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SYNTHESIS AND CHARACTERISATION OF SOME NOVEL SCHIFF BASE METAL COMPLEXES WITH POLYOXYETHYLENE GLYCOLS AS SUBSTITUENTS

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ABSTRACT

Two novel Schiff base ligands containing oxyethylene glycol chains, *N*-(4-pentaoxyethyleneglycolphenyl)salicylaldimine, HL^1, and *N*-(4-nonaoxyethyleneglycolphenyl)salicylaldimine, HL^2, were synthesized by reacting salicylaldehyde with 4-aminophenylpentaoxyethylene glycol or 4-aminophenylnonaoxyethylene glycol, respectively. Their nickel(II), copper(II) and cobalt(II) complexes were synthesised. The novel Schiff base ligands and their complexes were characterized by elemental analyses, ^{1}H NMR, infrared and

UV-Visible spectra. The analytical data show that the metal to ligand ratio in the complexes is 1:2.

INTRODUCTION

Transition metal complexes derived from Schiff bases have occupied a central role in the development of coordination chemistry[1-11]. Metal chelates of salicylaldehyde Schiff base have proven to be an excellent model system to study the enzymatic reactions of pyridoxal phosphate, because both of these systems effectively catalyze transamination and racemination reactions[12,13]. In this paper, we report the preparation of the two novel Schiff bases, *N*-(4-pentaoxyethyleneglycolphenyl)salicylaldimine, HL^1, and *N*-(4-nonaoxy ethyleneglycolphenyl)salicylaldimine, HL^2, shown in Fig. 1 and examine their complexing ability with Ni(II), Cu(II) and Co(II) ions.

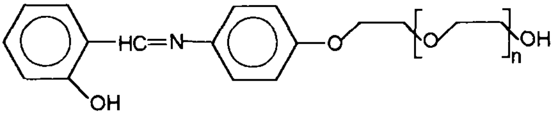
EXPERIMENTAL

Materials

Nickel(II) chloride hexahydrate, copper(II) chloride dihydrate, cobalt(II) chloride hexahydrate, 4-nitrophenol and salicylaldehyde were obtained from Merck. Tetraethylene glycol and polyethylene glycol were purchased from Fluka. 4-nitrophenylpentaoxyethylene glycol and 4-nitrophenylnonaoxy ethylene glycol were synthesised and purified in the laboratory[14,15]. Hydrazine monohydrate (Merck), metallic sodium (Merck), ethylene glycol (Merck), Pd/C 10% (Merck) were used as received. All solvents were reagent grade and used without purification.

Physical Measurements

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 elemental analyser. ^{1}H NMR spectra of the ligands were taken



n = 4 (HL^1) and n = 8 (HL^2)

Fig. 1. Suggested Structure of the Ligands HL^1 and HL^2

on a Bruker ARX 250 MHz spectrometer. The vibrational spectra in the 4000-400 cm^{-1} range were measured using KBr disks on a Bomem Michealson MB-series spectrophotometer. The electronic spectra in the 200-800 nm range were recorded in dioxan on a Shimadzu UV 2101 spectrophotometer.

Synthesis of 4-Aminophenylpentaoxyethylene Glycol, A

A 500 mL round bottom single neck flask was charged with 20 g (0.057 mol) of 4-nitrophenylpentaoxyethylene glycol, 16 mL (0.32 mol) of $NH_2NH_2.H_2O$, 1.68 g Pd/C (10%) and 100 mL of n-butanol. The reaction mixture was refluxed for 3 1/2 h under an atmosphere of nitrogen. The contents were then filtered to remove the catalyst. The solvent was concentrated under reduced pressure until the volume was 20 mL. The remaining solution was stored overnight at room temperature, resulting in the precipitation of white crystals. The product was removed by filtration, washed with diethyl ether and then dried in vacuo. It is soluble in ethyl alcohol and water and insoluble in chloroform and diethyl ether. Yield, 9 g (49%).

Synthesis of *N*-(4-Pentaoxyethylene Glycolphenyl)salicylaldimine, HL^1

To a solution of 0.25 g (0.754 mmol) 4-aminophenylpentaoxyethylene glycol (A) in 35 mL of ethyl alcohol was added 0.092 g (0.759 mmol) salicylaldehyde and the resulting mixture was refluxed for 2 h. After standing at room temperature for 1 h, the resulting yellow precipitate was seperated by filtration and washed with cold ethyl alcohol. The crude product was crystallized from ethyl alcohol and then dried in vacuo. The product is soluble in dioxan and hot ethyl alcohol. Yield, 0.22 g (66%).

Synthesis of 4-Aminophenylnonaoxyethylene Glycol, B

To a solution of 4-nitrophenylnonaoxyethylene glycol (20 g, 0.037 mol) in 150 mL of n-butanol was added 16 mL (0.32 mol) of hydrazine monohydrate and 1.68 g Pd/C (10%). This mixture was refluxed for 5 h under a nitrogen atmosphere. The contents were filtered to remove the catalyst. The solvent was concentrated under reduced pressure until the volume was 20 mL. The remaining solution was stood overnight at room temperature, resulting in the precipitation of white crystals. The product was removed by filtration, washed with diethyl ether and then dried in vacuo. It is soluble in ethyl alcohol and water and insoluble in chloroform and diethyl ether. Yield, 0.22 g (66%).

Synthesis of N-(4-Nonaoxyethylene Glycolphenyl)salicylaldimine, HL^2

This Schiff base ligand was prepared by the condensation of 0.5 g (1 mmol) of 4-aminophenylnonaoxyethylene glycol (B) with 0.122 g (1 mmol) of salicylaldehyde in 35 mL of ethyl alcohol by boiling the mixture under reflux for 3 h. After standing at room temperature for 3 h, the resulting yellow precipitate was seperated by filtration and washed with cold ethyl alcohol. The crude product was crystallized from ethyl alcohol and then dried in vacuo. The product is soluble in dioxan and hot ethyl alcohol. Yield, 0.35 g (58%).

Synthesis of the Complexes

To a hot solution of 2.0 mmol of the ligand (0.70 g of HL^1 or 1 g of HL^2) in ethyl alcohol (35 mL), an ethyl alcohol solution (25 mL) of 1.00 mmol of metal chloride (0.237 g $NiCl_2.6H_2O$, 0.170 g of $CuCl_2.2H_2O$ or 0.238 g $CoCl_2.6H_2O$) was added. After this addition, an alcoholic ammonia solution (1 N) was added dropwise to adjust the pH of the solution to the range 4-5 when the complexes started to precipitate. The mixture was then refluxed for 3 1/2 h, cooled to room temperature and the precipitate was filtered, washed several times with water, followed with ethyl alcohol and dried in vacuo over $CaCl_2$.

RESULTS AND DISCUSSION

We report here the reaction of salicylaldehyde with 4-amino phenylpentaoxyethylene glycol or with 4-aminophenylnonaoxyethylene glycol to give the two Schiff base ligands HL^1 and HL^2 and the synthesis of nickel(II), copper(II) and cobalt(II) complexes of these ligands, $Ni(L^1)_2$, $Cu(L^1)_2$, $Co(L^1)_2$, $Ni(L^2)_2$, $Cu(L^2)_2$ and $Co(L^2)_2$. The ligands HL^1 and HL^2 have been reacted with Ni(II), Cu(II) and Co(II) chlorides to give the complexes as described by the following equation.

$$MCl_2.\,mH_2O + 2HL^x \xrightarrow[\text{reflux}]{\text{EtOH}} M(L^x)_2 + 2HCl + mH_2O$$

(m = 2, 6 and x = 1 and 2)

The physical properties and elemental analyes of the ligands and complexes are recorded in Table I, their suggested structure is shown in Fig. 2.

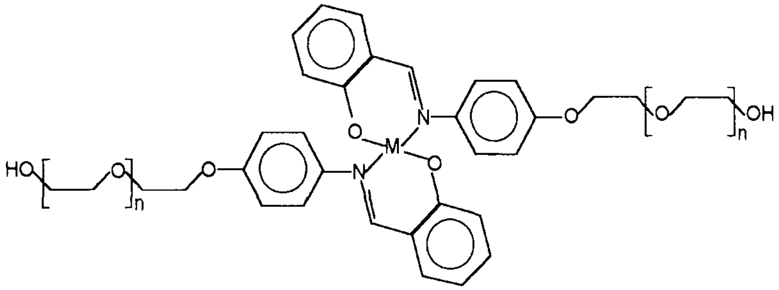
^{1}H NMR Spectra

The proton magnetic resonance spectral data of the ligands are compiled in Table II. The phenyl protons of salicylaldehyde and the aniline moiety are observed as broad signals at δ 6.80-7.40 ppm range in the the Schiff base ligands. The singlet at 8.70 ppm has been assigned to the proton of the

TABLE I.

The Elemental Analytical Results, Yields and Melting Point of the Ligands and Complexes.

Compound	Empirical Formula	Mol. Wt.	Yield %	M. p. °C	Elemental Analyses, % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
A	$C_{16}H_{27}N_1O_6$	329	49	75	58.35	8.20	4.25	58.47	8.13	4.33
HL[1]	$C_{23}H_{31}N_1O_7$	433	66	220	63.74	7.10	3.23	64.00	7.30	3.30
$Ni(L^1)_2$	$C_{46}H_{60}N_2O_{14}Ni$	922.5	71	280	59.83	6.50	3.03	59.90	6.20	3.35
$Cu(L^1)_2$	$C_{46}H_{60}N_2O_{14}Cu$	927.5	64	290	59.10	6.46	3.01	59.25	6.73	2.95
$Co(L^1)_2$	$C_{46}H_{60}N_2O_{14}Co$	918	69	300	59.80	6.50	3.03	59.45	6.05	3.15
B	$C_{24}H_{43}N_1O_{10}$	505	66	81	57.03	8.51	2.77	57.17	8.43	2.84
HL^2	$C_{31}H_{47}N_1O_{11}$	609	58	230	61.08	7.71	2.29	61.00	7.40	2.37
$Ni(L^2)_2$	$C_{62}H_{92}N_2O_{22}Ni$	1274.5	75	287	60.28	7.21	2.19	60.35	7.35	2.01
$Cu(L^2)_2$	$C_{62}H_{92}N_2O_{22}Cu$	1279.5	69	295	60.02	7.19	2.18	59.85	6.95	2.40
$Co(L^2)_2$	$C_{62}H_{92}N_2O_{22}Co$	1275	67	310	60.20	7.21	2.19	60.27	7.43	2.03



n = 4 (HL^1) and 8 (HL^2)

M = Ni(II), Cu(II) and Co(II)

Fig. 2. Suggested Structure of the Complexes

azomethine group. The signal at δ 11.20 ppm is assigned to the phenolic O-H protons in the ligands[16]. The ^1H NMR spectra of the ligands showed a triplet at 4.09 ppm for Ar-OCH_2- protons. The protons of the oxyethylene glycol group are found to appear as multiplet in the range of δ 3.62-3.75 ppm[17]. The results were consistent with those reported for oxyethylene groups attached to benzene rings as crown ethers or chains[18-24].

IR Spectra

A comparison of the characteristic IR absorption bands (Table III) of the ligands with those of the corresponding Ni(II), Cu(II) and Co(II) complexes reveals the following important features. In the infrared spectra of the Schiff base ligands, a relatively sharp band appearing at 3450 cm^{-1} may be assigned to the hydrogen bonded ν(OH) vibrations[25]. In the spectra of the metal complexes this band has disappeared, showing the chelation of the phenolic oxygen to the metal atom after deprotonation, suggesting the formation of a metal-oxygen bond.

TABLE II.

^{1}H NMR Data (δ, ppm) of the Compounds.

ligand	Ar-OH	-CH=N-	Ar-C-H	$-CH_2OH$	$Ar-OCH_2-$	OCH_2CH_2O
A	----	----	6.83-7.42 (m, 4 H)	4.78 (s, 1 H)	4.11 (t, J = 5.25 Hz, 2 H)	3.60-3.73 (m, 18 H)
B	---	----	6.79-7.43 (m, 4 H)	4.77 (s, 1 H)	4.08 (t, J = 5.21 Hz, 2 H)	3.65-3.74 (m, 34 H
HL^1	11.20 (bs, 1 H)	8.70 (s, 1 H)	6.80-7.40 (m, 8 H)	4.80 (s, 1 H)	4.09 (t, J = 5.23 Hz, 2 H)	3.62-3.75 (m, 18 H)
HL^2	11.20 (bs, 1 H)	8.72 (s, 1 H)	6.80-7.43 (m, 8 H)	4.80 (s, 1 H)	4.10 (t, J = 5.23 Hz, 2 H)	3.62-3.75 (m, 34 H

bs: broad singlet, s: singlet, t: triplet, m: multiplet

TABLE III. Infrared Data for the Schiff Base Ligands and Their Complexes (KBr, cm^{-1}).

Compound	υ(O-H)	υ(Ar-H)	υ(C-H)	υ(C=N)	υ(C-O-C)	υ(M-N)	υ(M-O)
A	3445 vs	3017 m	2929 s	----	1083 s	----	----
HL^1	3450 vs	3013 m	2929 s	1624 m	1080 s	----	----
$Ni(L^1)_2$	3392 s	3013 m	2930 s	1620 w	1090 s	565 w	425 w
$Cu(L^1)_2$	3373 s	3010 m	2900 s	1614 w	1095 s	560 w	423 w
$Co(L^1)_2$	3380 s	3000 m	2896 s	1618 w	1091 s	562 w	420 w
B	3440 vs	3015 m	2933 s	----	1080 s	----	----
HL^2	3450 vs	3000 m	2920 s	1624 m	1100 vs	----	----
$Ni(L^2)_2$	3390 s	3025 m	2890 s	1620 w	1100 s	565 w	425 w
$Cu(L^2)_2$	3395 s	3000 m	2930 s	1625 w	1110 s	560 w	420 w
$Co(L^2)_2$	3390 s	3010 m	2930 s	1620 w	1115 s	562 w	420 w

vs: very strong, s: strong, m: medium, w: weak

TABLE IV. The Electronic Absorption Spectral Data for the Schiff Bases and Their Complexes.

Compound	λ_{max}(nm) (ε, M^{-1} cm^{-1})
A	243 (5500), 287 (1300)
B	247 (5600), 293 (1270)
HL^1	240 (6300), 294 (3500), 364 (3300)
$Ni(L^1)_2$	244 (6000), 361 (1700), 409 (1300)
$Cu(L^1)_2$	240 (6500), 293 (1700), 360 (1350)
$Co(L^1)_2$	240 (6500), 294 (3400), 362 (1400)
HL^2	242 (7000), 295 (3450), 360 (3000)
$Ni(L^2)_2$	246 (6200), 293 (2560), 356 (1600)
$Cu(L^2)_2$	242 (4000), 290 (3200), 356 (1900)
$Co(L^2)_2$	242 (4170), 291 (3350), 355 (1690)

A strong band at 1080-1100 cm^{-1} due to the C-O-C linkage[17,26] and a band at 1624 cm^{-1} assignable to ν(C=N) are also observed in the spectrum of the two ligands[27]. A band of medium intensity at 1624±10 cm^{-1} in the complexes may be assigned to the ν(C=N) vibration which originally appears in the ligands at 1624 cm^{-1}. Several new bands at 565 cm^{-1} and 425 cm^{-1} may be attributed to ν(M←N) and ν(M-O), respectively, and tend to support the proposed coordination in the complexes[28,29].

Electronic Spectra

The UV and visible spectra of the Schiff bases (Table IV) show two intense maxima at 240 and 294 nm due to $\pi \rightarrow \pi^*$ transitions within the benzene ring and the double bond of the azomethine group, respectively. The third band observed around 360 nm may be assigned to the $n \rightarrow \pi^*$ transitions of the C=N chromophore.

The first two bands remain unchanged in the corresponding complexes, whereas an appreciable hypsochromic shift is observed in the third band due to the polarisation in the C=N bond caused by metal-ligand π electron interaction[16].

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