Synthesis and characterisation of some hexadentate Schiff-base ligands containing the piperazine moiety

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Ten hexadentate (N_4O_2, N_4S_2 and N_6) Schiff-base ligands have been prepared by condensation of various aldehydes and two different linear tetraamines containing the piperazine moiety. The products have been characterised by melting point, elemental analysis and various spectroscopic methods such as: FT-IR, ^{1}H, ^{13}C NMR, and EI mass spectrometry. The complex [Co{N, N'-bis[(pyridin-2-ylmethylene)ethyl]piperazine}][ClO_4]$_2$ has been prepared.

Keywords: hexadentate Schiff-base ligands; piperazine moiety; N,N'-bis(2-aminoethyl)piperazine; N, N'-bis(3-aminopropyl) piperazine; cobalt(II) complex.

Schiff-base ligands are of significant importance in chemistry, because Schiff-base ligands are potentially capable of forming stable complexes with metal ions.[1,2] A large number of Schiff-bases and their complexes had been studied for their interesting and important properties *e.g.* their ability to reversibly bind oxygen, catalytic activity in hydrogenation of olefins and transfer of an amino group, photochromic properties, and complexing ability towards some toxic metals.[3-7]

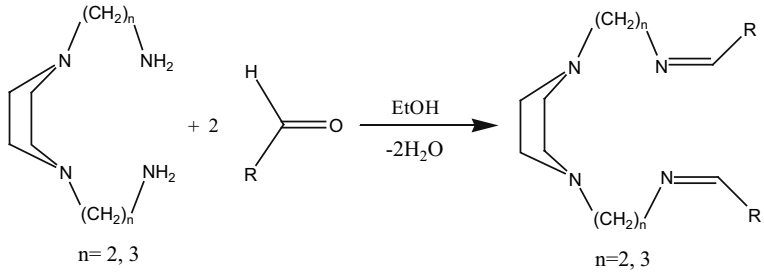
Schiff-base ligands, as a variety of compounds with the imine group, have gained importance because of physiological and pharmacological activities associated with them. They constitute an interesting class of chelating agents capable of coordination metal ions, which serves as models for biological system.[8-10]

The synthesis of Schiff-base is a classical reaction. It is often carried out with acid catalysis and generally by refluxing a mixture of aldehyde (or ketone) and amine.[11] Ghosh *et al.*[12] synthesised N, N'-bis[(pyridin-2-ylmethylene)ethyl]piperazin e by reflux for 10h. Ibers and co-workers[13] prepared a Schiff-base ligand from condensation of thiophene-2-carbaldehyde and N,N'-bis(3-aminopropyl)piperazine under reflux for 3 h. We recently reported[14] the synthesis and crystal structure of Mn(II) complexes with novel macrocyclic Schiff-base ligands containing the piperazine moiety. In this work, we report synthesis of 10 potentially hexadentate Schiff-base ligands containing the piperazine moiety. In these reactions, we used two different linear tetraaza-amines having the piperazine moiety with various aldehydes. The corresponding Schiff-base ligands were produced (Scheme 1). We also report a cobalt(II) complex with L^4 (Scheme 2), characterised by IR, elemental analysis and FAB mass spectroscopic methods.

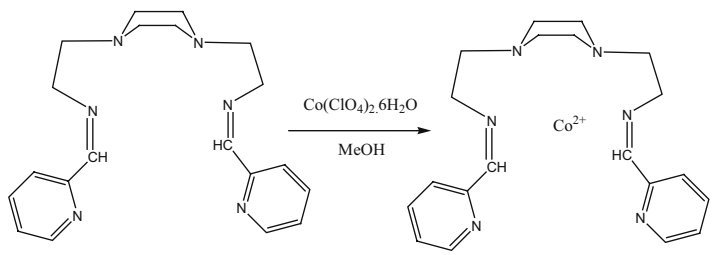
Experimental

Physical measurements

Melting points were measured on a SMPI apparatus. Elemental analysis for C, H and N was performed using a Perkin-Elmer series 2400 and Carlo-Erba EA analysers and IR spectra were recorded as liquid films between NaCl plates, using a Perkin–Elmer FT-IR Spectrum GX spectrophotometer (4000–500 cm^{-1}). ^{1}H and ^{13}C spectra were recorded on a 90 MHz Jeol and 400 MHz Bruker spectrometers in $CDCl_3$ at 25 °C. Mass spectra were obtained using a QP-1100EX Shimadzu GC–MS (EI at 70 eV). FAB mass spectrum was recorded using a Kratos-MS-50T spectrometer connected to a DS90 data system using 3-nitrobenzyl alcohol as the matrix. Conductivity measurements were carried out in 10^{-3} mol dm^{-3} dimethylformamide solutions at 20 °C using a CARISON GLP32 conductivimeter.



Scheme 1 Synthesis of some hexadentate Schiff-base ligands.



Scheme 2 Synthesis of cobalt(II) complex of L^4.

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Chemicals and starting materials

The aldehydes, such as salicaldehyde, 5-bromosalicaldehdes, 2-hydroxy-1-naphthaldehyde, pyridine-2-carabaldehyde and thiophene-2-carbaldehyde were obtained from Merck and *N,N′*-bis(3-aminopropyl)piperazine were obtained from Aldrich and all of them were used without further purification. 3,5-di-tert-butylsalicaldehyde (SATBU) and *N,N′*-bis(2-aminoethyl)piperazine were also prepared as previously described, respectively.[15,16]

Preparation of ligands

A solution of *N,N′*-bis(2-aminoethyl)piperazine or *N,N′*-bis(3-aminopropyl)piperazine (0.5 mmol) in absolute ethanol (30 mL) was added to a refluxing solution of salicaldehyde, 5-bromosalicaldehyde, 2-hydroxy-1-naphthaldehyde, pyridine-2-carabaldehyde or thiophene-2-carbaldehyde (1 mmol) in the same solvent (20 mL). After being refluxed for 3 h, the solution was concentrated in a rotary evaporator to *ca* 5–10 mL. A small volume of diethyl ether was slowly added into the solution producing powdery precipitates. The products were filtered off, washed with cold diethyl ether and dried.

N, N′-Bis{2-[(2-ethylimino)methyl]phenol}piperazine (L^1): Calcd for $C_{22}H_{28}N_4O_2$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.60; H, 7.34; N, 14.91%. ^{1}H NMR ($CDCl_3$) 2.71 (12H, m), 3.78 (4H, t), 6.85–7.33 (8H, m), 8.36 (2H, s), 13.27 (2H, br); ^{13}C NMR ($CDCl_3$) 53.08, 56.76, 58.50, 117.04, 118.59,118.74, 131.30, 132.32, 161.15, 165.85.

N, N′-Bis{2-[(2-ethylimino)methyl]-5-bromophenol}piperazine (L^2): Calcd for $C_{22}H_{26}Br_2N_4O_2$: C, 49.09; H, 4.87; N, 10.41. Found: C, 49.40; H, 5.0; N, 10.32%. ^{1}H NMR ($CDCl_3$) 2.58 (12H, br), 3.71 (4H, t), 6.82 (2H, d), 7.27 (4H, m), 8.21 (2H, s), 13.32 (2H, br); ^{13}C NMR ($CDCl_3$) 53.30, 56.83, 58.40, 109.91, 119.13, 120.10, 133.33, 134.90, 160.39, 164.40.

N, N′-Bis{2-[(2-ethylimino)methyl]-4,6-di-tert-butylphenol}piperazine (L^3): Calcd for $C_{38}H_{60}N_4O_2$: C, 75.45; H, 10.00; N, 9.26. Found: C, 76.02; H, 9.80; N, 9.76%. ^{1}H NMR ($CDCl_3$) 1.30 (18H, s), 1.44 (18H, s), 2.61 (12H, m), 3.74 (4H, t), 7.06 (2H, s), 7.38 (2H, s), 8.36 (2H, s), 13.72(2H, s); ^{13}C NMR ($CDCl_3$) 29.54, 31.59, 34.19, 35.09, 53.50, 57.12, 58.98, 118.04, 125.88, 126.94, 136.82, 140.08, 158.23, 166.78.

N, N′-Bis[(pyridin-2-ylmethylene)ethyl)]piperazine (L^4): Calcd for $C_{20}H_{26}N_6.0.5H_2O$: C, 66.82; H, 7.57; N, 23.38. Found: C, 67.23; H, 7.46; N, 23.50%. ^{1}H NMR ($CDCl_3$) 2.56 (8H, br), 2.68 (4H, t), 3.78 (4H, t), 7.27 (2H, t), 7.67 (2H, t), 7.90, (2H, d), 8.34 (2H, s), 8.58 (2H, d); ^{13}C NMR ($CDCl_3$) 52.80, 57.67, 57.99, 120.70, 125.09, 136.95, 149.34, 153.91, 162.39.

N, N′-Bis[2-(thiophen-2-ylmethyleneamino)ethyl]piperazine (L^5): Calcd for $C_{18}H_{24}N_4S_2$: C, 59.96; H, 6.71; N, 15.54. Found: C, 61.30; H, 6.58; N, 15.80%.^{1}H NMR ($CDCl_3$) 2.53 (8H, br), 2.63 (4H, t), 3.66 (4H, t), 6.86 (2H, d), 7.38 (4H, m), 8.28 (2H, s); ^{13}C NMR ($CDCl_3$) 53.68, 58.77, 58.85, 127.77, 128.77, 130.57, 142.39, 155.19.

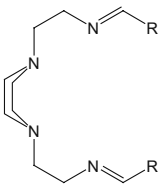
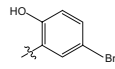
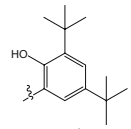
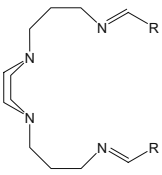
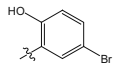
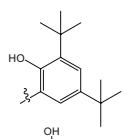
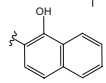
N, N′-Bis{2-[(3-propylimino)methy)]phenol}piperazine (L^6): Calcd for $C_{24}H_{32}N_4O_2$: C, 70.56; H, 7.90; N, 13.71. Found: C, 71.48; H, 8.02; N, 13.89%. ^{1}H NMR ($CDCl_3$) 1.87 (4H, m), 2.37 (12H, m), 3.58 (4H, t), 6.79–7.31 (8H, m), 8.20 (2H, s), 13.51 (2H, br); ^{13}C NMR ($CDCl_3$) 27.81, 53.08, 55.69, 57.27, 116.89, 118.29, 131.01, 131.96, 161.25, 164.88.

N, N′-Bis{2-[(3-propylimino)methyl]-5-bromophenol}piperazine (L^7): Calcd for $C_{24}H_{30}Br_2N_4O_2$: C, 50.90; H, 5.34; N, 9.89. Found: C, 51.40; H, 5.02; N, 10.24%. ^{1}H NMR ($CDCl_3$) 1.81 (4H, m), 2.35 (4H, t), 2.40 (8H, br), 3.58 (4H, t), 6.79 (2H, d), 7.28 (2H, s),7.31 (2H, d) 8.20 (2H, s), 13.49 (2H, br); ^{13}C NMR ($CDCl_3$) 27.79, 53.20, 55.76, 57.40, 109.83, 119.11, 120.09, 160.48, 163.77.

N, N′-Bis{2-[(3-propylimino)methyl]-4,6-di-tert-butylphenol}piperazine (L^8): Calcd for $C_{40}H_{64}N_4O_2.0.35\,H_2O$. C, 75.15; H, 10.20; N, 8.76. Found: C, 74.27; H, 11.10; N, 8.50%. ^{1}H NMR ($CDCl_3$) 1.33 (18H, s), 1.47 (18H, s), 1.90 (4H, br), 2.51 (12H, br), 3.64 (4H, t), 7.10 (2H, s), 7.39 (2H, b), 8.37(2H, b), 13.89(2H, s); ^{13}C NMR ($CDCl_3$) 27.80, 53.20, 53.30, 55.76, 57.40, 109.83, 119.11, 120.09, 133.24, 134.80, 160.48, 163.77.

N, N′-Bis{2-[(3-propylimino)methyl]naphthalen-1-ol}piperazine (L^9): Calcd for $C_{32}H_{36}N_4O_2.0.5\,CH_3CH_2OH$: C, 75.56; H, 7.13; N, 11.01. Found: C, 74.55; H, 7.60; N, 10.53%. ^{1}H NMR ($CDCl_3$) 1.81 (2H, m), 2.41 (12H, m), 3.58 (2H, t), 6.80–7.80 (12H, m), 8.64 (2H, s), 14.23

Table 1 Synthesis of L^1–L^{10}

Structure	Ligand	R	M.p/°C	Yield/%	MS *m/z*/% M^+	IR (νC=N)
	L^1		150	80	380(35)	1634
	L^2		188	85	538(50)	1634
	L^3		167	87	604(30)	1633
	L^4		102	80	350(43)	1647
	L^5		97	86	360(22)	1633
	L^6		97	82	408(65)	1634
	L^7		107	85	566(20)	1635
	L^8		125	84	632(35)	1631
	L^9		169	75	508(20)	1645
	L^{10}		[a]–	81	378(22)	1650

[a]The product was an oil.

(2H, b); ^{13}C NMR ($CDCl_3$) 27.44, 50.69, 53.03, 106.49, 117.73, 122.63, 125.22, 126.21, 127.94,129.27, 131.75, 133.99, 137.26, 158.22.

N, N'-Bis[(pyridin-2-ylmethylene)propyl]piperazine (L^{10}): Calcd for $C_{22}H_{32}N_6$: C, 69.44; H, 8.48; N, 22.09. Found: C, 70.25; H, 8.02; N, 22.09%. ^{1}H NMR ($CDCl_3$) 1.75 (4H, m), 2.33 (12H, m), 3.53 (4H, t), 7.13 (2H, t), 7.56 (2H, t), 7.78 (2H, d), 8.22 (2H, s), 8.47 (2H, d); ^{13}C NMR ($CDCl_3$) 26.98, 52.26, 55.21, 58.38, 120.20, 123.71, 135.53, 148.38, 153.70, 161.10.

Preparation of complex

$Co(ClO_4)_2.6H_2O$ (0.184 g, 0.5 mmol) was dissolved in methanol (20 mL) and added to a solution of L^4 (0.18 g, 0.50 mmol) in methanol (30 mL). The mixture was heated to reflux during 6 h and then it was cooled. As a precipitate did not develop immediately the solution was partially concentrated to give a solid. The product was filtered off and dried in a vacuum. (Scheme 2).

$[CoL^4](ClO_4)_2.0.5H_2O$ (62%). (Calcd for $C_{20}H_{26}Cl_2CoN_6O_6.0.5H_2O$: C, 38.91; H, 4.41; N, 13.61. Found: C, 38.60; H, 4.72; N, 13.39%). ν_{max}/cm^{-1} (KBr disc): 3418 (O–H), 1643 (C=N)imine, 1598, 1446 (C=N)py, 1088, 623 (ClO_4); FAB-MS *m/z* (%) 508 $[CoL^4]^+$ (ClO_4) (92.8), 409 $[CoL^4]^+$ (100). Λ_M/Ω^{-1} cm^2 mol^{-1} (in DMF): 126.4 (2 : 1).

Result and discussion

Here, we report synthesis of some hexadentate Schiff-base ligands, L^1–L^{10}, derived from the condensation of N,N-bis(3-aminopropyl) piperazine or N,N'-bis(2-aminoethyl)piperazine and a number of different aldehydes such as salicaldehyde derivatives, thiophene-2-carbaldehyde, 2-hydroxy-1-napthaldehyde and pyridine-2-carbaldehyde. Their spectral data are completely consistent with the proposed formulations. The yields, melting points, IR and EI mass data are given in Table 1.

The structure of the products has been assigned by spectroscopic data. The IR spectra of the new ligands confirm the formation of the compounds by the absence of bands characteristic of carbonyl and primary amine groups of the starting materials and exhibit a Schiff-base ν(C=N) vibration in the range of 1631–1647 m^{-1}. The stretching vibration of C–H in the alkyl groups appears in the region between 2800 and 2900 cm^{-1}. In the ^{1}H NMR spectra, protons of the imine bond have chemical shifts in the range 8.22–8.73 ppm. The signals around 6.5–8.4 ppm are assigned to C–H protons of aromatic rings. In the ^{13}C NMR spectra of the ligands, the imine bond C=N carbon appears at 158.21–166.78 ppm. Elemental analysis data and EI Mass spectra confirm the formation of Schiff-base ligands.

The Co(II) complex of L^4 is also reported and characterised by a variety of methods, such as: IR, elemental analysis and FAB Mass spectrometry. Positive-ion FAB mass spectrometry provided further evidence for formation of the Co(II) complex. The spectrum shows that the most intense peaks are observed at *m/z* 508 and 409 a.m.u corresponding to $[CoL^4]^+(ClO_4)$ and $[CoL^4]^+$, respectively. The molar conductance value of the complex measured in dimethylformamide lies in the range reported for 2 : 1 electrolytes in this solvent.[17]

Conclusion

In this work, we have prepared in high yield 10 potentially hexadentate Schiff-base ligands containing the piperazine moiety. All of the ligands and related cobalt(II) complex of L^4 were characterised by various spectroscopic methods.

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