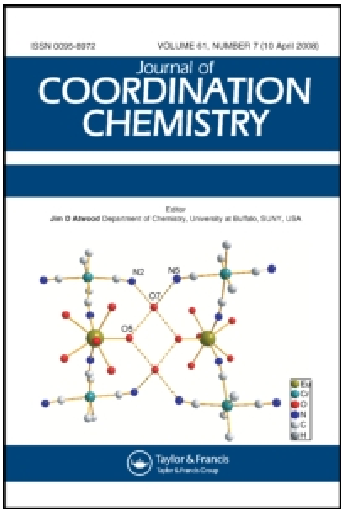

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Preparation and characterization of binuclear Cu^{II} complexes derived from diamines and dialdehydes

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Preparation and characterization of binuclear Cu^{II} complexes derived from diamines and dialdehydes

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New macrocyclic complexes were synthesized by template reaction of 1,7-*bis*(2-formylphenyl)-1,4,7-trioxaheptane, 1,4-*bis*(2-carboxyaldehydephenoxy)butane or 1,3-*bis*(2-carboxyaldehydephenoxy)propane with 1,4-*bis*(2-aminophenoxy)butane, 1,3-*bis*(2-aminophenoxy)butane, 1,4-*bis*(4-chloro-2-aminophenoxy)butane or 1,3-*bis*(4-chloro-2-aminophenoxy)butane and $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$, respectively. The complexes have been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR, UV–Vis spectra, magnetic susceptibility, conductivity measurements and mass spectra. All complexes are diamagnetic and binuclear.

Keywords: Macrocyclic Schiff base; Macrocyclic Schiff-base complex; Binuclear copper(II) complex

1. Introduction

Metal template syntheses of multidentate and macromonocyclic ligands have been established as offering high-yielding and selective routes to new ligands and their complexes. The various synthetic routes to potentially multidentate ligands have been extensively reviewed [1–3] and several types of template effects about transition-metal ions identified. Macrocyclic ligands with additional donor atoms appended to the ring have generated considerable interest because of their capacity to bind and transport metal ions, for the potential to prepare and study mixed-valence forms, and as models for metalloproteins [4]. Dinuclear complexes with metal ions close in proximity show interesting magnetic, catalytic and electron transfer properties. Efforts to synthesize ligands capable of generating such dinuclear complexes have resulted in a large number of dinucleating ligands [5]. Binuclear copper(II) complexes have attracted attention with studies of metalloproteins [6–9]. Proteins and enzymes have binuclear metallosites in which the metals are essential for biological activity [10–12]. Enzymes like hemocyanin [13], tyrosinase [14] etc. have binuclear cooper centers in their active sites. Copper(II) ions play a central role in biological redox metalloenzymes such as plastocyanin, hemocyanin, azurin and galactose oxidase [15, 16]. In the present work, I have

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synthesized new macrocyclic copper(II) complexes by template reaction of 1,7-*bis*(2-formylphenyl)-1,4,7-trioxaheptane, 1,4-*bis*(2-carboxyaldehydephenoxy)butane or 1,3-*bis*(2-carboxyaldehydephenoxy)propane with 1,4-*bis*(2-aminophenoxy)butane, 1,3-*bis*(2-aminophenoxy)butane, 1,4-*bis*(4-chloro-2-aminophenoxy)butane or 1,3-*bis* (4-chloro-2-aminophenoxy)butane and $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$. Spectral and magnetic properties of all complexes are reported.

2. Experimental

2.1. *Physical measurements*

Elemental analysis was carried out on a LECO CHNS model 932 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded using a BRUKER AVANCE DPX-400 NMR spectrometer. IR spectra were recorded on a PERKIN ELMER SPECTRUM RX1 FTIR spectrometer on KBr discs in the wavenumber range 4000–400 cm^{-1}. Electronic spectral studies were conducted on a SHIMADZU model 160 UV Visible spectrophotometer in the wavelength 200–600 nm. Molar conductivities were measured with a WTW LF model 330 conductivity meter using prepared solution of the complex in DMSO (10^{-3} M). Electrospray ionization mass spectrometric analyses (ESI–MS) were obtained on the AGILEND 1100 MSD spectrometer. Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model N0: MK1) at room temperature (30°C) using $Hg[Co(SCN)_4]$ as a calibrant; diamagnetic corrections were calculated from Pascal's constants [17].

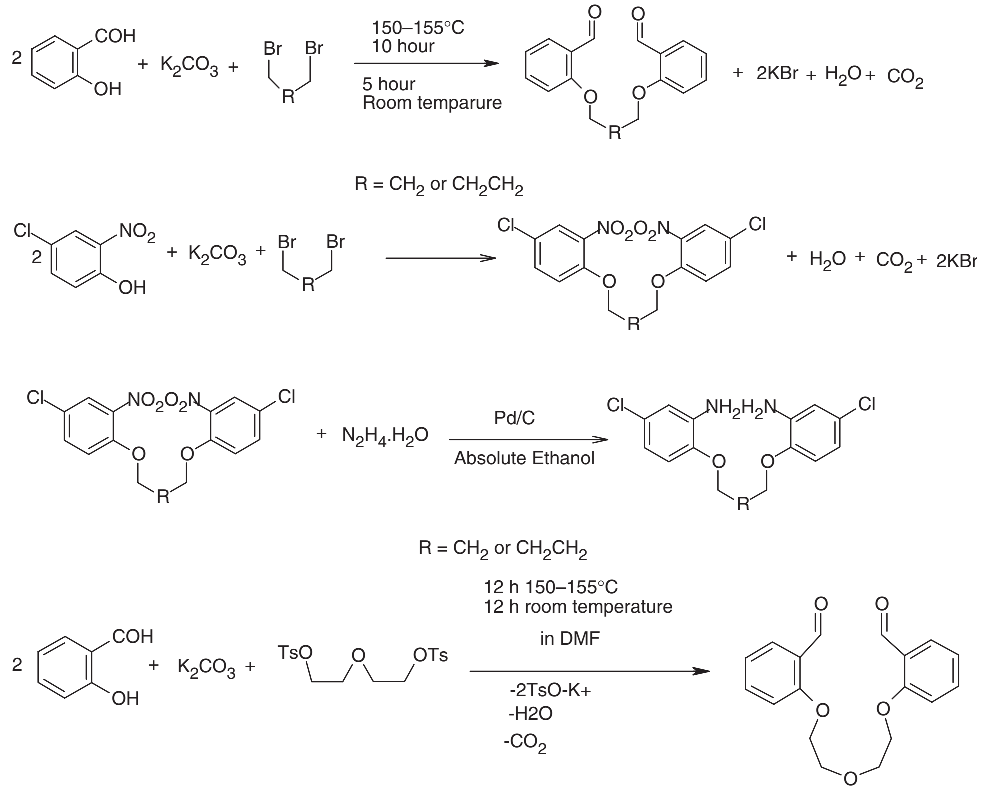
2.2. *Materials*

1,4-*bis*(2-carboxyaldehydephenoxy)butane, 1,4-*bis*(2-carboxyaldehydephenoxy)propane and 1,4-*bis*(2-aminophenoxy)butane, 1,3-*bis*(2-aminophenoxy)butane, 1,4-*bis*(4-chloro-2-aminophenoxy)butane, 1,3-*bis*(4-chloro-2-aminophenoxy)butane were prepared by the literature method as shown in Scheme 1 [18–21]. All other chemicals and solvents were of analytical grade and used as received.

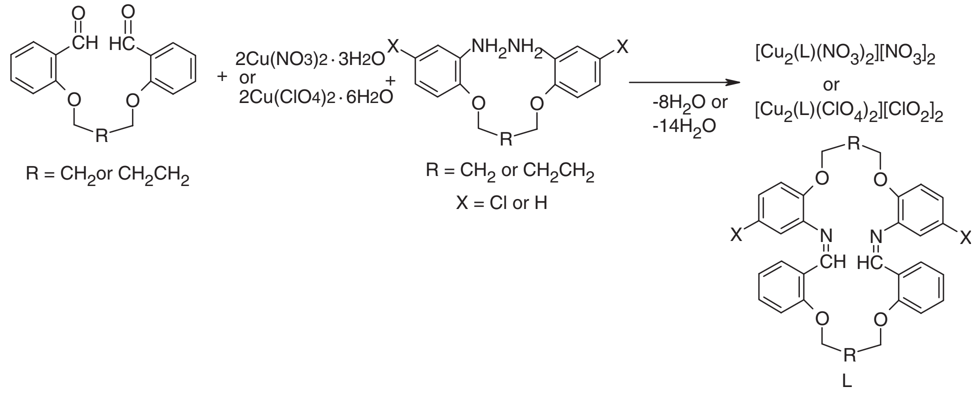
To a stirred solution of dialdehyde (2 mmol) and $Cu(ClO_4)_2 \cdot 6H_2O$ or $Cu(NO_3)_2 \cdot 3H_2O$ (4 mmol) in methanol (60 mL) was added dropwise diamines (2 mmol) in methanol (40 mL). After the addition was complete, stirring was continued for 2 h. Then precipitate was filtered and washed with methanol and dried in air (Scheme 2).

2.3. *Spectral characterization of $[Cu_2(L^1)(NO_3)_2][NO_3]_2$*

Yield: 0.98 g (54%). Anal Calcd for $Cu_2C_{34}H_{34}N_6O_{16}$: C, 44.86; H, 3.77; N, 9.26. Found: C, 44.45; H, 4.11; N, 10.03. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 27.5, OCH_2: 64.6, HC=N: 189.6. Aromatic C's: 114.1, 121.1, 124.6, 127.9, 135.8, 161.4. ^{1}H NMR (DMSO-d$_6$, δ ppm): $\delta = 2.0$ (p, 8H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 6.7$–7.9 (m, 16, Ar–H), $\delta = 10.4$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1642 ν(C=N), 1384 $\nu(NO_3^-)$, 752 ν(substituted benzene), 535 ν(Cu–O), 458 ν(Cu–N).



Scheme 1. Synthesis of the dialdehydes and diamines.



Scheme 2. General synthesis of the complexes.

$\Lambda_M = 172\,\Omega^{-1}\,\mathrm{mol}^{-1}\,\mathrm{cm}^2$. Mass spectra ($m/z$): (850, 0.3%, $[[Cu_2(L^1)(NO_3)_3] + 2H]^+$, (554, 2.8%, $[[Cu(L^1) - OCH_2CH_2] + H]^+$), (553, 7.9%, $[[Cu(L^1) - OCH_2CH_2]^+$), (535, 2.1%, $[L^1]^+$), (274, 18.2%, $[C_{16}H_{22}N_2O_2]^+$), (273, 100%, $[C_{16}H_{21}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 274, 322. $\mu_{eff} = \mathrm{Dia}$.

Table 1. Physical characterization, analytical, molar conductance and mass data of the complexes.

Compound	Yield gram (%)	(Calcd) Found %C	%H	%N	Λ_M (Ohm^{1}cm^2 mol^{-1})	Formula weight	MS/EI	Assignment (m/z)	μ_{eff} (BM)
$[Cu_2(L^1)(NO_3)_2][NO_3]_2$	0.98	(44.86)	(3.77)	(9.26)	172	910	850	$[[Cu_2(L^1)(NO_3)_3] + 2H]^+$	Dia
	(54)	44.45	4.11	10.03					
$[Cu_2(L^2)(NO_3)_2][NO_3]_2$	1.00	(41.63)	(3.26)	(8.57)	164	980	977	$[[Cu_2(L^2)(NO_3)_4] - 3H]^+$	Dia
	(51)	41.81	3.92	8.28					
$[Cu_2(L^3)(NO_3)_2][NO_3]_2$	0.82	(44.24)	(3.69)	(9.44)	166	896	893	$[[Cu_2(L^3)(NO_3)_4] - 3H]^+$	Dia
	(46.0)	44.31	3.62	9.33					
$[Cu_2(L^4)(NO_3)_2][NO_3]_2$	0.88	(44.24)	(3.64)	(9.42)	178	896	898	$[[Cu_2(L^4)(NO_3)_4] + 2H]^+$	Dia
	(49)	44.42	3.53	9.53					
$[Cu_2(L^5)(NO_3)_2][NO_3]_2$	0.91	(40.93)	(3.12)	(8.72)	186	967	962	$[[Cu_2(L^5)(NO_3)_4] - 5H]^+$	Dia
	(47)	41.12	3.24	8.59					
$[Cu_2(L^6)(NO_3)_2][NO_3]_2$	0.85	(40.94)	(3.09)	(8.74)	172	967	626	$[Cu(L^6) - OCH_2]^+$	Dia
	(44)	41.19	3.23	8.83					
$[Cu_2(L^1)(ClO_4)_2][ClO_4]_2$	1.2	(38.48)	(3.22)	(2.57)	182	1060	861	$[Cu_2(L^1)(ClO_4)_2]^+$	Dia
	(56)	38.66	3.16	2.47					
$[Cu_2(L^2)(ClO_4)_2][ClO_4]_2$	1.2	(36.14)	(3.04)	(2.47)	196	1131	935	$[[Cu_2(L^2)(ClO_4)_2] + 3H]^+$	Dia
	(52)	38.16	3.19	2.54					
$[Cu_2(L^3)(ClO_4)_2][ClO_4]_2$	1.1	(37.88)	(3.12)	(2.69)	168	1044	648	$[[Cu_2(L^3) + H]^+$	Dia
	(54)	37.81	3.03	2.74					
$[Cu_2(L^4)(ClO_4)_2][ClO_4]_2$	1.0	(37.86)	(3.14)	(2.73)	175	1044	647	$[Cu_2(L^4)]^+$	Dia
	(47)	38.08	3.25	2.64					
$[Cu_2(L^5)(ClO_4)_2][ClO_4]_2$	1.0	(35.44)	(2.68)	(2.54)	191	1115	717	$[Cu_2(L^5)]^+$	Dia
	(45)	35.57	2.76	2.43					
$[Cu_2(L^6)(ClO_4)_2][ClO_4]_2$	1.0	(35.39)	(2.73)	(2.52)	201	1115	653	$[Cu(L^6)]^+$	Dia
	(45)	35.44	2.62	2.59					
$[Cu_2(L^7)(ClO_4)_2][ClO_4]_2$	0.9	(37.94)	(3.18)	(2.56)	185	1075	631	$[[Cu_2(L^7)] - (OCH_2CH_2) - 2H]^+$	Dia
	(45)	38.03	3.23	2.34					
$[Cu_2(L^8)(ClO_4)_2][ClO_4]_2$	0.9	(35.56)	(2.83)	(2.44)	148	1143	845	$[Cu_2(L^8)(ClO_4) + H]^+$	Dia
	(42)	35.67	2.93	2.52					

Table 2. IR (cm^{-1}) and UV–Vis (nm) spectral data for the Cu(II) complexes.

Compound	ν(C=N)	$\nu(NO_3^-)$ or $\nu(ClO_4^-)$	ν(substitute benzene)	ν(Cu–O)	ν(Cu–N)	π–π* transition	n–π* transition
$[Cu_2(L^1)(NO_3)_2][NO_3]_2$	1642	1384	752	535	458	274	322
$[Cu_2(L^2)(NO_3)_2][NO_3]_2$	1643	1384	751	547	453	277	316
$[Cu_2(L^3)(NO_3)_2][NO_3]_2$	1642	1384	752	530	493	273	318
$[Cu_2(L^4)(NO_3)_2][NO_3]_2$	1641	1384	752	553	477	278	318
$[Cu_2(L^5)(NO_3)_2][NO_3]_2$	1642	1384	749	542	468	277	323
$[Cu_2(L^6)(NO_3)_2][NO_3]_2$	1644	1384	751	544	472	280	325
$[Cu_2(L^1)(ClO_4)_2][ClO_4]_2$	1641	1092, 623	751	542	474	274	321
$[Cu_2(L^2)(ClO_4)_2][ClO_4]_2$	1642	1092, 625	758	554	465	276	318
$[Cu_2(L^3)(ClO_4)_2][ClO_4]_2$	1646	1095, 623	756	536	490	273	319
$[Cu_2(L^4)(ClO_4)_2][ClO_4]_2$	1638	1094, 624	762	528	484	276	317
$[Cu_2(L^5)(ClO_4)_2][ClO_4]_2$	1640	1094, 623	758	527	482	278	324
$[Cu_2(L^6)(ClO_4)_2][ClO_4]_2$	1640	1094, 623	758	537	482	279	324
$[Cu_2(L^7)(ClO_4)_2][ClO_4]_2$	1653	1106, 624	758	535	486	276	321
$[Cu_2(L^8)(ClO_4)_2][ClO_4]_2$	1641	1101, 624	758	528	475	281	325

2.4. *Spectral characterization of* $[Cu_2(L^2)(NO_3)_2][NO_3]_2$

Yield: 1.00 g (51%). Anal Calcd for $Cu_2C_{34}H_{32}N_6O_{16}Cl_2$: C, 41.63; H, 3.26; N, 8.57. Found: C, 41.81; H, 3.92; N, 8.28. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 27.4, OCH_2: 64.5, HC=N: 189.6. Aromatic C's: 114.8, 122.1, 125.3, 128.2, 136.6, 162.1. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.0$ (p, 8H, CH_2CH_2), $\delta = 4.3$ (t, 8H, OCH_2), $\delta = 6.8$–7.8 (m, 16, Ar–H), $\delta = 10.4$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1643 ν(C=N), 1384 $\nu(NO_3^-)$, 751 ν(substituted benzene), 547 ν(Cu–N), 453 ν(Cu–O). $\Lambda_M = 164\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra ($m/z$): (977, 0.3%, $[[Cu_2(L^2)(NO_3)_4]\text{-}3H]^+$), (621, 3.0%, $[[Cu(L^2) - OCH_2CH_2] + 3H]^+$), (605, 2.3%, $[(L^1) + H]^+$), (450, 100%, $[C_{30}H_{29}N_2O_2]^+$), (341, 11.8%, $[C_{16}H_{20}N_2Cl_2O_2]^+$). UV–Vis ($\lambda_{max}$, nm) in DMSO: 277, 316. $\mu_{eff} =$ Dia.

2.5. *Spectral characterization of* $[Cu_2(L^3)(NO_3)_2][NO_3]_2$

Yield: 0.82 g (46%). Anal Calcd for $Cu_2C_{33}H_{32}N_6O_{16}$: C, 44.24; H, 3.69; N, 9.44. Found: C, 44.31; H, 3.62; N, 9.33. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 28.9, OCH_2: 65.6, HC=N: 189.8. Aromatic C's: 114.0, 121.2, 124.5, 128.2, 136.9, 161.3. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.4$ (p, 2H, CH_2CH_2), $\delta = 2.5$ (p, 4H, CH_2CH_2), $\delta = 4.3$ (t, 8H, OCH_2), $\delta = 7.0$–7.9 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1642 ν(C=N), 1384 $\nu(NO_3^-)$, 752 ν(substituted benzene), 530 ν(Cu–O), 493 ν(Cu–N). $\Lambda_M = 166\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra ($m/z$): (893, 1.2%, $[[Cu_2(L^3)(NO_3)_4] - 3H]^+$), (648, 3.4%, $[[Cu_2(L^3)]^+$), (521, 1.2%, $[(L^3)]^+$), (286, 100%, $[C_{17}H_{21}N_2O_2]^+$), (270, 12.8%, $[C_{16}H_{18}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 273, 318. $\mu_{eff} =$ Dia.

2.6. *Spectral characterization of* $[Cu_2(L^4)(NO_3)_2][NO_3]_2$

Yield: 0.88 g (49%). Anal Calcd for $Cu_2C_{33}H_{32}N_6O_{16}$: C, 44.24; H, 3.64; N, 9.42. Found: C, 44.42; H, 3.53; N, 9.53. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 25.9,

OCH_2: 67.9, HC=N: 189.6. Aromatic C's: 112.4, 120.8, 124.9, 128.6, 136.0, 161.2. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.2$ (p, 2H, CH_2CH_2), $\delta = 2.4$ (p, 4H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 7.0$–7.9 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1641 ν(C=N), 1384 $\nu(NO_3^-)$, 752 ν(substituted benzene), 553 ν(Cu–O), 477 ν(Cu–N). $\Lambda_M = 178\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m/z*): (898, 1.2%, $[[Cu_2(L^4)(NO_3)_4] + 2H]^+$), (773, 4.3%, $[[Cu_2(L^4)(NO_3)_2] + H]^+$), (708, 3.7%, $[[Cu(L^4)(NO_3)_2]]^+$), (584, 5.3%, $[[Cu(L^4)] - H]^+$), (521, 6.5%, $[L^4]^+$), (286, 100%, $[C_{17}H_{21}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 278, 318. μ_{eff} = Dia.

2.7. *Spectral characterization of $[Cu_2(L^5)(NO_3)_2][NO_3]_2$*

Yield: 0.91 g (47%). Anal Calcd for $Cu_2C_{33}H_{30}N_6O_{16}Cl_2$: C, 40.93; H, 3.12; N, 8.72. Found: C, 41.12; H, 3.24; N, 8.59. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 25.7, OCH_2: 68.4, HC=N: 189.6. Aromatic C's: 114.0, 121.0, 124.7, 128.1, 136.9, 161.4. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.0$ (p, 2H, CH_2CH_2), $\delta = 2.6$ (p, 4H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 7.0$–8.1 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1642 ν(C=N), 1384 $\nu(NO_3^-)$, 749 ν(substituted benzene), 542 ν(Cu–O), 468 ν(Cu–N). $\Lambda_M = 186\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m/z*): (962, 1.1%, $[[Cu_2(L^5)(NO_3)_4] - 5H]^+$), (654, 7.0%, $[[Cu(L^5) + H]^+$), (653, 10.7%, $[[Cu(L^5)]^+$), (589, 4.9%, $[[Cu(L^5) - H]^+$), (286, 100%, $[C_{17}H_{21}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 277, 323. μ_{eff} = Dia.

2.8. *Spectral characterization of $[Cu_2(L^6)(NO_3)_2][NO_3]_2$*

Yield: 0.85 g (44%). Anal Calcd for $Cu_2C_{33}H_{30}N_6O_{16}Cl_2$: C, 40.94; H, 3.09; N, 8.74. Found: C, 41.19; H, 3.23; N, 8.83. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 25.6, 25.9, 28.9, 30.9, OCH_2: 65.6, 67.5, HC=N: 189.8. Aromatic C's: 114.0, 116.7, 121.2, 124.8, 128.2, 135.7, 136.9, 161.3. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.0$ (p, 2H, CH_2CH_2), $\delta = 2.5$ (p, 4H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 7.0$–8.1 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1644 ν(C=N), 1384 $\nu(NO_3^-)$, 751 ν(substituted benzene), 544 ν(Cu–O), 472 ν(Cu–N). $\Lambda_M = 172\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m/z*): (626, 4.9%) $[Cu(L^6) - OCH_2]^+$), (654, 1.7%, $[Cu(L^6) + H]^+$), (625, 4.5%, $[Cu(L^6) - (CH_2CH_2)]^+$), (590, 3.9%, $[(L^6) + H]^+$), (287, 12.7%, $[C_{17}H_{22}N_2O_2]^+$), (286, 47.3%, $[C_{17}H_{21}N_2O_2]^+$), (259, 13.2%, $[C_{15}H_{17}N_2O_2]^+$), (258, 100%, $[C_{15}H_{16}N_2O_2]^+$), (79, 4.8%, $[C_6H_7]^+$). UV–Vis (λ_{max}, nm) in DMSO: 280, 325. μ_{eff} = Dia.

2.9. *Spectral characterization of $[Cu_2(L^1)(ClO_4)_2][ClO_4]_2$*

Yield: 1.2 g (56%). Anal Calcd for $Cu_2C_{34}H_{34}N_2O_{20}Cl_4$: C, 38.48; H, 3.22; N, 2.57. Found: C, 38.66; H, 3.16; N, 2.47. ^{13}C NMR (DMSO-d_6, δ ppm): CH_2CH_2: 28.1, OCH_2: 65.1, HC=N: 189.8. Aromatic C's: 114.2, 120.8, 124.3, 127.6, 135.6, 161.6. ^{1}H NMR (DMSO-d_6, δ ppm): $\delta = 2.1$ (p, 4H, CH_2CH_2), $\delta = 2.4$ (p, 4H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 7.1$–8.0 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1641 ν(C=N), 1092, 623 $\nu(ClO_4^-)$, 751 ν(substituted benzene), 542 ν(Cu–O), 474 ν(Cu–N). $\Lambda_M = 182\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m/z*): (861, 3.5%, $[Cu_2(L^1)(ClO_4)_2]^+$), (732, 1.3%, $[Cu_2(L^1)(ClO_4)) - OCH_2]^+$), (667, 0.8%,

$[Cu_2(L^1)+4H]^+$), (539, 0.9%, $[(L^1)+4H]^+$), (287, 2.0%, $[C_{17}H_{20}N_2O_2+2H]^+$), (286, 1.7%, $[C_{17}H_{21}N_2O_2]^+$), (274, 19.6%, $[C_{16}H_{22}N_2O_2]^+$), (273, 100%, $[C_{16}H_{21}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 274, 321. $\mu_{eff}=$ Dia.

2.10. *Spectral characterization of* $[Cu_2(L^2)(ClO_4)_2][ClO_4]_2$

Yield: 1.2 g (52%). Anal Calcd for $Cu_2C_{34}H_{32}N_2O_{20}Cl_6$: C, 36.14; H, 3.04; N, 2.47. Found: C, 38.16; H, 3.19; N, 2.54. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 28.4, OCH_2: 65.6, HC=N: 189.9. Aromatic C's: 115.0, 121.6, 125.1, 128.4, 135.9, 162.1. ^{1}H NMR (DMSO-d$_6$, δ ppm): $\delta=2.2$ (p, 4H, CH_2CH_2), $\delta=2.4$ (p, 4H, CH_2CH_2), $\delta=4.3$ (t, 8H, OCH_2), $\delta=7.2$–8.1 (m, 16, Ar–H), $\delta=10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1642 ν(C=N), 1092, 625 $\nu(ClO_4{}^-)$, 758 ν(substituted benzene), 554 ν(Cu–O), 465 ν(Cu–N). $\Lambda_M=196\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (935, 0.5%, $[[Cu_2(L^2)(ClO_4)_2]+3H]^+$), (838, 0.2%, $[[Cu_2(L^2)(ClO_4)]+5H]^+$), (768, 0.6%, $[Cu(L^2)(ClO_4)]^+$), (732, 0.6%, $[[Cu_2(L^2)]+H]^+$), (667, 2.0%, $[Cu(L^2)+H]^+$), (666, 0.9%, $[Cu(L^2)]^+$), (665, 1.4%, $[Cu(L^2)-H]^+$), (621, 5.3%, $[Cu(L^2)-OCH_2CH_2]^+$) (607, 2.0%, $[(L^2)+3H]^+$), (588, 10.5%, $[(L^2)\text{-}(O)]^+$), (587, 25.8%, $[(L^2)-(O)\text{-}H]^+$), (273, 49.9%, $[C_{16}H_{21}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 276, 318. $\mu_{eff}=$ Dia.

2.11. *Spectral characterization of* $[Cu_2(L^3)(ClO_4)_2][ClO_4]_2$

Yield: 1.1 g (54%). Anal Calcd for $Cu_2C_{33}H_{32}N_2O_{20}Cl_4$: C, 37.88; H, 3.12; N, 2.69. Found: C, 37.81; H, 3.03; N, 2.74. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 28.6, OCH_2: 65.6, HC=N: 189.8. Aromatic C's: 114.0, 121.2, 124.8, 128.2, 136.8, 162.3. ^{1}H NMR (DMSO-d$_6$, δ ppm): $\delta=2.4$ (p, 2H, CH_2CH_2), $\delta=2.3$ (t, 4H, CH_2CH_2), $\delta=4.3$ (t, 8H, OCH_2), $\delta=7.0$–7.9 (m, 16, Ar–H), $\delta=10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1646 ν(C=N), 1095, 623 $\nu(ClO_4^-)$, 756 ν(substituted benzene), 536 ν(Cu–O), 490 ν(Cu–N). $\Lambda_M=168\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (648, 0.9%, $[[Cu_2(L^3)+H]^+$), (607, 2.6%, $[[Cu_2(L^3)-(CH_2CH_2CH_2)-H]^+$), (583, 2.4%, $[[Cu(L^3)-H]^+$), (521, 0.6%, $[(L^3)]^+$), (400, 23.1%, $[C_{26}H_{26}NO_3]^+$), (399, 72.3%, $[C_{26}H_{25}NO_3]^+$), (286, 1.7%, $[C_{17}H_{21}N_2O_2]^+$), (285, 6.6%, $[C_{17}H_{21}N_2O_2]^+$), (274, 1.8%, $[C_{16}H_{22}N_2O_2]^+$), (273, 2.4%, $[C_{16}H_{21}N_2O_2]^+$), (101, 100%, $[C_7H_3N]^+$). UV–Vis (λ_{max}, nm) in DMSO: 273, 319. $\mu_{eff}=$ Dia.

2.12. *Spectral characterization of* $[Cu_2(L^4)(ClO_4)_2][ClO_4]_2$

Yield: 1.0 g (47%). Anal Calcd for $Cu_2C_{33}H_{32}N_2O_{20}Cl_4$: C, 37.86; H, 3.14; N, 2.73. Found: C, 38.08; H, 3.25; N, 2.64. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 25.7, OCH_2: 68.4, HC=N: 189.9. Aromatic C's: 114.0, 121.0, 124.8, 128.1, 137.2, 161.7. ^{1}H NMR (DMSO-d$_6$, δ ppm): $\delta=2.5$ (p, 2H, CH_2CH_2), $\delta=2.4$ (t, 4H, CH_2CH_2), $\delta=4.2$ (t, 8H, OCH_2), $\delta=7.0$–8.0 (m, 16, Ar–H), $\delta=10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1638 ν(C=N), 1094, 624 $\nu(ClO_4^-)$, 762 ν(substituted benzene), 528 ν(Cu–O), 484 ν(Cu–N). $\Lambda_M=175\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (647, 2.4%, $[Cu_2(L^4)]^+$), (585, 13.0%, $[Cu(L^4)+H]^+$), (522, 30.1%, $[(L^4)+H]^+$), (521, 67.7%, $[(L^4)]^+$), (286, 26.3%, $[C_{17}H_{20}N_2O_2+H]^+$), (271, 5.2%, $[C_{16}H_{20}N_2O_2-H]^+$), (259, 100%, $[C_{15}H_{17}N_2O_2]^+$), (101, 16.1%, $[C_7H_3N]^+$), (79, 18.6%, $[C_6H_7]^+$), (78, 7.4%,

$[C_6H_6]^+$), (64, 1.7%, $[Cu+H]^+$), (63, 5.4%, $[Cu]^+$). UV–Vis (λ_{max}, nm) in DMSO: 276, 317. $\mu_{eff} =$ Dia.

2.13. *Spectral characterization of* $[Cu_2(L^5)(ClO_4)_2][ClO_4]_2$

Yield: 1.0 g (45%). Anal Calcd for $Cu_2C_{33}H_{30}N_2O_{20}Cl_6$: C, 35.44; H, 2.68; N, 2.54. Found: C, 35.57; H, 2.76; N, 2.43. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 25.7, OCH_2: 68.4, HC=N: 189.6. Aromatic C's: 105.0, 113.1, 114.0, 116.2, 121.0, 124.7, 128.1, 136.9, 161.5. ^1H NMR (DMSO-d$_6$, δ ppm): $\delta = 2.3$ (p, 2H, CH_2CH_2), $\delta = 2.5$ (t, 4H, CH_2CH_2), $\delta = 4.3$ (t, 8H, OCH_2), $\delta = 7.0$–8.1 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1640 ν(C=N), 1094, 623 $\nu(ClO_4^-)$, 758 ν(substituted benzene), 527 ν(Cu–O), 482 ν(Cu–N). $\Lambda_M = 191\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (717, 0.6%, $[Cu_2(L^5)]^+$), (654, 11.4%, $[Cu(L^5)+H]^+$), (653, 31.7%, $[Cu(L^5)]^+$), (652, 6.1%, $[Cu(L^5)-H]^+$), (651, 12.7%, $[Cu(L^5)-2H]^+$), (590, 2.0%, $[(L^5)+H]^+$), (589, 5.4%, $[(L^5)]^+$), (521, 3.1%, $[(L^5)-Cl_2+2H]^+$), (414, 22.8%, $C_{27}H_{28}NO_3]^+$), (413, 100%, $C_{27}H_{27}NO_3]^+$), (259, 35.3%, $[C_{15}H_{17}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 278, 324. $\mu_{eff} =$ Dia.

2.14. *Spectral characterization of* $[Cu_2(L^6)(ClO_4)_2][ClO_4]_2$

Yield: 1.0 g (45%). Anal Calcd for $Cu_2C_{33}H_{30}N_2O_{20}Cl_6$: C, 35.39; H, 2.73; N, 2.52. Found: C, 35.44; H, 2.62; N, 2.59. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 25.6, OCH_2: 68.4, HC=N: 189.8. Aromatic C's: 114.0, 121.2, 124.7, 128.2, 136.9, 161.3. ^1H NMR (DMSO-d$_6$, δ ppm): $\delta = 2.4$ (p, 2H, CH_2CH_2), $\delta = 2.3$ (t, 4H, CH_2CH_2), $\delta = 4.2$ (t, 8H, OCH_2), $\delta = 7.0$–7.9 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1640 ν(C=N), 1094, 623 $\nu(ClO_4^-)$, 758 ν(substituted benzene), 537 ν(Cu–O), 482 ν(Cu–N). $\Lambda_M = 201\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (653, 0.9%, $[Cu(L^6)]^+$), (625, 8.7%, $[Cu(L^6)\text{-}(CH_2CH_2)]^+$), (589, 6.0%, $[(L^6)]^+$), (287, 18.0%, $[C_{17}H_{22}N_2O_2]^+$), (286, 87.7%, $[C_{17}H_{21}N_2O_2]^+$), (259, 19.1%, $[C_{15}H_{17}N_2O_2]^+$), (258, 100%, $[C_{15}H_{16}N_2O_2]^+$), (101, 2.1%, $[C_7H_3N]^+$), (79, 3.7%, $[C_6H_7]^+$). UV–Vis (λ_{max}, nm) in DMSO: 279, 324. $\mu_{eff} =$ Dia.

2.15. *Spectral characterization of* $[Cu_2(L^7)(ClO_4)_2][ClO_4]_2$

Yield: 0.9 g (42%). Anal Calcd for $Cu_2C_{34}H_{34}N_2O_{21}Cl_4$: C, 37.94; H, 3.18; N, 2.56. Found: C, 38.03; H, 3.23; N, 2.34. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 25.6, OCH_2: 65.6, 68.4, HC=N: 189.8. Aromatic C's: 114.1, 121.4, 124.8, 128.5, 137.3, 161.6. ^1H NMR (DMSO-d$_6$, δ ppm): $\delta = 2.3$ (p, 4H, CH_2CH_2), $\delta = 3.7$ (t, 4H, CH_2OCH_2), $\delta = 3.9$ (t, 4H, OCH_2Ph), $\delta = 4.2$ (t, 4H, OCH_2Ph), $\delta = 6.9$–8.0 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1653 ν(C=N), 1106, 624 $\nu(ClO_4^-)$, 758 ν(substituted benzene), 535 ν(Cu–O), 486 ν(Cu–N). $\Lambda_M = 185\,\Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (631, 3.9%, $[[Cu_2(L^7)]\text{-}(OCH_2CH_2)\text{-}2H]^+$), (613, 0.6%, $[Cu(L^7)]^+$), (570, 2.9%, $[Cu(L^7)\text{-}(OCH_2CH_2)]^+$), (569, 7.3%, $[Cu(L^7)\text{-}(OCH_2CH_2)\text{-}H]^+$), (552, 4.5%, $[(L^7)+H]^+$), (551, 14.4%, $[(L^7)]^+$), (274, 18.0%, $[C_{16}H_{22}N_2O_2]^+$), (273, 100%, $[C_{16}H_{21}N_2O_2]^+$), (258, 3.2%, $[C_{15}H_{16}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 276, 321. $\mu_{eff} =$ Dia.

2.16. *Spectral characterization of [$Cu_2(L^8)(ClO_4)_2$][ClO_4]$_2$*

Yield: 0.9 g (42%). Anal Calcd for $Cu_2C_{34}H_{32}N_2O_{21}Cl_6$: C, 35.56; H, 2.83; N, 2.44. Found: C, 35.67; H, 2.93; N, 2.52. ^{13}C NMR (DMSO-d$_6$, δ ppm): CH_2CH_2: 25.6, OCH_2: 65.6, 68.4, HC=N: 189.8. Aromatic C's: 114.3, 121.7, 125.0, 128.4, 137.2, 161.6. ^{1}H NMR (DMSO-d$_6$, δ ppm): $\delta = 2.2$ (p, 2H, CH_2CH_2), $\delta = 3.6$ (t, 4H, CH_2OCH_2), $\delta = 3.9$ (t, 4H, OCH_2Ph), $\delta = 4.2$ (t, 4H, OCH_2Ph), $\delta = 6.9$–8.0 (m, 16, Ar–H), $\delta = 10.5$ (s, 2H, HC=N). Selected IR data (KBr, ν cm^{-1}): 1641 ν(C=N), 1101, 624 ν(ClO_4^-), 758 ν(substituted benzene), 528 ν(Cu–O), 475 ν(Cu–N). $\Lambda_M = 148\ \Omega^{-1}\,mol^{-1}\,cm^2$. Mass spectra (*m*/*z*): (845, 1.4%, $[Cu_2(L^8)(ClO_4) + H]^+$), (740, 4.1%, $[Cu_2(L^8) - 4H]^+$), (687, 2.8%, $[Cu(L^8) + 3H]^+$), (686, 11.0%, $[Cu(L^8) + 2H]^+$), (685, 24.6%, $[Cu(L^8) + H]^+$), (621, 4.9%, $[(L^8) + H]^+$), (550, 1.0%, $[(L^8) - Cl_2]^+$), (431, 4.3%, $[C_{26}H_{24}N_2O_4]^+$), (430, 26.4%, $[C_{26}H_{23}N_2O_4]^+$), (429, 100%, $[C_{26}H_{22}N_2O_4]^+$), (287, 10.1%, $[C_{17}H_{22}N_2O_2]^+$), (286, 42.9%, $[C_{17}H_{21}N_2O_2]^+$), (259, 7.8%, $[C_{15}H_{17}N_2O_2]^+$), (258, 39.6%, $[C_{15}H_{16}N_2O_2]^+$). UV–Vis (λ_{max}, nm) in DMSO: 281, 325. μ_{eff} = Dia.

3. Results and discussion

Reaction between dialdehydes, diamines and $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$ in methanol give macrocyclic Schiff-base complexes which were characterized by elemental analysis, UV–Vis, magnetic susceptibility, IR and mass spectrometry. The mass spectrum of complexes confirm the monomeric [1 : 1 : 2] (dialdehyde : diamine: $Cu(NO_3)_2 \cdot 3H_2O$ or $Cu(ClO_4)_2 \cdot 6H_2O$) nature (Scheme 2). The crystals were unsuitable for single crystal X-ray structure determination and are insoluble in most common solvents, including water, ethanol, ethyl acetate and acetonitrile; however, suggested structures of the complexes are shown in figures 1 and 2.

3.1. *IR spectra*

The IR spectra of the complexes show ν(C=N) at 1685 cm^{-1} and the absence of a ν(C=O) peak at 1700 cm^{-1}, indicative of Schiff's base condensation. All of the complexes show ν(C=N) bands at ca 1645 cm^{-1}, due to coordination of azomethine nitrogens to copper [22, 23]. The presence of several bands associated with nitrate vibrations clearly identifies coordinated nitrate. The absorptions at ca 1460–1452 (ν_5), 1300 (ν_1) and 1040 (ν_2) cm^{-1} suggest the presence of bidentate nitrate; an intense band at ca 1384 cm^{-1} attributable to ionic nitrate is also present [24–26]. The IR spectra clearly demonstrated that the COC and CCO stretching vibrations are altered, compared to ligands, due to conformational changes. The C–O–C absorption is shifted to lower wavenumber in complexes providing more evidence of complexation [27]. The spectra of all the Cu(II) complexes are dominated by bands between 2955–2828 cm^{-1} due to ν(Alph.-CH) groups. A band appearing in the 1198–1088 cm^{-1} region was assigned to ν(R–O) [28]. Also, infrared spectra of the Cu(II) complexes exhibit an intense band at ca 1100 cm^{-1} along with a weak band at ca 625 cm^{-1} assigned to uncoordinated perchlorate for the perchlorate complexes [29]. The ν(Ar–C=C) show very strong bands in the 1494–1489 and 1458–1456 cm^{-1} range.

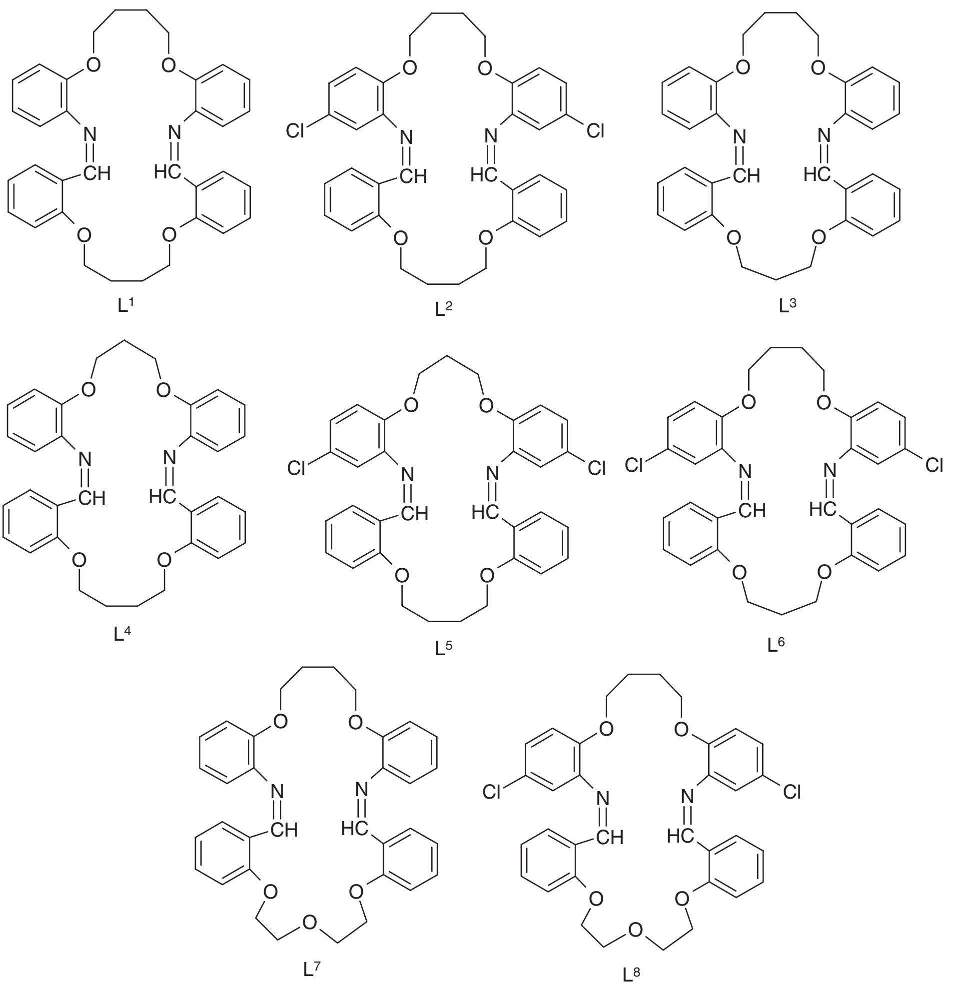
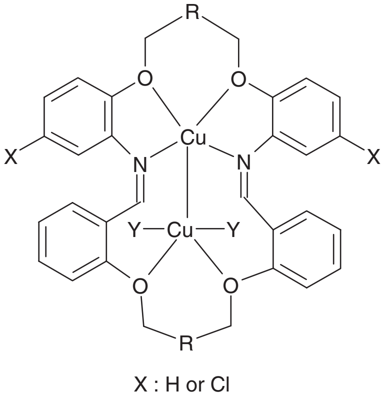


Figure 1. Structure of the ligands.



X : H or Cl
Y : NO_3 or ClO_4

Figure 2. Suggested structure of the complexes.

Conclusive evidence of the bonding is also shown by new bands at 554–527 cm^{-1} and 490–454 cm^{-1} assigned to ν(Cu–O) and ν(Cu–N) stretching vibrations [30].

3.2. ^{13}C and ^{1}H NMR spectra

The ^{13}C NMR spectra of complexes in the range ca 30 ppm are attributed to CH_2CH_2, ca 65 ppm to OCH_2, ca 190 ppm to imine carbon (HC=N) and ca 110–165 ppm to aromatic carbons. The ^{1}H NMR spectra show a singlet in the range ca 10.5 ppm attributable to imine protons (HC=N), multiplets ca 7.0–8.0 ppm to aromatic protons, pentet ca 2.5 ppm to CH_2CH_2 protons, a triplet ca 4.2 ppm to OCH_2 protons, a triplet ca 3.9 ppm to OCH_2Ph and a triplet ca 4.2 ppm to OCH_2Ph [31, 32] (Supplementary data).

3.3. *Electronic absorption spectroscopy*

The electronic spectra of the complexes in DMSO show absorption bands at ca 270 and 320 nm, indicative of benzene and other chromophores present in the complexes. A moderately intensive band at ca 320 nm is due to n–π* transition and the strong band in the range 270–280 nm is due to π–π* [31–33].

3.4. *Magnetic studies and conductivity measurements*

All the complexes are diamagnetic and binuclear [33]. Conductivity measurements of the complex 10^{-3} M in DMSO resulted in Λ_M value of 148–201 $\Omega^{-1}\,mol^{-1}\,cm^2$, indicating a 1 : 2 electrolyte [34].

3.5. *Mass spectra*

The fragments observed in the mass spectrum of the binuclear Cu^{II} complexes are given in the Supplementary data.

4. Conclusion

The 14 Schiff base macrocyclic binuclear Cu^{II} complexes were prepared and characterized by elemental analyses, IR and UV–Vis spectra, ^{13}C and ^{1}H NMR spectra, conductivity measurements, magnetic susceptibility and mass spectra. General structures of the complexes are shown in figure 2. The complexes probability have bipyramid geometry around the central metal ions.

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