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Synthesis and Characterization of Schiff Base Complexes of Cobalt(II)

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Two neutral Co(II) complexes have been synthesized from the Schiff bases derived from salicylaldehyde and *n*-aminopropane. In this study the syntheses, characterization and some of the theoretical investigations of two Co(II) complexes with two ligands 4-[(4-nitrophenyl)azo]-N-propylamine-salicylaldimine [HL^1] and 4-[(4-chlorophenyl)azo]-N-propylamine-salicylaldimine [HL^2] have been described. The structures of these compounds have been investigated by their microanalytical, FT-IR, UV-Vis studies. The spectral data of the two Co(II) complexes exhibit square-planar geometry.

Key Words: Synthesis, Characterization, Co(II), Schiff base complex.

INTRODUCTION

Schiff bases derived from condensation of aldehydes or ketones with amines represent an important class of complexing agents. Schiff base ligands and the corresponding metal ion complexes find interest in organic, bioorganic and inorganic chemistry. The transition metal ions have a great deal of interest in the synthesis and characterization of transition metal Schiff base chelates for their importantce as catalysts in many reactions such as carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis[1–3]. Transition metal complexes with bidentate ligands containing hydroxyl groups have attraction; most importantly, the bidentate (N, O) coordination sites are suitable for synthesis of square-planar, coplanar or tetrahedral configuration[4].

In recent years considerable interest has been shown in the syntheses of compounds with nonlinear optical property (NLO), because of their importance as dye lasers in laser technology and optical devices[5–9]. Recently the author has reported the syntheses, electronic structure and nonlinear optical properties (NLO) of two new Schiff base ligands[10]. In previous works, some theoretical calculations on the structure of Cd(II) complex with a bidentate symmetrical Schiff base ligand was reported[11]. In this work as part of a continuing project the author has designed two new Co(II) complexes with HL^1 and HL^2 ligands from her recent work[10] and will explain some of the structural properties of HL^1 and HL^2 Co(II) complexes [Co $(L^1)_2$ and Co $(L^1)_2$] (Figs. 1 and 2).

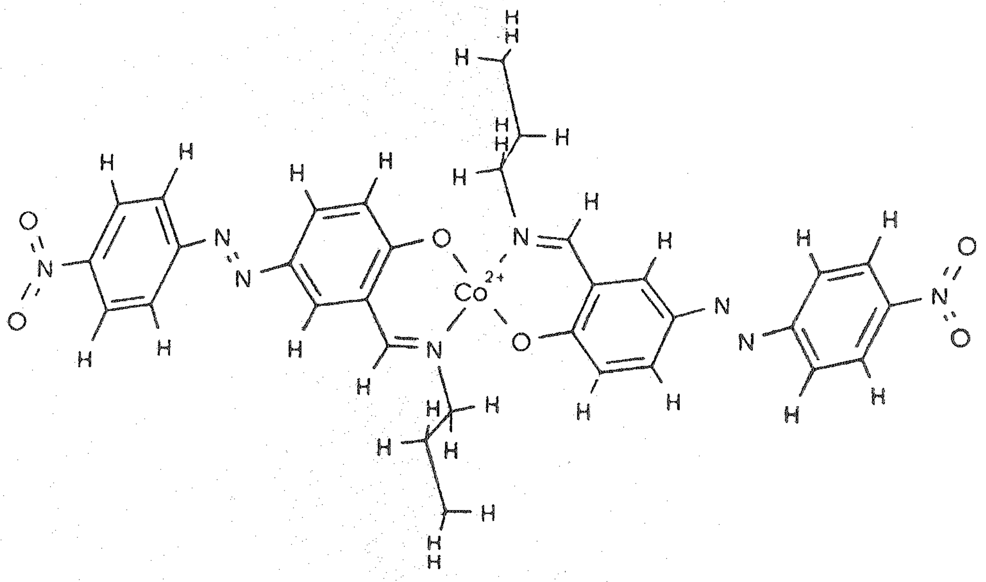


Fig. 1. Structure of Co(II) $(L^1)_2$ complex

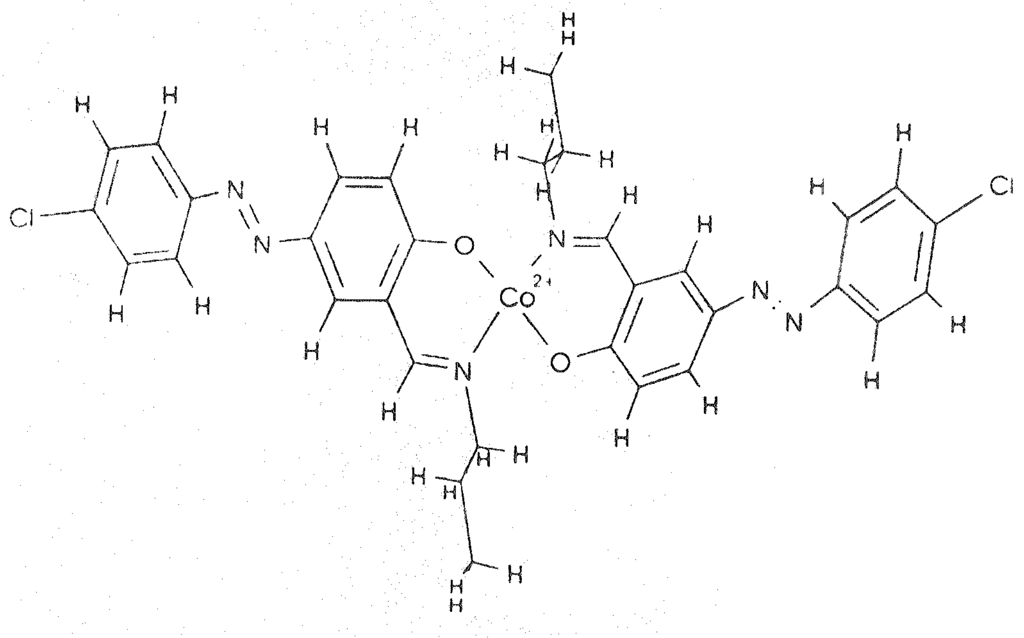


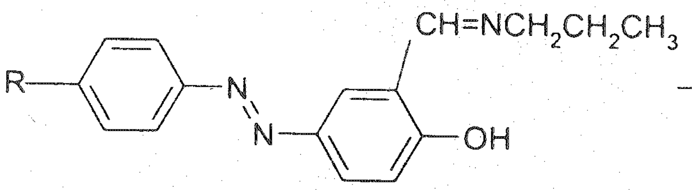
Fig. 2. Structure of Co(II) $(L^2)_2$ complex

EXPERIMENTAL

All reagents used for the preparation of ligands and their complexes were of Merck or Fluka products. All solvents were freshly purified by standard procedures and commercial chemicals such as *n*-propylamine, salicylaldehyde, 4-chloroamine and 4-nitroaniline were used as received.

Preparation of HL^1 and HL^2 Schiff base ligands: Two Schiff base ligands

4-[(4-nitrophenyl)azo]-N-propylamine-salicylaldimine [HL^1] and 4-[(4-chlorophenyl) azo]-N-propylamine-salicylaldimine [HL^2] (Fig. 3) were prepared according to the methods described in literature[12].



Schiff base	HL^1	HL^2
R	NO_2	Cl

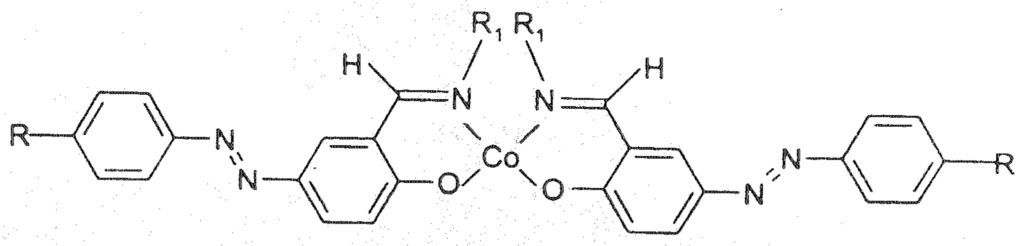
Fig. 3. Structures of HL^1 and HL^2 Schiff-base ligands

Preparation of mono azo Schiff base Co(II) complexes: A solution of 1 mmol of Co(II) acetate and 2 mmol Schiff base ligand in ethanol (20 mL) was refluxed under nitrogen gas in a dry box for *ca.* 2 h. The resulting solution was concentrated to *ca.* 10 mL, then 10 mL of light petroleum ether (60–80 mL) was added. The mixture was cooled at 0°C for *ca.* 10 h and the precipitated complexes were filtered, washed with ethanol and dried *in vacuo*. Yield for Co(L^1) 38% and for Co(L^2) 47%.

Microanalyses (C, H and N) were performed on a Perkin analyzer; UV-Vis spectra were reported in $CHCl_3$ with a Beckman Du-7000 spectrometer. FT-IR spectra were recorded on Shimadzu DR-8001 spectrophotometer in the range of 4000–500 cm^{-1} and using KBr discs. Conductivity measurements were performed using a Philips PW9509 digital instrument using DMF (dimethyl formamide) as a solvent at 25°C and melting points were obtained with a Metler PF 61 instrument. Computer was PC model Pentium-4 using Mopac 7.0 and Hyperchem 5.0 program packages[13, 14].

RESULTS AND DISCUSSION

All compounds were obtained from in suitable yields (38–47%). The analytical results and some of the physical properties of the isolated solid Co(II) complexes are listed in Table-1. The analytical data of the two complexes have good agreement with the general formula ML^2, where M = Co(II) and L = $C_{16}H_{15}N_4O_3$ or $C_{16}H_{15}N_3OCl$. The proposed structure of the complexes is given in Fig. 4.



R = Cl or NO_2 and R_1 = CH_2—CH_2—CH_3

Fig. 4. Structure of Co(II) Schiff base complexes

TABLE-1

ANALYTICAL DATA OF $Co(II)(L^1)_2$ AND $Co(II)(L^2)_2$ COMPLEXES

Compound (m.f.)	m.w. (g mol^{-1})	Colour	Yield (%)	m.p. (°C)	Analysis Found (Calcd.) %				Conductivity (ohm^{-1} cm^2 mol^{-1})[b]
					C	H	N	Co[a]	
$Co(L^1)_2$	680.93	Red	38	340.0[d]	56.40	4.10	15.90	9.10	29.40
$[Co(C_{32}H_{30}N_8O_6)]$					(56.39)	(4.40)	(16.44)	(8.65)	
$Co(L^2)_2$	659.93	Red-brown	47	291.5[d]	57.80	4.20	12.10	9.40	23.70
$[Co(C_{32}H_{30}N_6O_2Cl_2)]$					(58.18)	(4.54)	(12.72)	(8.39)	

[a]Cobalt was measured by atomic absorption Shimadzu spectrophotometer model AA-670G.
[b]Concentration *ca.* 1 × 10^{-3} M in DMF at 25°C.
[d]Decomposed.

Some of the important FT-IR spectral data for HL^1, HL^2, $Co(L^1)_2$ and $Co(L^2)_2$ are shown in Table-2.

TABLE-2

KEY FTIR (cm^{-1}) DATA FOR HL^1, HL^2 SCHIFF BASES AND THEIR Co(II) COMPLEXES

Compound	ν(O—H)	ν(C=N)	ν(Co—N)	ν(Co—O)
HL^1	3548	1622	—	—
HL^2	3540	1624	—	—
$Co(L^1)_2$	—	1604	400	478
$Co(L^2)_2$	—	1606	380	463

IR spectral data in Table-2 show the imine-stretching mode in HL^1, HL^2. Schiff-base ligands at 1624–1622 $cm^{-1}$and their Co(II) complexes are at 1606–1604 cm^{-1} confirm the presence of O—H group in the structures of the two Schiff base ligands. Spectral data indicate that when HL^1, HL^2 Schiff base ligands were coordinated with Co(II) ion, the adsorption band of O—H group was absent and absorption of C=N groups was shifted to lower frequency. The FTIR spectra of the metal chelates also show some new bonds in the region 400–380 cm^{-1} and 478–463 cm^{-1} which are probably due to the formation of (Co—N) and (Co—O) bonds respectively[15].

$Co(L^1)_2$ and Co $(L^2)_2$ are planar and paramagnetic (low spin d^7), thus having a single unpaired electron. The experimental optical spectra, relatively non-polar in $CHCl_3$ solution, showed a λ_{max} *ca.* 370–333 nm and both exhibited solvatochromism. The agreement between electronic spectral data for Co(II) complexes and theoretical data for its Schiff base ligands are very good. The semiempirical calculations in our previous work have shown that HL^1 Schiff base ligands have a large second-order nonlinear optical property, because the —NO_2 group in the structure of this ligand plays a major role in designing the NLO property for these salicylaldiminato Schiff base ligands[10, 16, 17]. The molecular hyperpolarizability β_μ of HL^1 is 18.774 × 10^{-30} esu and this amount of hyperpolarizability is comparable with that of *p*-nitroaniline (PNA, 6.3 × 10^{-30}

esu). However, the β value of $Co(L^1)_2$ compound is larger than of the HL^1 ligand by more than two to three times.

The ^1H NMR spectra of the Schiff bases in DMSO-d_6 show phenyl group multiplets at 6.9–7.8 δ range. Two peak sets 10.97 and 10.98 are attributable to the OH groups present in HL^1 and HL^2 ligands. The absence of these peaks, noted in the Co(II) complexes, indicates the loss of the —OH proton due to complexation. There are no important changes in all other signals in these complexes.

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