UDC: 546.96-386.057
546.73-386.057
Conference Paper

Synthesis and Characterization of Ru(II) and Co(III) Complexes with Schiff Bases Derived from Salicylaldehyde

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Abstract

New complexes of Ru(II) and Co(III) have been synthesized with Schiff bases, 2-((phenylimino)methyl) phenol and 2-((4H-1,2,4-triazol-4-ylimino) methyl) phenol. Ru(II) complexes have been synthesized from $[Ru(NH_3)_6]$ Cl_2, an ammonia complex formed from the reduction of ruthenium(III) chloride with hydrazine, whereas Co(III) complexes have been synthesized from $[Co(NH_3)_6]$ Cl_3. In both cases the bidentate ligand of the Schiff base replaces two ammonia molecules in the ammonia complex. The reactions are carried out at room temperature. Schiff bases and complexes have been characterized by elemental analysis, IR and UV-VIS spectra. The results have shown that the ammonia complexes have reacted with the Schiff bases in molar ratio 1:2 (metal: ligand). Ru(II) complexes are molecular (neutral), whereas cobalt complexes are cationic. The results are in accordance with an octahedral environment around the Ru(II) and Co(III) ions.

Keywords: Ruthenium and Cobalt Schiff base complexes; IR and UV-VIS spectroscopy

Introduction

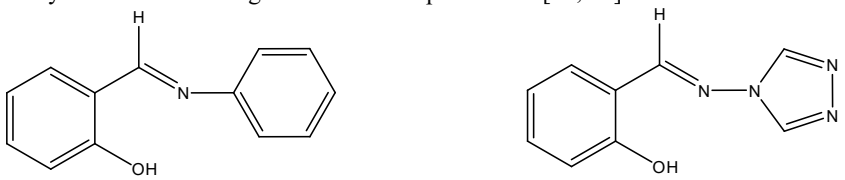
Schiff bases are organic molecules derived from amines and carbonyl compounds, which contain azomethine group. They are versatile ligands that may be used for different purposes. For example, Hodnett and Dunn (1970), El-masry et al. (2000), Jarrahpour et al. (2007) and Hania (2009) investigated antitumoral, antimicrobial, antibacterial, antifugal, antiviral and anticancer properties of Schiff bases as free ligands [1-5]. Schiff bases are also used as ligands in the complexes with transit metals [6,7]. Many metal complexes with various Schiff bases have been intensively studied mostly because of their pharmaceutical, microbiological and biochemical importance. The metal complexes generally exhibit significant activity against Gram-positive bacteria, especially S. aureus [8,9]. Cobalt complexes with salicylideneimine ligands exhibit considerable inhibition of bacterial growth [10,11], while ruthenium corresponding complexes kill pathogens as well [9]. On the other hand, some ruthenium complexes have shown promising anticancer activity and have been continuously investigated as the most important non-platinum based anticancer candidates in clinical trials [12,13].
We started synthesis of some new Ru(II) and Co(III) complexes with Schiff bases derived from salicylaldehyde. Here we report the preparation and characterization of Ru(II) neutral and Co(III) cationic complexes with 2-((phenylimino)methyl) phenol and 2-((4H-1,2,4-triazol-4-ylimino) methyl) phenol.

Materials and methods

All reagents and chemicals were used as obtained from Aldrich and Merck. The infrared spectra were determined on a Perkin-Elmer System 2000 FT-IR spectrometer with KBr pellets. The UV-Vis spectra were recorded on LKB, Ultraspec 5300.

Preparation of Schiff bases

Schiff bases were synthesized according to the literature procedures [14, 15].



a) b)

Scheme1. Schiff bases: a) 2-((phenylimino)methyl)phenol (HSB^{I}) b) 2-((4H-1,2,4-triazol-4-ylimino)methyl)phenol (HSB^{II})

Preparation of complexes

Ru(II) complex with HSB^{I}

To a water solution containing 1mmol of $[Ru(NH_3)_6]$ Cl_2, previously prepared as reported in the literature [16], was added 2mmol of HSB^{I} dissolved in 10 mL ethanol. The mixture was left for 2h at room temperature, with continuous stirring. Dark brown precipitate was formed after adding diethyl ether. The product was filtered and washed with diethyl ether. Yield: 60%. IR (KBr, cm^{-1}): 3210, 1607, 1423, 1094, 756, 684, 601. UV/VIS (λ_{max}/nm): 285, 302, 335, 348, 382, 540.

Ru(II) complex with HSB^{II}

To a water solution containing 1mmol of $[Ru(NH_3)_6]$ Cl_2 was added 2mmol of HSB^{II} dissolved in 15 mL methanol. The mixture was left for 2h at room temperature, with continuous stirring. The precipitate formed was filtered and washed with diethyl ether. Yield: 66%. IR (KBr, cm^{-1}): 3117, 1618, 1516, 1453, 1393, 1270, 1156, 1063, 756, 622. UV/VIS (λ_{max}/nm): 264, 281, 299, 318, 349, 387, 509.

Co(III) complex with HSB^{I}

$[Co(NH_3)_6]$ Cl_3, synthesized according to literature [17], was dissolved in 10mL of water. 2mmol HSB^{I} were dissolved in 5mL of water containing 10mL NaOH (c = 3M). The two solutions were mixed and left for 2h at room temperature, with continuous stirring. When adding NH_4Cl, brown precipitate was formed. After filtering, the product was washed with diethyl ether. Yield: 61%. IR (KBr, cm^{-1}): 3312, 1618, 1535, 1444, 1321, 1146, 898, 756. UV/VIS (λ_{max}/nm): 260, 283, 303, 336, 350, 388, 417, 576. Elemental Anal. Calc. for $C_{26}H_{26}CoN_4O_2$ (%): C, 64.33; H, 5.40; N, 11.54. Found (%): C, 64.10; H, 5.38; N, 11.49.

IR spectra

The IR spectra of the complexes **(1), (2), (3)** show bands at 3210, 3117 and 3312 cm^{-1} respectively, which can be attributed to NH_3 stretching vibration. A band at 1607 **(1),** 1618 **(2, 3)** cm^{-1} corresponds to the conjugated C=N stretching vibration. In the complexes, the Schiff bases are coordinated, therefore the C=N stretching frequency is displaced to a lower frequency, ~1620 cm^{-1}. The decrease in the frequency indicate a decrease in the C=N bond order due to the coordination of the azomethine nitrogen to the metals [18]. The IR spectra of the complexes **(1), (2)** and **(3)** are shown in figure 1, figure 2 and figure 3 respectively.

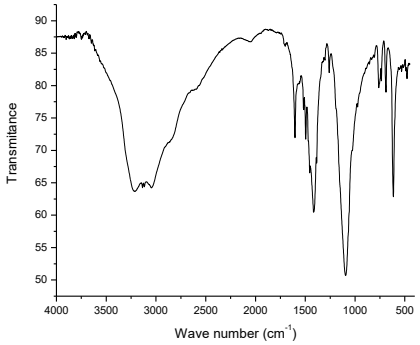


Fig. 1. The IR spectra of complex **(1)**

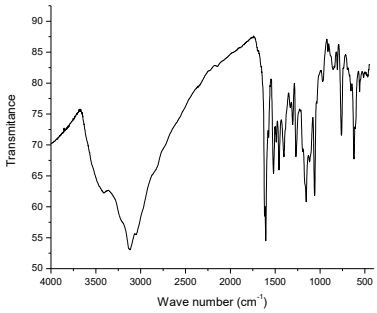


Fig. 2. The IR spectra of complex **(2)**

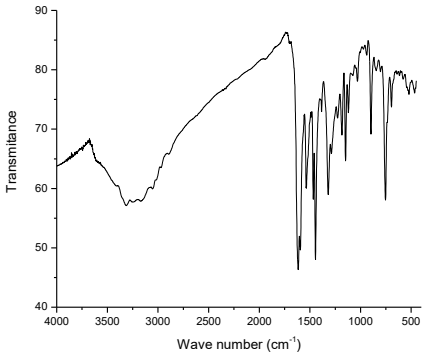
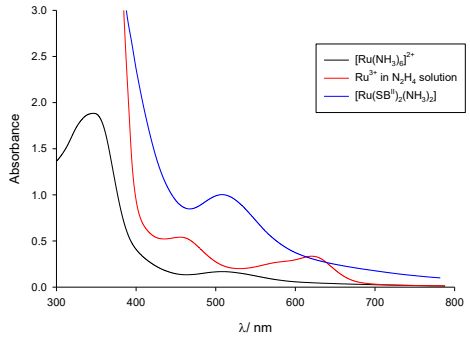


Fig. 3. The IR spectra of complex **(3)**

UV/VIS spectra

The comparison of the UV/VIS spectra of Ru^{3+} in hydrazine solution, hexammineruthenium(II) and complex **(2)**, are shown in figure 4. This figure clearly demonstrates the reduction of Ru^{3+} with hydrazine to $[Ru(NH_3)_6]^{2+}$, and the presence of ruthenium(II) in complex **(2)**. Ru^{3+} in these spectra absorbs at 622 nm, while $[Ru(NH_3)_6]^{2+}$ absorbs at 512 nm. This value of Ru^{2+} corresponds with the absorption of Ru^{2+} in complex **(2)** at 509 nm [19].

For the free ligand HSB^{I}, as shown in figure 5, the bands in the region of 294-435 nm in UV/VIS spectra are attributed to a $\pi \rightarrow \pi^*$ transition of the azomethine chromophore and to a $\pi \rightarrow \pi^*$ transition of the benzene ring of salicylaldehyde. The d-d bands of Co(III) are not observed due to the overlapping of the ligand bands with those of the metal. These bands should be low in intensity in the region of 500-600 nm [20].



Fi 4. The UV/VIS spectra of Ru^{3+} in hydrazine solution, ($[Ru(NH_3)_6]^{2+}$ and Ru^{2+} in complex **(2**

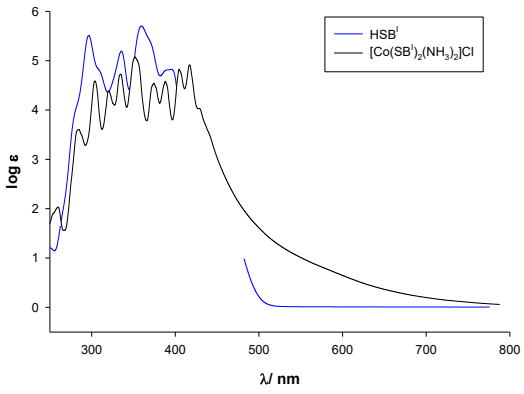
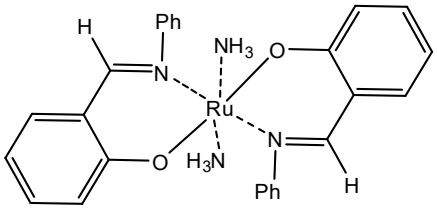


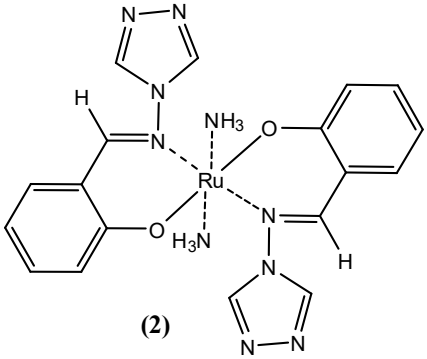
Fig. 5. The UV/VIS spectra of HSB^{I} and complex **(3)**

Based on these results, the formula $[MeL_2(NH_3)_2]$ (Me = Ru(II), Co(III); L = HSB^I, HSB^{II}) was suggested for the complexes. Co (III) complex with HSB^I is cationic, therefore the chloride ion acts as counterion.



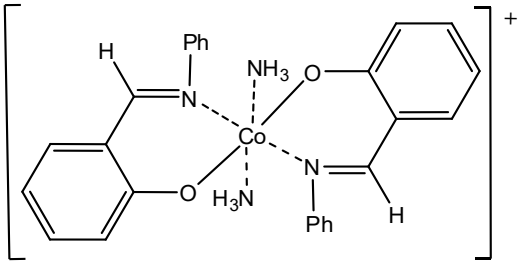
(1)

2-((phenylimino)methyl)phenolruthenium(II)



(2)

2-((4H-1,2,4-triazol-4
ylimino)methyl)phenolruthenium(II)



(3)

2-((phenylimino)methyl)phenolcobalt(III)

Scheme2. Suggested structures of the complexes

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