Characterisation of novel macroacyclic hexadentate (N_4O_2 and N_2O_4) Schiff base ligands and their zinc(II), copper(II) and cobalt(II) complexes, with ligands derived from reduction

Hassan Keypour[a]*, Hadi Amiri Rudbari[a], Reza Azadbakht[b] and Ebrahim Abouzari Lotf[c]

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran*

[b]*Department of Chemistry, Payame Noor University, Hamedan, Iran*

[c]*Department of Chemistry, Tarbiat Moalem University, Tehran, Iran*

The macrocyclic, hexadentate (N_4O_2 and N_2O_4) Schiff base ligands, 1,2-bis(2'-nitrophenoxy)benzene, 1,2-bis (2'-nitrophenoxy)-4-*t*-butylbenzene), 1,2-bis(2'-aminophenoxy)benzene and 1,2-bis(2'-aminophenoxy)-4-*t*-butyl-benzene have been synthesised, together with macroacyclic hexadentate ligands formed from their reduction. Zinc(II), copper(II) and cobalt(II) complexes of the Schiff base ligands have also been prepared and all compounds have been characterised by spectroscopy and elemental analysis.

Keywords: *ortho*-aminophenyl diamines, Schiff-base ligands, complexes, reduction

The chemistry of metal complexes with chelate ligands containing nitrogen or oxygen donors has been studied extensively in order to mimic the redox function of various metalloenzymes in living systems and the formation and reactivity of dioxygen in synthetic, industrial and biological processes. In enzymes, metal ions have several functions: (i) redox as in superoxide dismutase-like activity;[1-6] and (ii) structural and catalytic.[7-11] The complexation sites of these proteins are often N or O donors. Therefore, for many years there has been great interest in the study of metal complexes of bulky polydentate ligands that are able to mimic the active sites of metalloproteins. We have prepared and characterised four novel macroacyclic Schiff-base ligands derived from diamines with 2-pyridinecarboxaldehyde and salicylaldehyde. Compounds L_5, L_6, H_2L_7 and H_2L_8 were prepared by the reduction of Schiff base ligands. During the course of this work, we have prepared and characterised Co^{2+}, Cu^{2+} and Zn^{2+} complexes of L_1, L_2 and H_2L_3 ligands, and Co^{2+} and Cu^{2+} complexes of the H_2L_4 ligand. The diamines 1,2-bis (2'-aminophenoxy)benzene (**3**) and 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene (**4**) were synthesised by the reaction of diols (catechol or 4-*tert*-butylcatechol) with 1-fluoro-2-nitrobenzene in the presence of potassium carbonate (K_2CO_3) under a dinitrogen atmosphere, and then reduced by zinc dust and ammonium chloride.

Results and discussion

Bis(nitrophenoxy)benzenes

1,2-Bis(2'-nitrophenoxy)benzene (**1**) and 1,2-bis(2'-nitro-phenoxy)-4-*t*-butylbenzene (**2**) were prepared by an S_NAr reaction between 1-fluoro-2-nitrofluorobenzene and simple aromatic diols (catechol and 4-*tert*-butylcatechol). The IR spectrum of (**1**) and (**2**) reveals absorption bands at *ca* 1348 and 1524 cm^{-1} due to symmetric and asymmetric stretching of the -NO_2 group.[12,13] In the ^1H NMR spectrum, the absorption signals of aromatic protons of (**1**) and (**2**) appear in the region of 6.9–8 and ppm 6.8–7.8, respectively, and the butyl group of (**2**) appears at 1.3 ppm. 20 main peaks are expected in the ^{13}C NMR spectrum of (**2**), but only 16 main signals appeared because of overlap of carbon resonances. The ^{13}C NMR of (**1**) showed the expected nine aromatic signals.

Bis(aminophenoxy)benzenes

Aromatic nitro compounds can be reduced in high yield to the corresponding diamines using zinc metal and NH_4Cl in H_2O/MeOH.[14] After reduction, the characteristic absorptions of nitro groups disappeared and the amino groups showed NH stretching bands at 3426, 3408, 3313 cm^{-1} and 3461, 3405, 3376, 3304 cm^{-1} for (**3**) and (**4**), respectively. In the ^1H NMR spectra, all the aromatic protons of (**3**) and (**4**) resonated in the 7–6.6 ppm and 7.2–6.6 ppm region, respectively. Hydrogens of the *t*-butyl group appeared at 1.3 ppm and the signal appearing at 3.7 ppm corresponds to the amine group. Comparing the ^{13}C NMR spectra of (**3**) and (**4**) with the spectra of the precursors (**1**) and (**2**), the ^{13}C absorptions of the central three benzene rings move downfield as a result of the change to the electron-donating amino groups from the electron-withdrawing nitro groups.[12,13]

Schiff base ligands

The Schiff base ligands (L_1, L_2, H_2L_3 and H_2L_4) were prepared by condensation of the diamines with 2-pyridinecarboxaldehyde and salicylaldehyde in a 1 : 2 ratio (Fig. 1). The reactions are almost quantitative and produce yellow solids that are soluble in common organic solvents. L_1, L_2 are unstable in air but H_2L_3 and H_2L_4 are stable in air. The chemical structures of the L_1, L_2, H_2L_3 and H_2L_4 ligands were confirmed by elemental analysis and IR, ^1H and ^{13}C NMR spectroscopies, with results in good agreement with the designed compounds. The formation of Schiff base ligands is evidenced by the presence of a strong IR band at ~1639 cm^{-1} for L_1, L_2 and a strong band at ~1618 for H_2L_3 and H_2L_4, due to ν(C=N), while no bands attributable to ν(C=O) or to ν(NH_2) have been detected. For L_1, L_2 ligands the bands at 1600 and 1488 cm^{-1} of the pyridine ring vibrations are also present.[5] The ^1H NMR spectra are consistent with the IR spectroscopy. The ^1H NMR spectra in $CDCl_3$ show a peak at ~9.3 ppm for L_1, L_2 and at ~8.5 ppm for H_2L_3 and H_2L_4 corresponding to the imine protons.[16,17]

Complexes

The prepared complexes are stable in air. The elemental analysis, yield, IR and FAB mass data of the complexes are compared in Tables 1, 2 and 3. The presence of ν(C=N) bands in the correct positions for Schiff base linkages of this kind, and the absence of C=O and NH_2 indicate that the required macroacyclic Schiff base complexes have indeed formed.[18] For complexes containing 2-pyridinecarboxaldehyde, all the spectra exhibit medium to strong bands at ~1597 and 1485 cm^{-1} as expected for the two highest energy pyridine-ring vibrations. The shift of the imine and pyridine bands to lower wavenumbers by complexation suggests coordination via the imine and pyridine nitrogen atoms.[19,20] For the

* Correspondent. E-mail: haskey1@yahoo.com

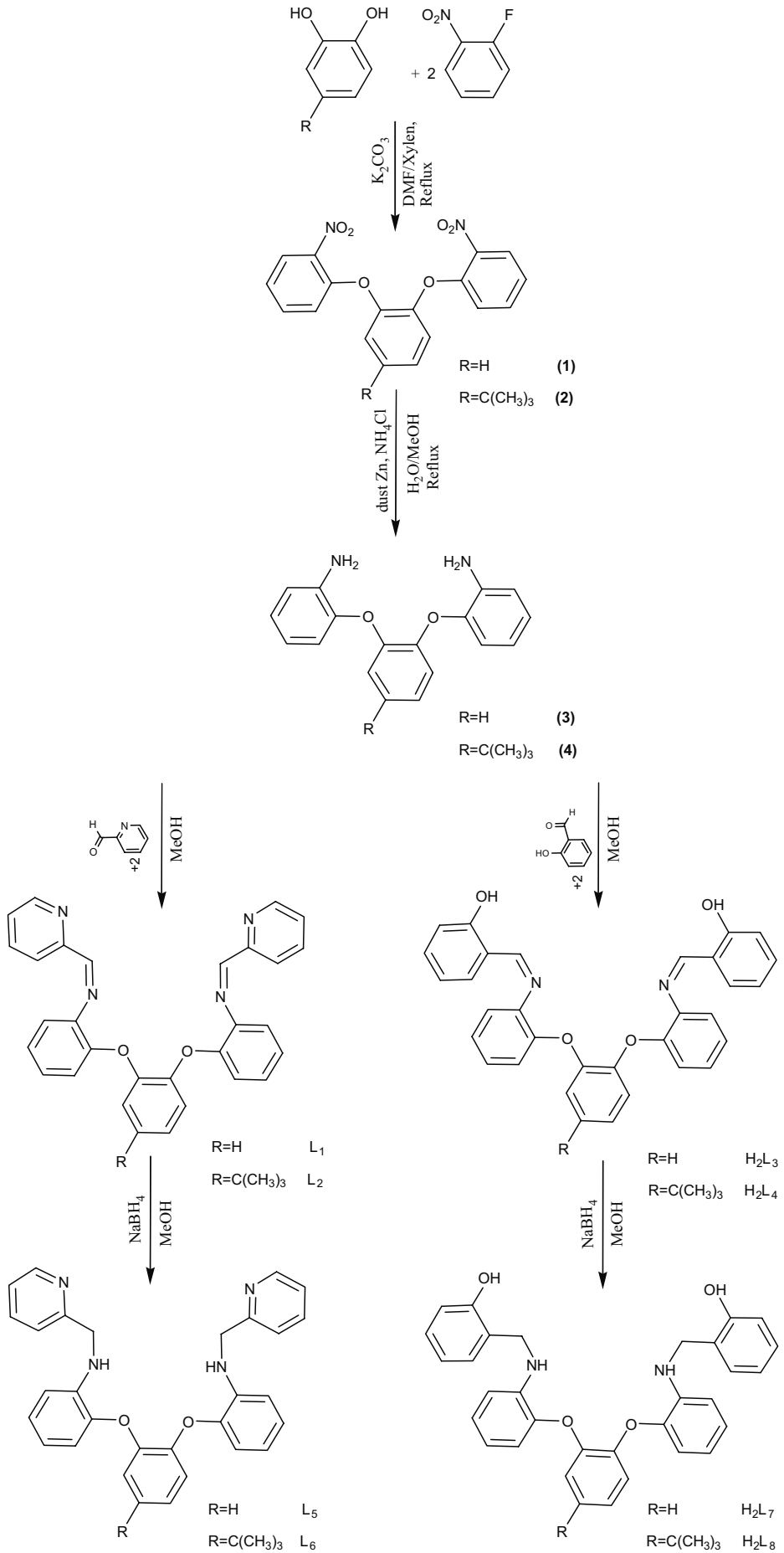

Fig. 1 Synthetic route used for the preparation of (**1**, **2**, **3** and **4**) compounds, and ligands.

Table 1 Elemental analysis (%) and yield of the complexes

Complex	Formula	C	H	N	Yield/%
$[Co(L_1)](NO_3)_2.H_2O$	$C_{30}H_{24}CoN_6O_9$	53.7(53.7)	3.5(3.6)	12.5(12.5)	82
$[Cu(L_1)](ClO_4)_2.H_2O$	$C_{30}H_{24}Cl_2CuN_4O_{11}$	48.1(48.0)	3.3(3.2)	7.4(7.5)	47
$[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$	$C_{34}H_{34}N_6O_{10}Zn$	54.4(54.3)	4.5(4.6)	11.1(11.2)	78
$[Co(L_2)](NO_3)_2.1.5H_2O$	$C_{34}H_{33}CoN_6O_{9.5}$	55.3(55.4)	4.4(4.5)	11.3(11.4)	54
$[Cu(L_2)](ClO_4)_2.2H_2O$	$C_{34}H_{34}Cl_2CuN_4O_{12}$	49.4(49.5)	4.2(4.15)	6.9(6.8)	38
$[Zn(L_2)](NO_3)_2.2CH_3OH$	$C_{36}H_{38}N_6O_{10}Zn$	55.4(55.4)	5.0(4.9)	10.7(10.8)	48
$[CoL_3].0.5CHCl_3$	$C_{65}H_{45}N_4Cl_3O_8Co_2$	63.2(63.25)	3.7(3.7)	4.6(4.5)	51
$[CuL_3].CH_3OH$	$C_{33}H_{26}N_2O_5Cu$	66.6(66.7)	4.4(4.4)	4.8(4.7)	37
$[ZnL_3]$	$C_{32}H_{22}N_2O_4Zn$	68.1(68.2)	3.9(3.9)	5.0(5.0)	43
$[CoL_4].CHCl_3$	$C_{37}H_{31}N_2Cl_3O_4Co$	60.7(60.6)	4.2(4.3)	3.8(3.8)	38
$[CuL_4].2CH_3OH$	$C_{38}H_{38}N_2O_6Cu$	67.0(66.9)	5.6(5.6)	4.1(4.1)	25

perchlorate complexes, absorptions attributable to ionic perchlorate were found at approximately 1100 and 624 cm^{-1}. The lack of splitting of these bands suggests that the perchlorate anions are not coordinated.[21] The band at ~1384 cm^{-1} for the nitrate complexes is due to ionic NO_3^-.[22,23] The shift of the imine band to lower and higher wavenumbers by complexation suggests coordination via the nitrogen atoms for complexes containing salicylaldehyde.[24] The diamagnetic zinc complexes were studied by ^1H, ^{13}C, COSY, HMQC and DEPT NMR experiments. The ^1H and ^{13}C NMR were run immediately after solution in DMSO-d_6 and gave the expected simple spectrum, indicating the integrity of the complexes. The spectra obtained after 12, 24 and 120 h were similar to the initial spectra indicating that the complexes are stable in solution. The ^1H NMR spectra of complexes, containing 2-pyridinecarboxaldehyde, show a peak at ~ 9.20 ppm due to the formation of the iminic bond. The ^{13}C NMR spectra show 14 and 19 signals for $[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$ and $[Zn(L_2)](NO_3)_2.2CH_3OH$ complexes respectively. The peak at ~163.3 ppm, assignable to the imine carbon atoms, confirms the presence of the Schiff base in the complexes. ^1H NMR spectrum of $[ZnL_3]$ shows a peak at 8.47 ppm corresponding to the imine protons. No signal corresponded to hydroxyl protons at ~13.1 ppm, suggested that the hydroxyl groups are fully deprotonated and the oxygen is most likely coordinated to the metal ions. The ^{13}C NMR spectrum of the Zn^{2+} complex with H_2L_3 is very simple and exhibited 16 signals, as expected; the peak at 172.8 ppm corresponds to the imine carbon for such a zinc complex.[25] The FAB mass spectral results serve an important role in confirming the [1 + 1] nature of the complexes (Tables 2 and 3). The FAB mass spectra for $[Co(L_1)](NO_3)_2.H_2O$, $[Cu(L_1)](ClO_4)_2.H_2O$, $[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$, $[Co(L_2)](NO_3)_2.1.5H_2O$, $[Cu(L_2)](ClO_4)_2.2H_2O$ and $[Zn(L_2)](NO_3)_2.2CH_3OH$ complexes indicate the presence of the macroacyclic ligand and metal ion and, as is common with complexes of this type, a characteristic fragmentation pattern resulting from stepwise loss of counterions from the neutral parent ion is observed.[26-32] For these complexes, the highest-mass and more intense peak in each case corresponds to the general formulation $[MLX]^+$ and the loss of a second counterion occurs to generate $[ML]^+$. In the $[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$ complex, the FAB mass spectra gave a highest-mass and more intense peak at *m/z* 598 assignable to $[Zn(L_1)NO_3]^+$. The spectrum also shows a peak due to $[ZnL_1]^+$ and $[L_1 + H]^+$ at 536 and 471, respectively. For $[CoL_3].0.5CHCl_3$, $[CuL_3].CH_3OH$, $[ZnL_3]$, $[CoL_4].CHCl_3$ and $[CuL_4].2CH_3OH$ complexes the highest-mass and more intense peak in each case corresponds to the general formulation $[ML + H]^+$. Unfortunately, we could not prepare zinc complexes with H_2L_4.

Experimental

Materials and physical measurements

NMR spectra were recorded using Jeol FX-Q 90 MHZ, Bruker FT NMR 350 and 500 MHZ spectrometers. The IR spectra were recorded as KBr discs, using a Perkin Elmer FT-IR GX spectrophotometer (4000–4600 cm^{-1}). Positive ion FAB mass spectra were recorded on a Kratos-MS-50 spectrometer with 3-nitrobenzyl alcohol as the matrix solvent. Solvents were of reagent grade and were purified by the usual methods. Catechol, 4-*tert*-butylcatechol, 1-fluoro-2-nitrobenzene, 2-pyridinecarboxaldehyde, salicylaldehyde and metal salts were obtained from Merck Chem.Co. and used without further purification.

Ligand synthesis

Synthesis of 1,2-bis(2'-nitrophenoxy)benzene (**1**): Catechol (11 g, 0.1 mol) was dissolved in DMF (100 cm^3)/xylene (10 cm^3) before K_2CO_3 (42 g, 0.3 mol) and 1-fluoro-2-nitrobenzene (28.2 g, 0.2 mol) were added. The mixture, refluxed at 130–135 °C under a dinitrogen atmosphere for 24 h with stirring, was then allowed to cool and poured

Table 2 IR data (cm^{-1}) and FAB mass spectral of the complexes

Compound	ν(C=N)[a]	ν(C=N)[b]	ν(C=C)[c]	NO_3^-	ClO_4^-	Peak	Assignment
$[Co(L_1)](NO_3)_2.H_2O$	1628	1596	1486	1384		592	$[Co(L_1)(NO_3)]^+$
$[Cu(L_1)](ClO_4)_2.H_2O$	1631	1599	1487		1100, 623	634	$[Cu(L_1)(ClO_4)]^+$
$[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$	1634	1597	1485	1384		598	$[Zn(L_1)(NO_3)]^+$
$[Co(L_2)](NO_3)_2.1.5H_2O$	1635	1597	1485	1384		648	$[Co(L_2)(NO_3)]^+$
$[Cu(L_2)](ClO_4)_2.2H_2O$	1635	1597	1487		1100, 624	690	$[Cu(L_2)(ClO_4)]^+$
$[Zn(L_2)](NO_3)_2.2CH_3OH$	1637	1597	1491	1384		654	$[Zn(L_2)(NO_3)]^+$

[a]Schiff base. [b,c]Pyridine ring.

Table 3 IR data (cm^{-1}) and FAB mass spectral of the complexes

Compound	Sol. for crystallisation	ν(C=N)	ν(C=C)	ν(C-H)	Peak	Assignment
$[CoL_3].0.5CHCl_3$	$CHCl_3/CH_3OH$	1607	1581	–	559	$[CoL_3 + H]^+$
$[CuL_3].CH_3OH$	CH_3OH	1609	1581	–	563	$[CuL_3 + H]^+$
$[ZnL_3]$	CH_3CN	1612	1584	–	565	$[ZnL_3 + H]^+$
$[CoL_4].CHCl_3$	$CHCl_3/CH_3OH$	1611	1590	2963	615	$[CoL_4 + H]^+$
$[CuL_4].2CH_3OH$	CH_3OH	1609	1588	2965	619	$[CuL_4 + H]^+$

into H_2O (500 cm^3). The precipitate was isolated by filtration. After drying, the crude product was recrystallised from EtOH to give pure 1,2-bis(2'-nitrophenoxy)benzene. Yield: 31.3 g (89%). Anal. Calcd for $C_{18}H_{12}N_2O_6$: C, 61.4; H, 3.4; N, 7.95. Found: C, 61.3; H, 3.5; N, 7.8%. M.p. 110 °C. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 6.9–8 (m, Ar, 12H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 150.1, 145.8, 140.0, 134.2, 126.3, 125.5, 123.1, 121.9, 118.9. IR: 1524, 1348 (–NO_2), 1179 (C–O–C str).

Synthesis of 1,2-bis(2'-nitrophenoxy)-4-t-butylbenzene (**2**): 4-*tert*-Butylcatechol (16.6 g, 0.1 mol) was dissolved in DMF (100 cm^3)/xylene (10 cm^3) before K_2CO_3 (42 g, 0.3 mol) and 1-fluoro-2-nitrobenzene (28.2 g, 0.2 mol) were added. The mixture was refluxed at 130–135 °C under a dinitrogen atmosphere for 24 h with stirring, then the obtained mixture was poured into MeOH/H_2O (440 cm^3, vol. ratio 10:1) and left overnight at 0 °C to give a solid, which was collected, washed thoroughly with MeOH and H_2O, and dried under vacuum. After drying, the crude product was recrystallised from EtOH to give pure 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene. Yield: 37.21 g (91%). Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.7; H, 4.9; N, 6.9. Found: C, 64.7; H, 4.9; N, 6.9%. M.p. 52 °C. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 7.8–6.8 (m, Ar, 11H), 1.3 (s, $C(CH_3)_3$, 9H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$):150.3, 144.7, 143.2, 139.8, 139.5, 134.1, 125.4, 123.4, 122.8, 122.6, 121.7, 119.8, 118.5, 118.0, 34.5, 31.1. IR: 2964, 2868 (C–H)$_{aliph}$, 1524, 1348 (–NO_2), 1186 (C–O–C str).

Synthesis of 1,2-bis (2'-aminophenoxy)benzene (**3**): A mixture of 1,2-bis(2'-nitrophenoxy) benzene (3.52 g, 10 mmol), NH_4Cl (1.07 g, 20 mmol) and H_2O (10 cm^3) in MeOH (100 cm^3) was heated to boiling and zinc dust (2 g, 30 mmol) in 0.1 g portions at intervals of several minutes was added. The mixture was then refluxed for 5 h. The resulting solution was filtered, extracted with H_2O (300 cm^3) and dried. The precipitate was dissolved in CH_3CN, the solution was filtered and the solvent was the removed. Yield: 2.1 g (73%). Anal. Calcd for $C_{18}H_{16}N_2O_2.0.25H_2O$: C, 72.8; H, 5.6; N, 9.4 Found: C, 72.7; H, 5.5; N, 9.5%. M.p. 110 °C. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 7–6.6 (m, Ar, 12H), 3.7 (s, NH_2, 4H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 147.2, 144.3, 137.5, 124.2, 120.1, 118.8, 117.8, 116.8. IR: 3426, 3408, 3313 (NH str), 1199 (C–O–C str).

Synthesis of 1,2-bis(2'-aminophenoxy)-4-t-butylbenzene (**4**): A mixture of 1,2-bis(2'-nitrophenoxy)-4-*t*-butylbenzene (4.09 g, 10 mmol), NH_4Cl (1.07 g, 20 mmol) and H_2O (10 cm^3) in MeOH (100 cm^3) was heated to boiling and zinc dust (2 g, 30 mmol) was added in 0.1 g portions at intervals of several minutes. The mixture was reflux for 5 h. The solution was evaporated to dryness and the residue extracted with H_2O/$CHCl_3$. The organic layer was evaporated to yield an organic solid. Yield: 2.71 g (77%). Anal. Calcd for $C_{22}H_{24}N_2O_2.H_2O$: C, 72.1; H, 7.15; N, 7.6. Found: C, 72.2; H, 7.1; N, 7.7%. M.p. 89–91 °C. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 7.2–6.6(m, Ar, 11H), 3.7(br, NH_2, 4H), 1.3(s, $C(CH_3)_3$, 9H). ^{13}C NMR δ_C (90 MHz, CD_3CN): 148.5, 147.3, 146.4, 145.2, 144.6, 140.1, 139.7, 125.4, 124.9, 122.1, 119.7, 119.2, 118.5, 118.1, 116.9, 35.1, 31.7. IR: 3461, 3405, 3376, 3304 (–NH_2), 3041 (C–H)$_{ar}$, 2962, 2867 (C–H)$_{aliph}$.

Synthesis of L_1 and L_2: 2-Pyridinecarboxaldehyde (2 mmol) in dry MeOH (25 cm^3) was slowly added to a stirred solution of the appropriate diamine [1,2-bis(2'-aminophenoxy)benzene or 1,2-bis (2'-aminophenoxy)-4-*t*-butylbenzene; 1 mmol] in dry MeOH (25 cm^3). The yellow solution was stirred for 5 h. The solvent volume was reduced, cooled in an ice bath for 3 h and the yellow precipitate formed was filtered off and dried *in vacuo*.

L_1: Yield: 0.27 g (57%). Anal. Calcd for $C_{30}H_{22}N_4O_2$ C, 76.6; H, 4.7; N, 11.9. Found: C, 76.5; H, 4.8; N, 11.8%.^{1}H NMR δ_H (90 MHz, $CDCl_3$): 9.29 (2H, HC=N), 8.87 (2H, py), 8.16 (2H, py), 8.01–6.63 (ar (12H) and py (4H)). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 163.51 (C=N)$_{imi}$, 150.34–115.34 (ar and py rings). IR: 1637 (CH=N)$_{imi}$, 1601 (CH=N)$_{py}$, 1488 (C=C)$_{py}$.

L_2: Yield: 0.32 g (61%). Anal. Calcd for $C_{34}H_{30}N_4O_2.2CH_3OH$ C, 73.2; H, 6.5; N, 9.5. Found: C, 73.3; H, 6.4; N, 9.6%. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 9.31 (2H, HC=N), 8.87 (2H, py), 8.26 (2H, py), 8.20–6.51 (ar(11H) and py(4H)), 1.33 (9H, CCH_3). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 163.49 (C=N)$_{imi}$, 150.21–115.31 (ar and py rings), 34.56 (CCH_3), 31.08 (CCH_3). IR: 1639 (CH=N)$_{imi}$, 1600 (CH=N)$_{py}$, 1488 (C=C)$_{py}$.[32]

Synthesis of H_2L_3 and H_2L_4

The salicylaldehyde (0.244 g, 2 mmol) in absolute EtOH (25 cm^3) was added dropwis to hot solution in absolute EtOH (50 cm^3) of the appropriate diamine [1,2-bis (2'-aminophenoxy)benzene or 1,2-bis(2'-aminophenoxy)-4-t-butylbenzene; 1 mmol]. The solution was gently refluxed for 6 h. The colour of the solution changed to yellow. The solution was then concentrated in a rotary evaporator to a volume of ca 15 cm^3. The precipitate was obtained by standing overnight at 0 °C.

H_2L_3: Yield: 0.39 g (73%). Anal. Calcd for $C_{32}H_{24}N_2O_4.CH_3CH_2OH$ C, 74.7; H, 5.5; N, 5.1. Found: C, 74.8; H, 5.5; N, 5.1%. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 6.8–7.4 (m, Ar, 20 H), 8.5 (s, CH=N, 2H), 13.1 (s, OH, 2H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 163.4, 161.2, 149.8, 146.9, 138.6, 132.9, 132.2, 127.5, 124.9, 123.6, 121.1, 120.7, 119.3, 118.7, 118.1, 117.1. IR: 3408 (OH), 1618 (CH=N), 1592 (C=C)$_{ar}$.

H_2L_4: Yield: 0.36 g (64%). Anal. Calcd for $C_{36}H_{32}N_2O_4.2CH_3CH_2OH$ C, 74.05; H, 6.8; N, 4.3. Found: C, 74.1; H, 6.8; N, 4.4%. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 13.2 (s, OH, 2H), 8.4 (s, CH=N, 2H), 7.4–6.4 (m, Ar, 19 H), 1.3 (s, $C(CH_3)_3$, 9H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 163.2, 161.2, 160.2, 148.9, 145.8, 144.3, 138.0, 132.8, 132.1, 127.4, 123.0, 122.1, 121.4, 121.0, 120.6, 119.4, 118.6, 117.1, 34.4, 31.3. IR: 3410 (OH), 2959, 2864 (C–H)$_{aliph}$, 1619 (CH=N), 1590 (C=C)$_{ar}$.

Synthesis of L_5 and L_6

2-Pyridinecarboxaldehyde (2 mmol) in dry MeOH (25 cm^3) was slowly added to a stirred solution of the appropriate diamine [1,2-bis (2'-aminophenoxy)benzene or 1,2-bis(2'-aminophenoxy)-4-*t*-butylbenzene; 1 mmol] in dry MeOH (25 cm^3). The yellow solution was stirred for 5 h and then $NaBH_4$ (6 mmol) was added in small portions to the solution. The resulting mixture was stirred at room temperature for 35 h. The solvent was reduced to dryness by rotary evaporation, extracted by $CHCl_3$ (3 × 50 cm^3) and dried *in vacuo*.

L_5: Yield: 0.35 g (73%). Anal. Calcd for $C_{30}H_{26}N_4O_2.2H_2O$ C, 70.6; H, 5.9; N, 11.0. Found: C, 70.5; H, 6.0; N, 11.1%. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 8.53 (2H, py), 8.00 (2H, py), 7.79–6.37 (ar (12H) and py (4H)), 4.67 (4H, CH_2NH). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 148.76–113.18 (ar and py rings), 45.81 (H_2C–NH). IR: 3359 (NH), 1600 (CH=N)$_{py}$, 1488 (C=C)$_{py}$.

L_6: Yield: 0.36 g (67%). Anal. Calcd for $C_{34}H_{34}N_4O_2.2H_2O$ C, 72.1; H, 6.8; N, 9.9. Found: C, 72.0; H, 6.7; N, 10.0%. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 8.50 (2H, py), 8.06 (2H, py), 7.66–6.48 (ar (11H) and py (4H)), 4.64 (4H, CH_2NH), 1.36 (9H, CCH_3). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 149.01–112.89 (ar and py rings), 45.93 (H_2C–NH), 34.51 (CCH_3), 31.10 (CCH_3). IR: 3363 (NH), 1598(CH=N)$_{py}$, 1493 (C=C)$_{py}$.

Synthesis of H_2L_7 and H_2L_8

$NaBH_4$ (0.15 g, 4 mmol) was added in small portions to a solution of Schiff base ligand (H_2L_1 or H_2L_2, 1 mmol) in absolute EtOH (50 cm^3). The resulting mixture was stirred at room temperature for 30 h. The solvent was then removed and extracted by $CHCl_3$ (3 × 50 cm^3) and dried.

H_2L_7: Yield: 0.26 g (51%). Anal. Calcd for $C_{32}H_{28}N_2O_4.CHCl_3$ C, 63.5; H, 4.7; N, 4.5. Found: C, 63.5; H, 4.7; N, 4.55%. ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 7.4–6.5(m, Ar, 20 H), 4.2 (s, CH_2, 4H). ^{13}C NMR δ_C (90 MHz, $CDCl_3$): 156.2, 146.6, 145.4, 138.3, 128.8, 128.6, 124.8, 124.1, 123.2, 120.7, 119.9, 119.5, 116.3, 114.4, 47.4. IR: 3331 (NH), 1585 (C=C)$_{ar}$.

H_2L_8: Yield: 0.35 g (63%). Anal. Calcd for $C_{36}H_{36}N_2O_4$ C, 77.1; H, 6.5; N, 5.0. Found: C, 77.0; H, 6.4; N, 5.05%. ^{1}H NMR δ_H (90 MHz, $CDCl_3$): 7.4–6.6 (m, Ar, 19 H), 4.2 (s, CH_2, 4H), 1.3 (s, $C(CH_3)_3$, 9H). ^{13}C NMR δ_C (500 MHz, $CDCl_3$): 156.4, 148.6, 146.0, 145.6, 144.2, 138.3, 128.7, 128.6, 123.8, 123.3, 120.6, 119.8, 118.9, 115.9, 115.7, 115.1, 114.3, 47.5, 34.4, 31.3. IR: 3340 (NH), 1587 (C=C)$_{ar}$.

Preparation of complexes

Metal complexes of L_1 and L_2 ligands

General synthesis

A MeOH solution (25 cm^3) of 2-pyridinecarboxaldehyde (2 mmol) was added dropwise to a MeOH solution (25 cm^3) of the appropriate diamine (1 mmol). The yellow solution was stirred for 5 h; then the appropriate salt (1 mmol) in MeOH (15 cm^3) was added dropwise. The resulting solution was stirred for 4 h at 40–45 °C and allowed to stand overnight. The precipitate was filtered, washed with EtOH and Et_2O and dried *in vacuo*.

$[Zn(L_1)](NO_3)_2.2CH_3CH_2OH$: ^{1}H NMR δ_H (350 MHz, DMSO-d_6): 6.65, 6.78, 6.89, 6.97, 7.46, 7.70, 7.97, 8.04, 8.30, 8.84, 9.20. ^{13}C NMR δ_C (350 MHz, DMSO-d_6): 115.41, 122.14, 125.77, 126.47, 127.23, 128.28, 129. 68, 129.86, 133.34, 142.05, 146.26, 148.83, 150.50, 163.37.

$[Zn(L_2)](NO_3)_2$. $2CH_3OH$: ^{1}H NMR δ_H (350 MHz, DMSO-d_6): 1.33, 6.56, 6.61, 6.67, 6.84, 6.95, 7.46, 7.52, 7.90, 8.02, 8.25, 8.76, 9.26. ^{13}C NMR δ_C (350 MHz, DMSO-d_6): 31.01, 34.56, 115.18, 121. 48, 121.84, 123.62, 125.65, 127.20, 128.06, 129.20, 129.30, 133.10, 141.76, 143.76, 145.85, 146.17, 148.79, 150.19, 163.20.

Metal complexes of H_2L_3 and H_2L_4 ligands

General synthesis

The salicylaldehyde (0.244 g, 2 mmol) in absolute EtOH (25 cm^3) was added dropwise to a hot solution in absolute EtOH

(50 cm^3) of diamine [1,2-bis (2'-aminophenoxy)benzene or 1,2-bis (2'-aminophenoxy)-4-t-butylbenzene; 1 mmol]. The solution was gentlly refluxed for 6 h. After cooling to 55–60 °C temperature a solution of triethylamine (0.2 g, 2 mmol) in absolute EtOH (5 cm^3) was added to the solution. The solution was essentially red at this time. The mixture stirred for 10 min, and then a solution of appropriate metal salt (1 mmol) in absolute EtOH (20 cm^3) was added dropwise. The solution was refluxed for 6 h, concentrated in a rotary evaporator until approximately 10–15 cm^3. The precipitation obtained was filtered off.

[ZnL_3]: ^{1}H NMR δ_H (500 MHz, DMSO-d_6): 6.46, 6.53, 7.06, 7.15, 7.21, 7.28, 7.56, 8.47. ^{13}C NMR δ_C (500 MHz, DMSO-d_6): 114.4, 119.3, 120.6, 123.0, 123.1, 123.4, 126.3, 126.7, 128.5, 136.7, 138.2, 140.7, 148.9, 151.1, 170.9, 172.8.

IR and NMR spectra of dinitro and diamine compounds, ligands and zinc complexes of L_1, L_2 and H_2L_3 and FAB-Mass spectra of complexes are available upon request from the authors.

We are grateful to the Department of Chemistry of Bu–Ali Sina, Tarbiat Moalem Universities and Sharif University of Technology for support of this work.

Received 18 December 2008; accepted 1 April 2009
Paper 09/0369 doi: 10.3184/030823409X457528
Published online: 22 June 2009

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