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Synthesis and Characterization of Copper(II) Complexes of New Potentially Binuclear Schiff Base Ligands

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Three new decadentate potentially binucleating Schiff base ligands have been synthesized by condensation of 3,5-di-*tert*-butyl salicylaldehyde with branched EDTA like hexamines, which, in terms of their structure, corresponded to dimethylene, tetramethylene and hexamethylene-linked 1,5-diamino-3-aza-pentane units. These ligands have two sets of quinquedentate coordination sites separated by polymethylene diamines. The ligands have been characterized by IR, ^{1}H and ^{13}C NMR, UV-Vis and elemental analysis data. The binuclear Cu(II) complexes of these ligands have been prepared and their spectral properties have been studied.

Key Words: Binuclear ligands, Copper(II) complexes, Hexamine, Schiff base.

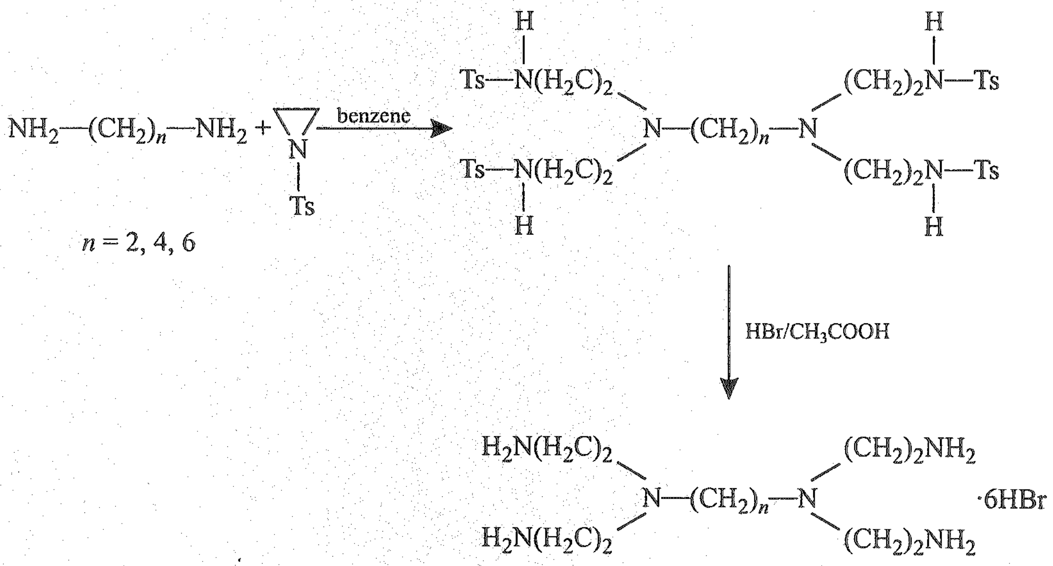
INTRODUCTION

In recent years the study of binuclear copper(II) complexes has been a subject of considerable interest because of their structural, magnetic and catalytic properties. Some of these complexes already have some interesting applications, *e.g.*, in catalytic oxidation reactions and electrochemical reduction processes[1–3], in metalloenzyme-mediated catalysis[4] and asymmetric catalysis[1–5].

In the development of the synthetic strategy of binuclear systems an important role is played by the Schiff bases owing to their relatively easy preparation, through the well known condensation reaction of formyl or carbonyl derivatives with a primary amine and their versatility in metal complexation. To this aim suitable keto and/or amine precursors have been prepared[6, 7].

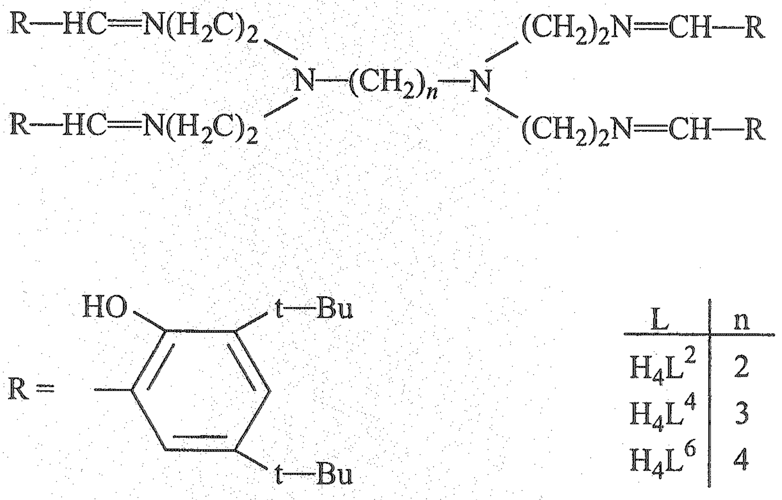
According to the results of previous workers[8, 9] the binuclear Cu(II) complexes containing open chain quinquedentate chelating groups exhibit the catalytic activities. The catalytic activity of these complexes, with a flexible bridge, is highly dependent on the length and flexibility of the bridging groups and also on the flexibility of the chelating group. In recent years there has been considerable and growing interest in the coordination chemistry of transition metal complexes with bulky di-*t*-butylate salen class ligands prepared from ethylene, polymethylene, cyclohexylene and aromatic diamines[10–13]. But transition metal complexes with bulky salen ligands derived from flexible EDTA type hexamines,

$(H_2NCH_2CH_2)_2N\text{-}(CH_2)_nN(CH_2CH_2NH_2)_2$ (n = 2, 4, 6) **(Scheme-1)** and 3,5-di-*t*-butylsalicylaldehyde have not yet been extensively studied.



Scheme-1

As a part of our investigation into complexes of binuclear ligands capable of encapsulating metal ions[14] in the present work a new series of binucleating ligands with two quinquedentate sites separated by polymethylene diamines **(Scheme-2)** have been prepared from the condensation of 3,5-di-*t*-butyl salicylaldehyde with various branched EDTA like hexamines which, in terms of their structure, corresponded to dimethylene, tetramethylene and hexamethylene-linked 1,5-diamino-3-aza-pentane units.



L	n
H_4L^2	2
H_4L^4	3
H_4L^6	4

Scheme-2

EXPERIMENTAL

All chemicals and solvents were of reagent grade quality and were used without further purification. 3,5-Di-tert-butyl salicylaldehyde was prepared from commercially available 2,4-di-tert-butylphenol according to literature[15].

N,N,N′,N′-tetrakis(2-aminoethyl)ethane-1,2-diamine hexahydrobromide (ten. 6HBr),N,N,N′,N′-tetrakis(2-aminoethyl)butane-1,4-diamine hexahydrobromide (ttmd. 6HBr) and N,N,N′,N′-tetrakis (2-aminoethyl)hexane-1,6-diamine (thm. 6HBr) were prepared by reaction of the appropriate linear diamines with *N*-tosylaziridine in benzene at room temperature for 3 days followed by detosylation with HBr/AcOH as described previously[16]. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance 300 MHz spectrometer. IR spectra were recorded as KBr pellets, using Unicam Galaxy Series FTIR 5000 spectrophotometer. Electronic spectra were measured on a Perkin-Elmer Lambda 15 UV-Vis spectrophotometer.

General procedure for synthesis of H_4L^n ligands: The ligands were readily prepared by the following general procedure. 3,5-Di-*t*-butyl salicylaldehyde (2.05 mmol) in methanol (10 mL) was added to a stirring solution of hexamine hexahydrobromide (0.5 mmol) and triethylamine (3 mmol) in methanol (15 mL). The solution was refluxed for 2 h and volume of methanol was reduced to 10 mL. The yellow products were washed with small amount of water and recrystallized from a mixture of hexane/methanol (1/1) and dried *in vacuo.*

H_4L^2: N,N,N′N′-tetrakis(3,5-di-*tert*-butyl salicylideneaminoethyl)ethane-1-2-diamine: Anal. %: Calcd. (Found) for $C_{70}H_{108}N_6O_4$: C, 76.70 (76.50); H, 9.85 (9.90); N, 7.66 (7.50). ^{13}C NMR, δ_C (CDCl$_3$, ppm): 166.7, 158.2, 139.9, 136.6, 126.6, 125.8, 117.9, 58.1, 55.7, 54.0, 35.0, 34.1, 31.5, 29.5.

H_4L^4: N,N,N′,N′-tetrakis(3,5-di-*tert*-butyl salicylideneaminoethyl)butane-1,4-diamine: Anal. %: Calcd. (Found) for $C_{72}H_{112}N_6O_4$: C, 76.93 (76.70); H, 9.96 (10.10); N, 7.47 (7.70). ^{13}C NMR, δ_C (CDCl$_3$, ppm): 167.0, 158.1, 140.0, 136.6, 126.9, 125.9, 117.8, 58.1, 55.0, 54.0, 35.0, 34.1, 31.5, 29.4, 18,9.

H_4L^6.: N,N,N″,N″-tetrakis(3,5-di-*tert*-butyl salicylideneaminoethyl)hexane-1,6-diamine: Anal. %: Calcd. (Found) for $C_{74}H_{116}N_6O_4$: C, 77.14 (76.90); H, 10.07 (10.30); N, 7.29 (7.10). ^{13}C NMR, δ_C (CDCl$_3$, ppm): 169.7, 157.7, 140.7, 136.7, 127.9, 126.7, 117.5, 58.2, 54.5, 53.8, 35.0, 34.2, 31.5, 29.6, 21.4, 15.3.

General procedure for synthesis of Cu_2L^n complexes: To a stirring warm solution of H_4L^n (0.5 mmol) and NEt$_3$ (3 mmol) in CH$_3$Cl (3 mL) and EtOH (20 mL), copper(II) acetate monohydrate (1 mmol) in hot methanol (10 mL) was added. The resulting mixture was heated at *ca.* 50–55°C with stirring for about 40–50 min and allowed to cool to room temperature. The precipitated product was collected by filtration, washed several times with methanol and recrystallized from methanol/chloroform and dried in air.

$Cu_2L^2 \cdot H_2O$ (1): Anal. %: Calcd. (Found) for $C_{70}H_{108}N_6O_5Cu_2$: C, 67.92 (67.70); H, 8.56 (8.70); N, 6.78 (6.50); Cu, 10.27 (9.78).

$Cu_2L^4 \cdot H_2O$ (2): Anal. %: Calcd. (Found) for $C_{72}H_{110}N_6O_5Cu_2$: C, 68.31 (68.20); H, 8.69 (8.80); N, 6.63 (6.50); Cu, 10.04 (9.90).

$Cu_2L^6 \cdot 1.5H_2O$ (3): Anal. %: Calcd. (Found) for $C_{74}H_{115}N_6O_{5.5}Cu_2$: C, 68.21 (68.00); H, 8.82 (9.00); N, 6.45 (6.40); Cu, 9.75 (9.40).

RESULTS AND DISCUSSION

The binuclear Schiff base ligands have been prepared by condensation reaction of the appropriate hexamines with 3,5-di-*t*-butyl salicylaldehyde in methanol

(Scheme-2). These ligands can incorporate suitable metal ions, such as Cu(II). The ligands and complexes were isolated as solids and readily characterized.

The infrared spectra of ligands and complexes taken in the region 4000–400 cm^{-1} are all similar and provide some information regarding the bonding in the compounds. The bands assigned are shown in Table-2.

TABLE-1
ANALYTICAL DATA FOR H_2L^n AND Cu_2L^n (n = 2, 4, 6)

Compd.	Colour	Yield (%)	Elemental analysis (%) Calcd. (Found)		
			C	H	N
H_4L^2	Yellow	84	76.70 (76.50)	9.85 (9.90)	7.66 (7.50)
H_4L^4	Yellow	78	76.93 (76.70)	9.96 (10.10)	7.47 (7.70)
H_4L^6	Yellow	79	77.14 (76.90)	10.07 (10.30)	7.29 (7.10)
$Cu_2L^2 \cdot H_2O$	Green	72	67.92 (67.70)	8.56 (8.70)	6.78 (6.50)
$Cu_2L^4 \cdot H_2O$	Green	73	68.31 (68.20)	8.69 (8.80)	6.63 (6.50)
$Cu_2L^6 \cdot 1.5H_2O$	Green	68	68.21 (68.00)	8.82 (9.00)	6.45 (6.40)

TABLE-2
IR AND ELECTRONIC SPECTRAL DATA FOR H_4L^n AND Cu_2L^n (n = 2, 4, 6)

Compd.	IR spectra (cm^{-1})					Electronic spectra λ_{max} (nm)
	ν(C=N)	ν(C–O)	ν(–CH$_2$–N=C)	ν(Cu–O)	ν(Cu–N)	
H_4L^2	1632	1275	1171	–	–	274, 325, 430
H_4L^4	1632	1277	1175	–	–	274, 326, 425
H_4L^6	1630	1273	1175	–	–	274, 325, 427
Cu_2L^2	1620	1317	1169	460–354	545–494	230, 277, 334, 395, 652
Cu_2L^4	1613	1310	1171	432–351	550–491	235, 274, 341,398, 645
Cu_2L^6	1614	1320	1170	420–345	552–490	234, 270, 347, 407, 640

A medium intensity broad band at 3100–2600 cm^{-1} in the spectra of free ligands, due to ν(OH) of the intramolecularly bonded N·····HO, is lacking in the spectra of the complexes, indicating deprotonation of the salicylaldehyde moiety of H_4L^n.[13] The IR spectra of the ligands and complexes all contained a strong band in the region 1632–1630 cm^{-1} attributable to the azomethine group[17]. Complexation was accompanied by a bathochromic shift in the ligand core frequency, indicating the bonding of imine nitrogens to Cu(II). In the IR spectra of the ligands also a strong band was observed in the region 1280–1269 cm^{-1}. This may be assigned to the C—O (phenolic) stretching vibration[18]. After the coordination of the ligand to the metal ion these bands are shifted to high frequency (1320–1317 cm^{-1}), indicating possibly a slightly stronger than normal single bond in C—O, presumably by a resonance in the ring[19]. In addition, the ligands and complexes exhibit a series of bonds in the region 1240–1150 cm^{-1} may be assigned to methylene group adjacent to imine nitrogen (—H_2C—N═C) stretching vibrations. The position of these bands remains largely unchanged upon coordination of the ligands to the metal ions[18]. The IR spectra of all the complexes show two absorption bands in the far infrared region, 460–340 cm^{-1} and 560–490 cm^{-1}, which are assignable to ν(Cu—O)and ν(Cu—N) vibrations, respectively[22].

Electronic absorption spectral data of H_4L^n ligands are very similar to each other because of their structural identity (Table-2). Their electronic spectra in DMF solutions along with bands assigned to intraligand $\pi \to \pi^*$ and $n \to \pi^*$ transitions also display the absorption maxima at 425–430 nm attributable to an $n \to \pi^*$ transition of dipolar zwitter ionic keto-amine tautomeric structures of ligands[20, 21].

The electronic spectra of Cu_2L^n complexes in DMF solution exhibit broad bands in the 410 and 640 nm regions. The band at 400 nm corresponds to a charge-transfer transition which involves the Cu(II) ion and both, the imine and phenolate, groups of the ligand. The less intense band at approximately 640 nm is assigned to the expected *d-d* transition involving Cu(II) ion[23].

The ^1H NMR spectra of ligands in $CDCl_3$, presented in Table-3, are in accordance with their formulations. All H_4L^n ligands showing a singlet in the region δ 13.73–13.95 ppm are removed by shaking with D_2O and may be assigned to hydrogen bonded salicylic proton. The CH═N imine protons exhibit a singlet resonance in the region δ 8.35–8.41 ppm in keeping with their identity. Protons of the methylene groups attached to a nitrogen atom, N—CH_2— show resonances in the region δ 3.63–4.08 ppm. Salicylic protons at 4 and 6 positions appeared as meta-coupled doublets from ring protons on salicylic moiety at δ 7.08 ppm and δ 7.39–7.40 ppm. The spectra of H_4L^n contain only two single resonances at δ 1.29–1.31 and at δ 1.43–1.47 ppm corresponding to each of the unique *t*-Bu groups.

TABLE-3

^1H NMR SPECTRAL DATA FOR THE H_4L^n (δ ppm) (n = 2, 4, 6)

	H_4L^2		H_4L^4		H_4L^6	
—OH	13.95	s, 4H	13.73	s, 4H	13.90	s, 4H
—CH═N—	8.35	s, 4H	8.38	s, 4H	8.41	s, 4H
C_6H_2	7.40	d(2.15), 4H	7.39	d (2.27), 4H	7.39	d (2.22), 4H
C_6H_2	7.08	d(2.15), 4H	7.08	d (2.27), 4H	7.08	d (2.22), 4H
—$C(CH_3)_3$	1.31	s, 36H	1.31	s, 36H	1.29	s, 36H
	1.47	s, 36H	1.46	s, 36H	1.43	s, 36H
—CH_2—N═C—	3.63	8H	4.08	8H	3.74	8H
Others	2.85. 8	H ; 2.69, 4H	2.89	8H; 2.62, 4H	2.84,	8H; 2.63. 4H
			1.28	4H	1.12–1.26	8H

Conclusion

The syntheses of potentially binuclear Schiff base ligands and their copper(II) complexes were confirmed with elemental analysis, IR, ^1H NMR, ^{13}C NMR and electronic spectra. On the basis of spectroscopic data, it can be concluded that all the complexes assume a binuclear structure.

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