr): 1616 (s, νC=N). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 234(50390), 281(26420), 338(22310). Mass spectral parent ion; *m*/*z* 616.

2.4.3. $[CuL^1]\cdot 0.5CH_2Cl_2$. A methanol solution (15 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 1 mmol) and a moderate excess of NEt_3 were added to a warm solution of H_2L^1 (0.560 g, 1 mmol) in methanol (50 mL). The mixture was stirred and heated to reflux for 4 h. The resultant green solid was collected by filtration and washed with diethyl ether and cold methanol. Green crystals of $[CuL^1]\cdot 0.5CH_2Cl_2$ were obtained by liquid diffusion of *n*-hexane into a solution of the complex in dichloromethane. Yield: 0.5 g (75%); m.p. 260°C. Anal. Calcd for $C_{34}H_{26}CuN_2O_6\cdot 0.5\ CH_2Cl_2$: C, 62.3; H, 4.1; N, 4.2. Found: C, 62.3%; H, 4.2%; N, 4.5%. IR (cm^{-1}, KBr): 1611 (s, νC=N), 427–470 (M–N), 540–582 (M–O). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 301(39030), 415(13840), 690(60). $\Lambda M = 9\ \Omega^{-1}\,cm^2\,mol^{-1}$. ESI–MS (*m*/*z*): 622 ($[CuL^1+H]^+$, 100%).

2.4.4. $[CuL^2]$. Similarly, H_2L^2 (0.617 g, 1 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ yielded green crystals. Yield: 0.4 g (59%); m.p. 285°C. Anal. Calcd for $C_{38}H_{34}CuN_2O_6$: C, 67.3; H, 5.0; N, 4.1. Found: C, 67.3%; H, 5.2%; N, 4.4%. IR (cm^{-1}, KBr): 1610 (s, νC=N), 445–476 (M–N), 523–553 (M–O). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 298(33110), 425(8220), 651(109). $\Lambda_M = 11.5\ \Omega^{-1}\,cm^2\,mol^{-1}$. ESI–MS (*m*/*z*): 678 ($[CuL^2+H]^+$, 100%).

2.4.5. $[ZnL^1]\cdot 0.5CH_2Cl_2$. In the same way, a methanol solution (15 mL) of $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1 mmol) and a moderate excess of NEt_3 were added to a warm solution of H_2L^1 (0.560 g, 1 mmol) in methanol (50 mL). The resultant yellow solid was collected by filtration and washed with cold methanol. Yellow crystals of $[ZnL^1]\cdot 0.5CH_2Cl_2$ were obtained by liquid diffusion of *n*-hexane into a solution of the complex in dichloromethane. Yield: 0.4 g (60%); m.p. 266°C. Anal. Calcd for $C_{34}H_{26}ZnN_2O_6\cdot 0.5CH_2Cl_2$: C, 62.2; H, 4.1; N, 4.2. Found: C, 62.2%; H, 4.3%; *N*, 4.4%. IR (cm^{-1}, KBr): 1612 (s, νC=N), 440–473 (M–N), 532–560 (M–O). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 317(30560), 435(15220). $\Lambda_M = 12.4\ \Omega^{-1}\,cm^2\,mol^{-1}$. ESI–MS (*m*/*z*): 561 ($[H_2L^1+H]^+$, 100%).

2.4.6. $[ZnL^2]$. Similarly, H_2L^2 (0.617 g, 1 mmol) and $Zn(NO_3)_2\cdot 6H_2O$ (0.297 g, 1 mmol) yielded yellow crystals. Yield: 0.5 g (73%); m.p. 242°C. Anal. Calcd for $C_{38}H_{34}ZnN_2O_6$: C, 67.1; H, 5.0; N, 4.1. Found: C, 67.3%; H, 5.2%; N, 4.2%. IR (cm^{-1}, KBr): 1610 (s, νC=N), 437–466 (M–N), 529–548 (M–O). UV-Vis [λ (nm), ε ((mol L^{-1})$^{-1}$ cm^{-1})]: 315(19710), 435(11750). $\Lambda_M = 14.2\ \Omega^{-1}\,cm^2\,mol^{-1}$. ESI–MS (*m*/*z*): 617 ($[H_2L^2+H]^+$, 100%).

3. Results and discussion

Two new potentially octadentate N_2O_6 Schiff-base ligands, H_2L^1 and H_2L^2, have been prepared from the reaction of o-Vaniline with 1,2-*bis*(2′-aminophenoxy)benzene or 1,2-*bis*(2′-aminophenoxy)-4-t-butylbenzene, respectively. The analytical and spectral data are consistent with the proposed formulation. The neutral Cu(II) and Zn(II) complexes of these ligands were also synthesized. All complexes were characterized by IR spectra, elemental analyses, magnetic susceptibility measurements, mass spectra, molar conductances (Λ_m), UV-Vis spectra and, in the case of $[ZnL^1]\cdot 0.5CH_2Cl_2$, with X-ray diffraction.

3.1. *IR spectra*

IR spectra of H_2L^1 and H_2L^2 (400–4000 cm^{-1}) show a strong absorption band at 1615 cm^{-1} and 1616 cm^{-1}, respectively, assigned to C=N stretch, indicating the formation of the Schiff-base linkages. The absence of C=O and N–H stretches in spectra of the ligands, related to aldehyde and diamine, respectively, indicate Schiff-base condensation. Reactions of copper(II) or zinc(II) salts with H_2L^1 and H_2L^2 yield $[CuL^1]\cdot 0.5CH_2Cl_2$, $[CuL^2]$, $[ZnL^1]\cdot 0.5CH_2Cl_2$, and $[ZnL^2]$. Deprotonation of all phenolic functions is confirmed by lack of O–H stretching bands at 3300–3400 cm^{-1} for all complexes [25, 26]. The strong ν(C=N) bands are shifted to lower frequencies compared with free imine bonds, indicating coordination of the ligands to copper(II) and zinc(II) *via* azomethine nitrogen. Bands at 1188 cm^{-1} for H_2L^1 and H_2L^2 ascribed to phenolic C–O stretches are shifted to lower frequencies due to O-metal coordination. Conclusive evidence of the bonding is also shown by the observation that new bands in IR spectra of the complexes appear at 525–590 and 410–485 cm^{-1} assigned to ν(M–O) and ν(M–N) [27–30].

3.2. *Magnetic measurements*

The magnetic moment values (at room temperature) of $[CuL^1]\cdot 0.5CH_2Cl_2$ and $[CuL^2]$ are 1.63 and 1.68 BM, respectively, in agreement with the magnetic moment for a single unpaired electron [31]. Due to a weak intermolecular antiferromagnetic exchange interaction between the copper centers in the crystal structure, these values are slightly less than the spin-only values [20, 32]. Zn(II) complexes are diamagnetic as expected.

3.3. *NMR spectra*

^1H- and ^{13}C-NMR spectroscopies have proved useful in establishing the nature and structure of many Schiff bases as well as their complexes in solutions. The ^1H- and ^{13}C-NMR spectra of the Schiff bases were recorded in chloroform ($CDCl_3$) using tetramethylsilane (TMS) as an internal standard; ^1H-NMR spectra of $[ZnL^1]\cdot 0.5CH_2Cl_2$ and $[ZnL^2]$ and ^{13}C-NMR spectrum of $[ZnL^1]\cdot 0.5CH_2Cl_2$ were recorded in DMSO-d_6. ^1H- and ^{13}C-NMR spectra of H_2L^1 and H_2L^2 and their diamagnetic Zn(II) complexes are listed in table S1. The NMR numbering of the atoms is shown in figure 1. ^1H-NMR spectrum of H_2L^1 shows only single –CH=N– resonance

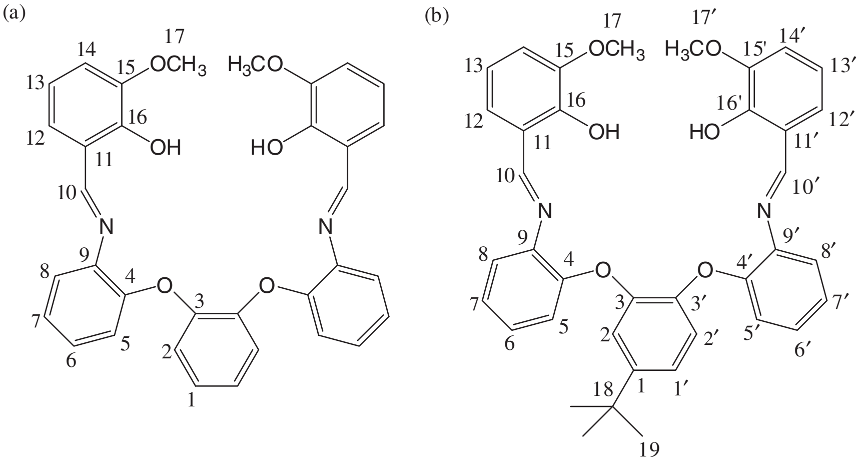

Figure 1. Structure of (a) H_2L^1 and (b) H_2L^2, along with NMR numbering.

at *ca* 8.35 ppm, demonstrating equivalence of the two imine environments. The ^{13}C-NMR spectrum shows that the imine carbon (162.8 ppm) are chemically equivalent. In the region corresponding to aromatic ring carbons (114.672–151.761 ppm), 15 peaks are observed as expected. The ^{1}H-NMR spectrum of H_2L^2 shows two singlet –CH=N– resonances at *ca* 8.30 and 8.35 ppm, supporting the non-equivalence of the two imine environments. ^{13}C-NMR spectrum shows that in the region corresponding to signals of aromatic rings (114.479–151.827 ppm) 22 peaks instead of 30 expected peaks are observed, due to similarity of some carbons and low resolution of the instrument. The spectra of the complexes are examined in comparison with those of the parent Schiff base. Phenolic-OH signals of H_2L^1 and H_2L^2 at 13.692 and 13.794 ppm disappear in spectra of their Zn(II) complexes, indicating that OH protons are removed completely upon coordination. Also, an upfield shift of 0.1 ppm for imine proton in $[ZnL^1]\cdot 0.5CH_2Cl_2$ and 0.2 and 0.3 ppm for two imine protons of $[ZnL^2]$ was observed. All the spectral changes supported the formation of the complex between Zn(II) and these ligands. Representative spectra of $[ZnL^1]\cdot 0.5CH_2Cl_2$ and $[ZnL^2]$ are presented in figure S1.

3.4. *Electronic absorption spectroscopy*

Electronic spectra of the ligands and complexes were recorded in $CHCl_3$. Bands below 345 nm are attributable to intramolecular $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Electronic spectra of the Cu(II) complexes show an absorption at 651–690 nm attributed to the $^2E_g \rightarrow {}^2T_g$ transition, characteristic for square-planar geometry [33, 34]. The band assigned to d–d transitions provides a rough estimate of the ligand field strength, since one electronic transition in the band envelope is $d_{x^2-y^2} - d_{xy}$ and the energy associated with this transition is 10Dq-C [28, 33, 34]. Spectra of the Zn(II) and Cu(II) complexes show an intense band at *ca* 415–435 nm, which can be assigned to a charge transfer transition [35–38].

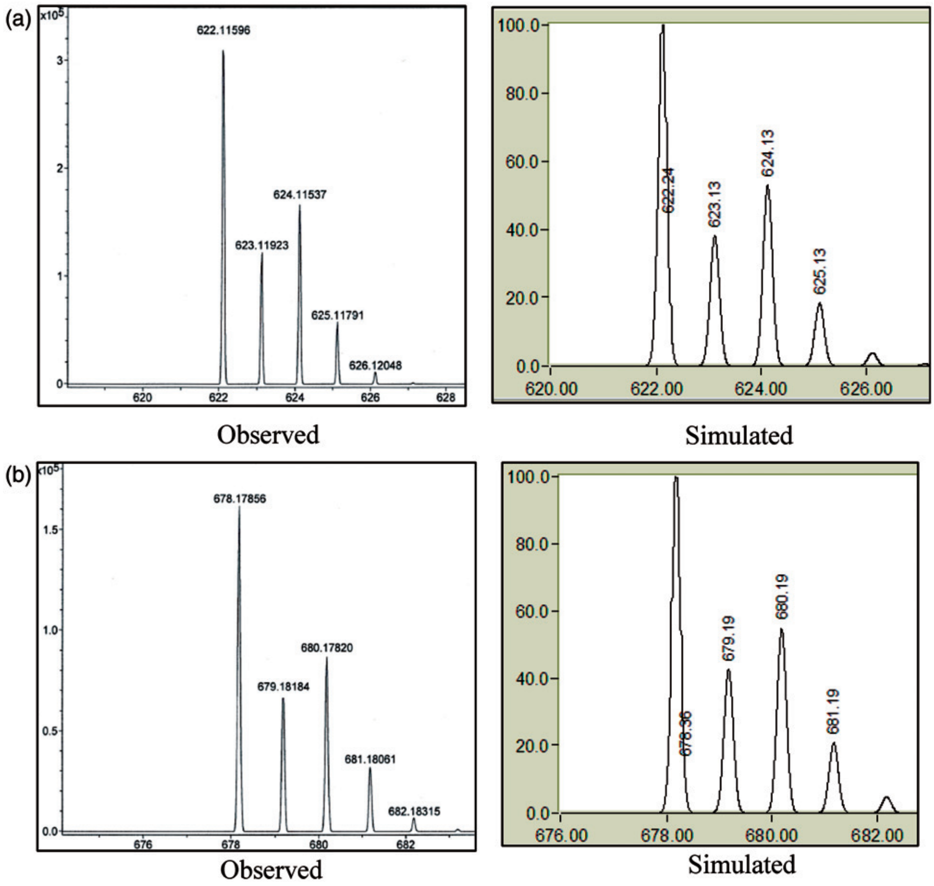

Figure 2. The observed and simulated isotopic patterns of ESI–MS spectra of (a) [CuL^1] and (b) [CuL^2].

3.5. *Molar conductivity*

The molar conductivities (Λ_m) of the Cu(II) and Zn(II) complexes in CH_2Cl_2 at $10^{-3}\,mol\,L^{-1}$ were 9–14.2 $\Omega^{-1}\,cm^2\,mol^{-1}$, indicating non-electrolytes [39, 40]. The molar conductance values of these complexes indicate that H_2L^1 and H_2L^2 are coordinated to copper(II) and zinc(II) as doubly negatively charged anions. Therefore, two phenolic OH have been deprotonated and bonded to the metals [41].

3.6. *ESI–MS spectra*

ESI–MS spectra of ([CuL^1] · 0.5CH_2Cl_2, [CuL^2], [ZnL^1] · 0.5CH_2Cl_2, and [ZnL^2]) confirm formation of the complexes. In the ESI–MS spectra of the Cu complexes, the peaks at m/z 622.12 and 678.18 correspond to $[CuL^1 + H]^+$ and $[CuL^2 + H]^+$ species, respectively. The spectra of latter complexes are shown in figure 2. The observed isotopic patterns of the ESI–MS spectra of these complexes are completely consistent with simulated patterns. The ESI–MS spectra of the Zn complexes showed the parent ion peak at *m*/*z* 561.20 and 617.26, corresponding to $[H_2L^1 + H]^+$ and $[H_2L^2 + H]^+$ species, respectively, which compares well with the calculated formula weight of metal free ligands. These results seem to be quite common, since ESI–MS is very rich in energy and may push the equilibrium to the uncomplexed side [42].

3.7. *X-ray structure*

Slow diffusion of *n*-hexane into dichloromethane solution of $[ZnL^1] \cdot 0.5CH_2Cl_2$ resulted in single crystals suitable for X-ray structure determination. An ORTEP of the Zn(II) complex is shown in figure 3. The complex is five coordinate with four normal bonds and one weak interaction, resulting in a ZnN_2O_3 core with highly distorted trigonal bipyramidal geometry. The base of the trigonal bipyramid is occupied with two nitrogens of 1,2-*bis*(2′-aminophenoxy)benzene and one oxygen of phenolate. Two oxygens, one of phenolate and one of the mentioned amine occupy the apical sites. The four normal bonds are from phenolate oxygen and imine nitrogen of ligand toward Zn(II). The weak interaction was from one oxygen of the 1,2-*bis*(2′-aminophenoxy)benzene.

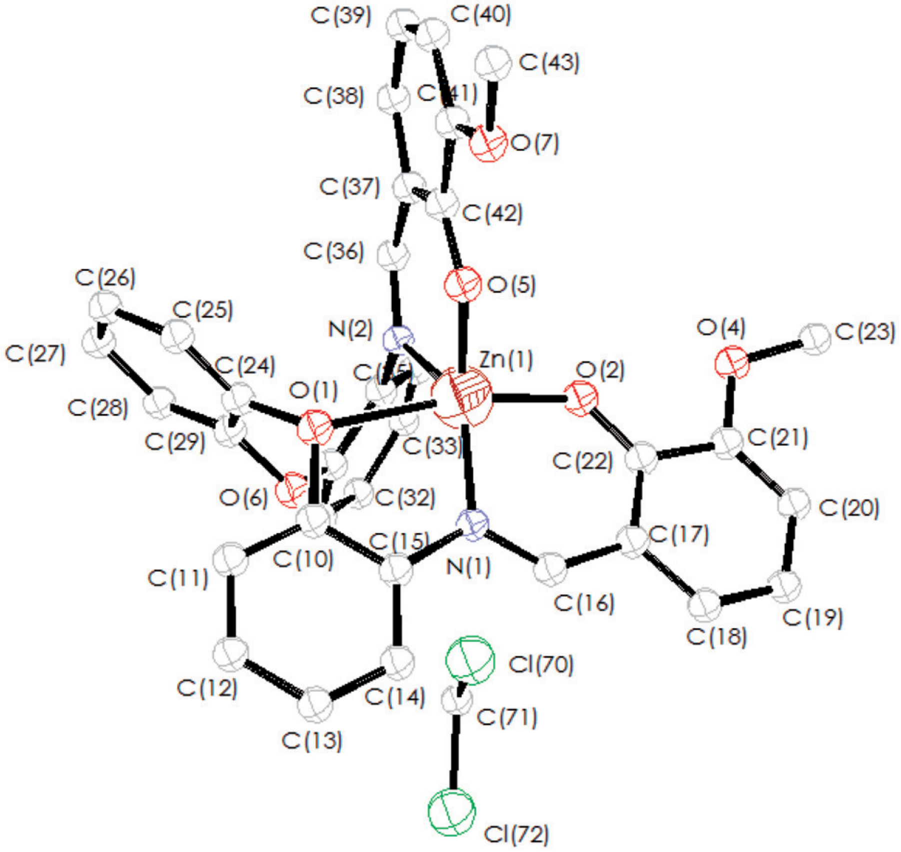

Figure 3. Molecular structure of $[ZnL^1] \cdot 0.5CH_2Cl_2$ showing 50% probability thermal ellipsoids using ORTEP.

Selected bond lengths and angles are given in table 2. It has been noted from O– and N–bound Zn(II) complexes in the literature that the common coordination number is four, and when this number increases, the additional coordinations are generally weak with Zn(II) $\cdots$ O distances ranging from 2.34 to 2.91 Å and the corresponding geometries are highly distorted [39–43]. Such observations include the Zn(II) $\cdots$ $O_{phosphato}$ distance of 2.71 Å observed in a Zn(II)–ATP complex [43] (distorted octahedral), Zn(II) $\cdots$ $O_{carboxylato}$ distance of 2.91 and 2.79 Å observed in two Zn(II)–histidino complexes [44, 45] (distorted octahedral), Zn(II) $\cdots$ $O_{perchlorato}$ distance of 2.528 and 2.818 Å observed with the two crystallographically independent molecules present in the lattice of a Zn(II)–triazacyclododecane complex [46] (distorted trigonal bipyramid), Zn(II) $\cdots$ $O_{crown\ ether}$ distances of 2.34, 2.56 and 2.60 Å observed for a Zn–crown ether complex [47] (highly distorted trigonal bipyramid). In this case, Zn(II) exhibits a distorted trigonal bipyramidal geometry with a *trans* angle ($O_{phenoxo}$–Zn–$O_{phenolic}$) of 168.87(10)° (156.8(3)° and 146.1(6)° [47] and 150.7(1)° [48]). The average angle observed in the basal plane of 118.05° (65.1° and 68.1° [47] and 112.0(1)° [48]) and the average angle between apical and basal atoms of 90.69° are all within the reported range. However, if only the four normal bonds are considered, the Zn^{2+} complex revealed a highly distorted tetrahedral geometry, wherein five of the angles (95.31°, 94.30°, 96.09°, 122.59° and 137.26°) are quite off from the expected ones.

Sixty-three structures with $[ZnN_2O_3]$ core have been described. In 61 cases, the Zn(II) coordination is a trigonal bipyramid ($\tau = 0.51$–1.0) and only in two cases does N occupy the axial position [49, 50].

3.8. *Electrochemical studies*

Electrochemical behavior of H_2L^2 and its Cu(II) complex, $[CuL^2]$, were studied by cyclic voltammetry. Figure S2 shows the cyclic voltammogram obtained for 1 mmol L^{-1} H_2L^2 in acetonitrile, containing 0.2 mol L^{-1} tetra-n-butylammonium perchlorate (Bu_4NClO_4) as supporting electrolyte. At this condition, cyclic voltammogram of

Table 2. Selected bond lengths (Å) and angles (°) for $[ZnL^1] \cdot 0.5CH_2Cl_2$.

Zn(1)–O(5)	1.938(3)
Zn(1)–O(2)	1.967(2)
Zn(1)–N(1)	2.013(3)
Zn(1)–N(2)	2.045(3)
Zn(1)–O(1)	2.421(2)
O(5)–Zn(1)–O(2)	103.47(11)
O(5)–Zn(1)–N(1)	122.59(10)
O(2)–Zn(1)–N(1)	95.31(11)
O(5)–Zn(1)–N(2)	94.30(11)
O(2)–Zn(1)–N(2)	96.09(11)
N(1)–Zn(1)–N(2)	137.26(12)
O(5)–Zn(1)–O(1)	85.18(9)
O(2)–Zn(1)–O(1)	168.87(10)
N(1)–Zn(1)–O(1)	73.95(10)
N(2)–Zn(1)–O(1)	90.15(10)

$$\mathrm{Cu^{II}L} + 2\mathrm{e} \xrightarrow[-1.08\ \mathrm{V}\ vs.\ \mathrm{Ag\ wire}]{\text{Peak } \mathrm{C_0}} \mathrm{Cu^0} + \mathrm{L} \qquad (1)$$

$$\mathrm{Cu^0} - 2\mathrm{e} \xrightarrow[0.04\ \mathrm{V}\ vs.\ \mathrm{Ag\ wire}]{\text{Peak } \mathrm{A_1}} \mathrm{Cu^{II}} \qquad (2)$$

$$\mathrm{Cu^{II}} + 2\mathrm{e} \xrightarrow[-0.43\ \mathrm{V}\ vs.\ \mathrm{Ag\ wire}]{\text{Peak } \mathrm{C_1}} \mathrm{Cu^0} + \mathrm{L} \qquad (3)$$

Scheme 1. Electrochemical reduction of [CuL^2].

H_2L^2 is the same as a voltammogram of background (figure S2, inset) showing no clear oxidation or reduction peaks.

The electrochemical behavior of [CuL^2] was studied by cyclic voltammetry. Figure S3 shows the first cyclic voltammogram obtained for a 1 mmol L^{-1} solution. The voltammogram exhibits one cathodic peak C_0 (-1.08 V *vs.* Ag wire) which corresponds to reduction of Cu(II) in [CuL^2] to Cu(0) (scheme 1, equation (1)). On the reverse scan, one anodic peak (A_1) was observed at 0.04 V *versus* Ag wire which corresponds to oxidation of Cu(0) to Cu(II) (scheme 1, equation (2)).

In the second cycle, a new cathodic peak (C_1) appears with an E_p value of -0.43 V *versus* Ag wire and the current increases with increasing number of scans. This new peak is related to reduction of Cu^{II} to Cu^0 (scheme 1, equation (3)). This peak was confirmed with the addition of $Cu(ClO_4)_2$ to the previous solution. Under this condition, the current of peak C_1 increases.

The following equation is used to determine the formation constant of [CuL^2] [51]:

$$\Delta E_{pc} = (RT/2F) \ln K,$$

where K is the formation constant for:

$$\mathrm{Cu^{II}} + \mathrm{L} \rightleftharpoons \mathrm{CuL}.$$

ΔE_{pc} is $[(E_{pc})^M - (E_{pc})^C]$, where $(E_{pc})^M$ is the cathodic peak potential of Cu^{II} ($E_{pc1} = -0.43$ V) and $(E_{pc})^C$ is the cathodic peak potential of [CuL^2] ($E_{pc0} = -1.08$ V); R, T, and F have their usual meanings. The calculated logarithmic value of formation constant, $\log K$, is 21.9 (at 25°C).

4. Conclusion

The condensation of o-Vaniline with 1,2-*bis*(2′-aminophenoxy)benzene or 1,2-*bis*(2′-aminophenoxy)-4-t-butylbenzene afforded H_2L^1 and H_2L^2. Reactions of the Schiff bases with copper(II) and zinc(II) in 1 : 1 molar ratio (ligand : metal) were studied. On comparison to similar structures and on the basis of spectroscopic data, the Schiff-base ligands in Cu(II) complexes are dianionic tetradentate through two azomethine nitrogens and the two oxygens of phenolic groups; square-planar structures were assigned to these complexes. The crystal structure of [ZnL^1]$\cdot 0.5CH_2Cl_2$ shows that Zn(II) is coordinated by two azomethine nitrogens and two phenolic oxygens of the octadentate ligand to form a distorted trigonal bipyramidal geometry. In this complex, one oxygen of the initial amine exhibits a weak interaction with Zn(II) giving a ZnN_2O_3 core. All spectroscopic data show that ZnL^2 has similar structure with ZnL^1. From the study of the Schiff bases derived from salicylaldehyde (salens) and also its derivatives as polydentate ligands, we conclude that, in the mononuclear complexes related to these ligands, the metal ions prefer the N_2O_2, N_2O_3, and/or N_2O_4 sites depending on the flexibility of the ligands and the nature of metal. In more rigid ligands, due to a stronger coordination of azomethine nitrogens and phenolate oxygens, N_2O_2 is preferred and other donor atoms are usually too far from the metal to form strong coordination bonds. In more flexible ligands, both N_2O_3 and N_2O_4 sites can be observed.

Supplementary material

CCDC 744569 contains the supplementary crystallographic data for [ZnL^1]. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

Acknowledgments

We are grateful to the Faculty of chemistry of Bu-Ali Sina University, National Foundation of elites (BMN), and Ministry of Science, Research & Technology of Iran for the financial support. The authors thank Mr. Reza Farhadi for the help in the CV measurements.

References

[1] Q. Shi, L. Xu, J. Ji, Y. Li, R. Wang, Z. Zhou, R. Cao, M. Hong, A.S.C. Chan. *Inorg. Chem. Commun.*, **7**, 1254 (2004).
[2] B. Witkop, L.K. Ramachandran. *Metabolism*, **13**, 1016 (1964).
[3] R.A. Morton, G.A.J. Pitt. *Biochem. J.*, **59**, 128 (1955).
[4] E. Grazi, R.T. Rowley, T. Cheng, O. Tchola, B.L. Horecker. *Biochem. Biophys. Res. Commun.*, **9**, 38 (1962).
[5] I. Fridovitch, F.H. Westheimer. *J. Am. Chem. Soc.*, **84**, 3208 (1962).
[6] G.G. Hammes, P. Fasella. *J. Am. Chem. Soc.*, **84**, 4644 (1962).
[7] B.S. Tovrog, D.J. Kitko, R.S. Drago. *J. Am. Chem. Soc.*, **98**, 5144 (1976).
[8] Z.-L. You, H.-L. Zhu, W.-S. Liu. *Z. Anorg. Allg. Chem.*, **630**, 1617 (2004).
[9] Z.-L. You, H.-L. Zhu. *Z. Anorg. Allg. Chem.*, **630**, 2754 (2004).
[10] N. Raman, A. Sakthivel, R. Jeyamurugan. *J. Coord. Chem.*, **62**, 3969 (2009).
[11] Z.-L. You, L.-L. Ni, P. Hou, J.-C. Zhang, C. Wang. *J. Coord. Chem.*, **63**, 515 (2010).
[12] R. Pagadala, P. Ali, J.S. Meshram. *J. Coord. Chem.*, **62**, 4009 (2009).
[13] M. Rajasekar, S. Sreedaran, R. Prabu, V. Narayanan, R. Jegadeesh, N. Raaman, A.K. Rahiman. *J. Coord. Chem.*, **63**, 136 (2010).
[14] A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley. *Inorg. Chim. Acta*, **358**, 1785 (2005).
[15] E.J. Cambel, S.T. Nguyen. *Tetrahedron Lett.*, **42**, 1221 (2001).
[16] A.J. Stemmler, C.T. Burrows. *J. Am. Chem. Soc.*, **121**, 6956 (1999).
[17] R. Klement, F. Stock, H. Elias, H. Paulus, M. Valko, M. Mazur. *Polyhedron*, **18**, 3617 (1999).

[18] C.R. Choudhury, A. Datta, V. Gramlich, G.M.G. Hossain, K.M.A. Malik, S. Mitra. *Inorg. Chem. Commun.*, **6**, 790 (2003).
[19] A. Erxleben, J. Hermann. *J. Chem. Soc., Dalton Trans.*, **4**, 569 (2000).
[20] H. Keypour, M. Shayesteh, A. Sharifi-Rad, S. Salehzadeh, H. Khavasi, L. Valencia. *J. Organomet. Chem.*, **693**, 3179 (2008).
[21] C.-P. Yang, C.-H. Wei. *Polymer*, **42**, 1837 (2001).
[22] D.-J. Liaw, B.-Y. Liaw. *Polymer*, **39**, 1597 (1998).
[23] G.C. Eastmond, J. Paprotny. *Polymer*, **45**, 1073 (2004).
[24] H. Tsuzuki, T. Tsukinoki. *Green Chem.*, **3**, 37 (2001).
[25] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Edn, Wiley Interscience, New York, NY (1977).
[26] S.A. Ali, A.A. Soiman, M.M. Aboaly, R.M. Ramandan. *J. Coord. Chem.*, **55**, 1161 (2002).
[27] J.R. Ferraro. *Low Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, NY (1971).
[28] S. Ilhan, H. Temel. *J. Mol. Struct.*, **891**, 157 (2008).
[29] E. Bermejo, A. Castineiras, L.M. Fostiak, I.G. Santos, J.K. Swearingen, D.X. West. *Polyhedron*, **23**, 2303 (2004).
[30] R.P. John. PhD thesis, Cochin University of Science and Technology (2001).
[31] J. Hathaway. In *Comprehensive Coordination Chemistry*, G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds), chap. 53, p. 533, Pergamon, New York, NY (1987).
[32] V.T. Getova, R.P. Bontchev, D.R. Mehandjiev, P.R. Bontchev. *Polyhedron*, **25**, 2254 (2006).
[33] S. Ilhan, H. Temel, A. Kilic, E. Tas. *Transition Met. Chem.*, **32**, 1012 (2007).
[34] H. Temel, S. Ilhan, A. Kilic, E. Tas. *J. Coord. Chem.*, **61**, 1443 (2008).
[35] V. Suni, M.R. Prathapachandra Kurup, M. Nethaji. *Polyhedron*, **26**, 5203 (2007).
[36] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, New York (1984).
[37] A.H. Maki. *J. Chem. Phys.*, **28**, 651 (1958).
[38] A.M. Guidote Jr, K.-I. Ando, K. Terada, Y. Kurusu, H. Nagao, Y. Masuyama. *Inorg. Chim. Acta*, **324**, 203 (2001).
[39] W. Geary. *J. Chem. Rev.*, **7**, 81 (1971).
[40] E. Tas, M. Aslanoglu, A. Kilic, O. Kaplan, H. Temel. *J. Chem. Res.*, **(S) 4**, 242 (2006).
[41] M.A. Ali, A.H. Mirza, R.J. Butcher. *Polyhedron*, **20**, 1037 (2001).
[42] W. Amrein (2009) (personal communication).
[43] P. Orioli, R. Cini, D. Donati, S. Mangani. *J. Am. Chem. Soc.*, **103**, 4446 (1981).
[44] M.M. Harding, S.J. Cole. *J. Acta Crystallogr.*, **16**, 643 (1963).
[45] R.H. Kretsinger, F.A. Cotton, R.F. Bryan. *Acta Crystallogr.*, **16**, 651 (1963).
[46] S.C. Rawle, A.J. Clarke, P. Moore, N.W. Alcock. *J. Chem. Soc., Dalton Trans.*, **18**, 2755 (1992).
[47] A.B. Charette, J.-F. Marcoux, F. Bélanger-Gariépy. *J. Am. Chem. Soc.*, **118**, 6792 (1996).
[48] A.K. Sah, C.P. Rao, E.K. Wegelius, E. Kolehmainen, K. Rissanen. *Carbohydr. Res.*, **336**, 249 (2001).
[49] J. Skorsepa, K. Gyoryova, M. Melnik, K. Somolander, M. Ahlgren. *Acta Crystallogr., Sect. C*, **51**, 1069 (1995).
[50] R.B. Wilson, P. de Meester, D.J. Hodjson. *Inorg. Chem.*, **16**, 1498 (1977).
[51] K. Izutsu. *Electrochemistry in Nonaqueous Solutions*, p. 122, Wiley-VCH, Weinheim (2002).