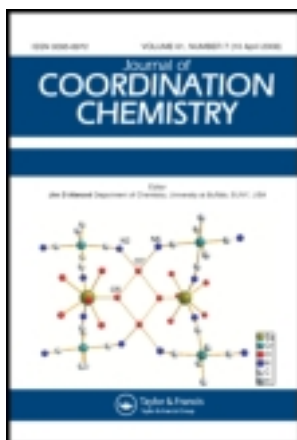


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Synthesis and characterization of nitro-Schiff bases derived from 5-nitro-salicylaldehyde and various diamines and their complexes of Co(II)

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Some neutral tetradentate N_2O_2 type complexes of Co(II) have been synthesized using Schiff bases formed by condensation of 5-nitro-salicylaldehyde with various diamines in alcohol. The nature of the ligands and complexes was established by spectroscopic techniques. The Schiff bases are bivalent anions with tetradentate ONNO donors derived from phenolic oxygen and azomethine nitrogen. IR and UV-Vis spectral data suggest that all the complexes are square-planar.

Keywords: Synthesis; Nitro-Schiff base; Ligand; Complex; Salicylaldehyde

1. Introduction

Schiff-base macroligands synthesized from reaction of dialdehydes and amino compounds [1–6] form stable complexes, perhaps selective to specific metallic ions with applications in electrochemistry, bioinorganic, antimicrobial activity, fluorescence properties, catalysis, metallic deactivators, separation processes, and environmental chemistry among others [7–14].

Preparation of new ligands is an important step in development of metal complexes, which exhibit unique properties and reactivity. For example, in asymmetric catalyst systems, small changes in donating ability of the ligand or the size of its substituents can have a dramatic effect on catalyst efficiency and enantioselectivities [15–18]. The nitro group is a strong electron-withdrawing group and due to its steric effects it has played an important role in affecting the reactivity and enantioselectivities in asymmetric cyclopropanation and allylic alkylation reactions [19].

In continuation of our research on preparation of Schiff bases [20–22] and their complexes [23–26], we decided to prepare new Schiff bases containing electron-withdrawing substituents.

This article describes the synthesis and spectroscopic characterization of several nitro-Schiff bases and their complexes with transition metal ions. The corresponding

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materials were characterized by spectroscopic (IR, UV-Vis, ^1H - and ^{13}C -NMR, mass spectra) and physical (melting point) data.

2. Experimental

2.1. Materials

Chemicals were purchased from Fluka and Merck Chemical Companies. Solvents were purified by standard methods and dried before use by conventional methods. 5-Nitro-salicylaldehyde has been prepared and characterized by our previously reported procedure [26].

2.2. Physical measurements

IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FTIR spectrophotometer. ^1H - and ^{13}C -NMR spectra were recorded in d_6 -DMSO on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded on a Finnigan MAT 44S by electron ionization (EI) mode with an ionization voltage of 70 eV. Melting points were obtained with a Yanagimoto micromelting point apparatus and are uncorrected. Purity determination of the substrates and reaction monitoring were accomplished by thin layer chromatography (TLC) on silica-gel polygram SILG/UV 254 plates (from Merck Company).

2.3. Synthesis of ligands

To prepare *N,N'*-bis(5-nitro-salicylidene)-1,3-propanediamine (L2), a solution of 5-nitro-salicylaldehyde (0.67 g, 4 mmol) in methanol (20 mL) was slowly added over a solution of 1,3-diaminopropane (0.15 g, 2 mmol) in the same solvent (20 mL). The mixture was stirred at 30°C for 45 min and the precipitated product was obtained as a yellowish orange solid. The crude solid was filtered off and washed with ethanol twice (2×20 mL) and recrystallized from a dichloromethane/methanol mixed solvent to give pure crystals, conversion 98%, yield 90.5% (0.67 g), m.p. 210–213°C.

2.4. Synthesis of Schiff-base complexes of Co(II)

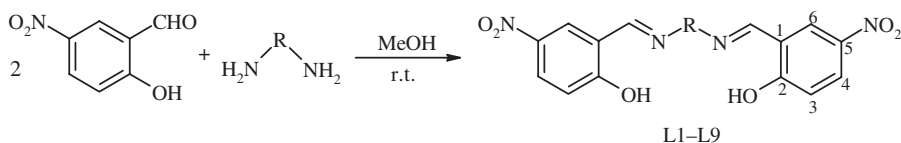
A flask containing a stirred suspension of cobalt(II) acetate tetrahydrate (0.25 g, 1 mmol) in methanol (20 mL) was purged with nitrogen, warmed to 50°C, *N,N'*-bis(5-nitrosalicylidene)-1,6-hexanediamine (L4) (0.42 g, 1 mmol) was added in one portion, and the resulting black suspension was stirred at room temperature for 90 min. Then the mixture was filtered under reduced pressure and the collected solid was washed with diethyl ether and dried in air to give dark green crystalline complex (L4-M) which was purified by recrystallization from chloroform, yield 87.0% (0.43 g).

3. Results and discussion

The tetradentate Schiff bases were prepared by condensation of 5-nitro-salicylaldehyde with various diamines in methanol (scheme 1). When 2 mol of 5-nitro-salicylaldehyde and 1 mol diamine were reacted, the corresponding products (L1–L9) were obtained under mild conditions; confirmation of these products was demonstrated by spectroscopic and physical data (table 1).

To prepare complexes, the Schiff bases were treated with cobalt(II) acetate in equal mole amounts at low temperature in methanol (scheme 2). The reactions proceeded without reflux under mild conditions preventing oxidation of metal(II) to metal(III). The progress of reaction was monitored by TLC. After disappearance of the ligand on TLC, the products were collected (table 2).

Complexes were insoluble in water and most organic solvents, but soluble in DMF and DMSO. The electron-withdrawing paranitro substituents on phenyl cause the

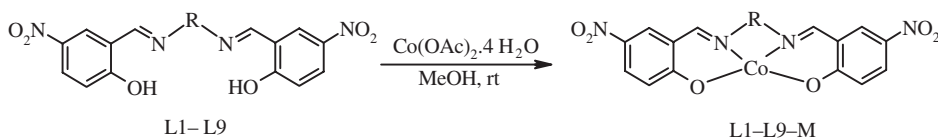


Scheme 1. Synthesis of nitro-Schiff bases from nitro-salicylaldehyde.

Table 1. Reactions for preparation of nitro-Schiff bases.

R	Ligand	Time (min)	Yield (%) ^a	m.p (°C)
(CH ₂) ₂	L1	45	91.0	272–274
(CH ₂) ₃	L2	45	90.5	210–213
(CH ₂) ₄	L3	45	88.5	173–176
(CH ₂) ₆	L4	45	88.0	159–161
(CH ₂) ₈	L5	45	85.0	161–164
	L6	40	92.0	261–264
	L7	50	92.0	193–195
	L8	50	93.0	281–283
	L9	50	91.5	204–206

^aIsolated yields.



Scheme 2. Preparation of complexes from nitro-Schiff bases.

Table 2. Reactions for preparation of nitro Schiff-base complexes with Co(II) acetate.

Ligands	Products	Time (min)	Yield (%) ^a	m.p (°C)
L1	L1-M	80	89.0	>350
L2	L2-M	85	90.0	>350
L3	L3-M	90	88.5	312–315
L4	L4-M	90	87.0	295–300
L5	L5-M	100	85.0	282–286
L6	L6-M	75	91.5	>330
L7	L7-M	90	88.0	274–276
L8	L8-M	100	88.5	>350
L9	L9-M	100	90.0	255–258

^aIsolated yields.Table 3. UV-Vis spectral data (DMF, nm) and IR bands (cm⁻¹) of ligands and their complexes with Co(II).

Entry	$n \rightarrow \pi^*$ (C=N)	$\pi \rightarrow \pi^*$ (arom. ring)	d → d	$\nu(\text{C}=\text{N})$	$\nu(\text{Ph}-\text{O})$	$\nu(\text{O}-\text{H})$	$\nu(\text{NO}_2)$	$\nu_{(\text{M}-\text{N}, \text{M}-\text{O})}$
L1	416	282	—	1649	1328	3384	1521, 1334	—
L1[Co(II)]	433	274	576	1624	1332	—	1522, 1347	470–496
L2	408	287	—	1643	1325	3353	1530, 1342	—
L2[Co(II)]	429	280	570	1617	1338	—	1534, 1352	464–490
L3	420	285	—	1658	1333	3338	1524, 1351	—
L3[Co(II)]	414	272	563	1625	1324	—	1520, 1343	460–487
L4	409	284	—	1640	1326	3355	1533, 1340	—
L4[Co(II)]	430	271	581	1602	1339	—	1537, 1350	469–484
L5	411	295	—	1647	1321	3340	1527, 1355	—
L5[Co(II)]	419	285	574	1615	1329	—	1529, 1353	458–494
L6	412	287	—	1641	1327	3359	1534, 1348	—
L6[Co(II)]	432	282	584	1600	1334	—	1527, 1349	462–481
L7	401	298	—	1642	1328	3294	1531, 1357	—
L7[Co(II)]	428	284	561	1603	1338	—	1529, 1352	459–495
L8	405	289	—	1648	1322	3358	1531, 1343	—
L8[Co(II)]	430	279	570	1607	1336	—	1530, 1354	460–490
L9	414	308	—	1645	1322	3354	1538, 1356	—
L9[Co(II)]	426	302	587	1614	1335	—	1537, 1359	462–487

phenolic OH to become more acidic, affecting the conditions of synthesis. Basically, the aldehyde group becomes more active, increasing yields of the obtained Schiff bases. Furthermore, formation of complexes occurred in short reaction times and without reflux. Ligands involving nitro are more stable in acidic and basic solution with solubility in hot water. The UV-Vis and IR data of ligands and their complexes are indicated in table 3.

3.1. Electronic spectra

Electronic spectra of complexes show intense absorptions in UV-region assigned to charge transfer from π orbitals of the donor to d orbitals of the metal, $d \rightarrow \pi^*$ [27], and intraligand $n \rightarrow \pi^*$ transition [28].

In complexes, the $n \rightarrow \pi^*$ transitions due to azomethine shift to lower energy, indicating the atom of imine group appears to be coordination of nitrogen [29]. The bands due to the $n \rightarrow \pi^*$ transition of the C=N appear between 380 and 410 nm in ligands and shift to lower energy upon complexation. The bands between 320 and 350 nm are assigned as an $n \rightarrow \pi^*$ transition involving C=N and benzene. The remainder of the observed bands at about 290–320 nm are assigned as $\pi \rightarrow \pi^*$ type transitions involving molecular orbital located on the phenolic chromophore.

A common feature of these spectra is the presence of three absorptions, two at lower frequencies ascribed to $\pi \rightarrow \pi_1^*$ and $\pi \rightarrow \pi_2^*$ transitions, in increasing energy [30]. Theoretical analysis of transitions of salicylideneimine suggests that the additional peak found at higher frequencies corresponds to the $\pi \rightarrow \pi_3^*$ transition, where π_3^* is the third unoccupied π molecular orbital [31]. For the nitro-substituted ligands, considerable overlap between $\pi \rightarrow \pi_2^*$ and $\pi \rightarrow \pi_3^*$ is observed. The $\pi \rightarrow \pi_1^*$ transition has been assumed to be localized mainly on the azomethine chromophore [32, 33] and $\pi \rightarrow \pi_2^*$ band has been assigned to a transition involving mainly π molecular orbitals of the aromatic ring of salicylideneimine moiety [34, 35].

In the ligands, these bands were observed at 280–320 nm. This blue shift in the complexes may be due to electron donation from oxygen of the phenoxy group to the metal [36]. An apparent bathochromic shift of the $\pi \rightarrow \pi^*$ transitions is observed upon metal complex formation. All spectra of the metal complexes exhibit a d \rightarrow d band in the visible region whose maximum absorption lie in the wavelength range 555–595 nm (table 3).

3.2. IR spectra

Infrared spectra of the ligands and their respective metal complexes were very similar (table 3). The ligands and complexes were characterized mainly using imine and phenolic bands. The band at 1610–1640 cm^{-1} is characteristic of the azomethine nitrogen in the free ligand. The lowering in this frequency to 1590–1615 cm^{-1} in all the complexes indicates involvement of the azomethine nitrogen in coordination with metal [37, 38]. The disappearance of $\nu_{\text{O-H}}$ in spectra of all complexes indicates that chelation takes place via the phenolic OH.

The compounds containing water exhibit characteristic medium intensity absorption bands in the region 3200–3500 cm^{-1} , while these are absent in unsolvated compounds. Spectra of the ligands exhibit medium intensity bands at 2500–3360 cm^{-1} assigned to intramolecular H-bonding (O–H \cdots N). In spectra of the complexes (table 3) these bands disappear. In the ligands, bands at 1311–1350 cm^{-1} can be assigned to phenolic (C–O) vibrations [39–41]. In the metal complexes, these bands displace to higher or lower frequency, indicating chelation of oxygen to the metal. Upon coordination bands at 1512 and 1341 cm^{-1} that are typical of nitro in nitro ligands undergo minor changes, suggesting that the nitro is not coordinated to cobalt. In all the complexes, bands at 617–461 cm^{-1} and 461–420 cm^{-1} can be attributed to the $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$ modes, respectively.

3.3. Magnetic properties of complexes

Magnetism of transition metal complexes is strongly influenced by coordination geometry and electron configuration [42]. It should be noted that simple paramagnetism

will be found only if there is sufficient magnetic dilution. This is the case if, due to the presence of large organic ligands, the paramagnetic centers are well separated, thus avoiding cooperative interactions of the ferro and antiferromagnetic types.

Magnetic susceptibility amounts of the complexes, summarized in Supplementary material, show different magnetic behavior, also evident in magnetization curves, which show the net magnetization, M , of a sample *versus* applied field strength, H . Two hysteresis loops for $\text{L1}[\text{Co(II)}]$ complex is provided in Supplementary material.

3.4. ^1H - and ^{13}C -NMR spectra

Spectra of all the complexes (Supplementary material) were recorded in DMSO-d_6 solution at 400 MHz and chemical shifts are in units of ppm relative to TMS. DMSO resonates near 2.0 ppm. The ^1H NMR spectra of the Schiff bases show the following signals: a broad singlet for phenolic O–H group at δ 14.0–14.5 ppm, a singlet for azomethine hydrogen ($\text{HC}=\text{N}$) at δ 8.9 ppm, a doublet for Ar–H at δ 8.5–8.6 ppm, a dd for Ar–H at δ 8.1–8.2 ppm and a doublet for Ar–H at δ 6.9–7.1 ppm. The absence of peak near 14.0 ppm in the metal(II) complexes indicates loss of –OH on complexation [43].

Intramolecular hydrogen bonding accounts for the high frequency of the ortho-phenolic hydrogen signals in all the Schiff bases. By comparing the ^1H -NMR spectra of all the Schiff bases with those of their corresponding cobalt(II) complexes, there is a downfield shift in the frequency of azomethine protons of aromatic bridge and upfield shift in the aliphatic bridge, confirming coordination of cobalt to both groups.

4. Conclusions

We have synthesized and characterized new nitro-Schiff-base complexes derived from the Co(II) acetate and new N_2O_2 donor nitro-Schiff bases. Advantages for preparation of these complexes are simplicity of synthesis and high stability of complexes in the presence of nitro groups on ligands. Magnetic properties for all complexes confirm presence of Co(II) without oxidation during complex formation.

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