

Titanium(IV), Chromium(III) and Iron(III) Complexes of Schiff Base Derived from Aldehyde and Primary Amine

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Abstract : The preparation of Schiff base of salicylaldehyde and 2-amino-4-methylthiazol in ethanol over a period of 75 minutes and its complexes with TiO(IV), Cr(III) and Fe(III) ions were characterized by CHNS elemental analyses as well as molar conductivity, magnetic moments and spectroscopic tools. On basis of these studies. It is suggested that the geometry of the complexes is an octahedral. The molar conductivity data revealed them to be non-ionic in nature.

Keywords: Salicylaldehyde, 2-amino-4-methylthiazol, complexes, physiochemical tools.

Introduction

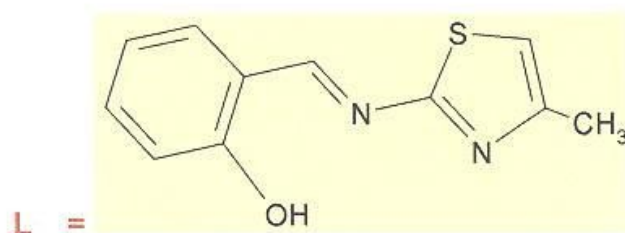
Salicylaldehyde and aminothiazol compounds can react to form Schiff base which coupled with transition and non- transition metal ions to form large amount of complexes.⁽¹⁾ Thiosemicarbazones and their complexes have received considerable attention since, because of their pharmacological properties they have numerous applications, for example as antibacterial and anticancer agents.⁽²⁾ Cobalt(II), nickel(II) and copper(II) complexes of the Schiff base derived from the reaction of salicylaldehyde with anthranilic acid or o-aminophenol have been synthesized and investigated by using different physiochemical techniques. A square planar geometrical structure was proposed for

all complexes⁽³⁾ Nickle(II) complexes with Schiff base obtained by the condensation of 1,3-propaneamine with salicylaldehyde and thiosalicylaldehyde which present as N₂OS or N₂S₂ coordination sphere have been prepared and studied.⁽⁴⁾

The aim of this work is to prepare and characterize the geometrical structures of the complexes by using some physiochemical techniques.

Results and Discussion

The condensation of salicylaldehyde and 2-amino-4-methylthiazol in ethanol yields the Schiff base, represented by the following formula:



The elemental analysis data (Table 1) are consistent with the calculated results from the empirical formula of each compound and showed the formation of 1:1 molar ratio. The molar conductance values of the complexes in 10^{-3} M DMSO solvent present the zero value. This value is a good evidence for the non-electrolytic nature, thus there is no inorganic anions are present outside the coordination sphere. The zero value also exhibits the high purity of the Schiff base complexes.⁽⁵⁾

The infrared spectra of the complexes exhibit three bands at 1609, 1594 and 1601 cm^{-1} due to ν (C=N) of azomethine. A slight change is observed for ν (C=N); 1611 cm^{-1} band after complexation, indicates the participation of the azomethine nitrogen atom in coordination.⁽⁶⁾ The spectral data of the complexes exhibit ν (OH) band in the range of 3297-3382 cm^{-1} region, which indicates the presence of water molecules in the chelate,⁽⁷⁾ Table 1. The infrared spectrum of TiO(IV) complex displays a band at 1031 cm^{-1} attributed to the presence of Ti=O vibration indicating the appearance of monomeric structures.⁽⁸⁾ The observed bands at 500-597 and 731-750 cm^{-1} are due to ν (M-N) and ν (M-O) vibrations, which are not present in the free Schiff base.⁽⁹⁾ The appearance of these bands support the involvement of nitrogen and

oxygen atoms of the Schiff base in coordination with metal ion.

The electronic spectral data of TiO(IV) chelate reveal a band at 314 nm (31847 cm^{-1}) which is due to charge transfer transition. The diamagnetic character and the intensity of the band support the presence of an octahedral structure.⁽¹⁰⁾ In octahedral ligand field, the 4F ground state of Cr(III) chelate splits into 4A_2 , 4T_1 and 4T_2 states. The spectrum of the chelate shows an intense band at 274 nm (36563 cm^{-1}) and a shoulder at 600 nm (16667 cm^{-1}). These two bands are corresponding to $\pi \rightarrow \pi^*$ and $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$ transitions. The obtained magnetic moment value of 4.40 BM which indicates the presence of three unpaired electrons in the chelate and the nature of the electronic absorption bands support the existence of an octahedral structure.⁽¹¹⁾ The magnetic moment value of 5.50 BM was obtained for Fe(III) chelate. This value indicates the presence of five unpaired electrons in the chelate. The electronic spectral data of the same chelate exhibit two bands at 327 nm (30581 cm^{-1}) and 265 nm (37665 cm^{-1}) due to charge transfer transition. The intensity of the bands and the magnetic moment value are consistent with an octahedral structure.⁽¹²⁾

Table-1: CHNS Elemental analyses, infrared and electronic spectral data of the Schiff base and its complexes

nm(cm^{-1})	ν (M-O)	ν (M-N)	ν (C-O)	ν (OH)	ν (C=N)	S%	N%	H%	C%	Schiff base/ Chelate
274 (36496), 382 (26178)	-	-	1263	3370	1611	14.70 15.20	12.84 12.19	4.58 4.84	60.60 59.97	$\text{C}_{11}\text{H}_{10}\text{N}_2\text{OS}$ (L)
314 (31847)	750	512	1390	3297	1609	9.61 8.87	8.41 8.62	3.90 4.79	39.64 38.78	[TiO(L).(OH). H_2O] H_2O
274 (36563), 600 (16667)	750	500	1375	3382	1594	8.96 8.75	8.84 8.62	4.76 4.78	36.97 36.78	[Cr(L).(OH) ₂ . H_2O]2 H_2O
265 (37665), 327 (30581)	731	597	1390	3367	1601	9.24 8.97	8.16 8.34	4.08 4.70	38.48 38.41	[Fe(L).(OH) ₂ . H_2O] H_2O

Bold= Experimental values

Experimental

The chemicals and solvents used in this study were pure materials (BDH).

Synthesis of Schiff base

To a solution of 2-amino-4-methylthiazol (1.14 g; 0.01 mole) in absolute ethanol (50 mL), a solution of salicylaldehyde (1.22 g; 0.01 mole) in the same amount of ethanol was added and few drops of dilute HCl was added to adjust pH 2-4. After the addition was complete, the mixture was stirred for 15 min at 100 °C. The resulting solution was evaporated in vacuum to remove the solvent. The solid residue was filtered and recrystallized from n-hexane. The obtained product yielded 60%.

Synthesis of Complexes

Hot ethanolic solutions of the Schiff base (2.18 g; 0.01 mole) and the metal salts [TiOSO₄.H₂O, CrCl₃.6H₂O and FeCl₃.6H₂O] in 1:1 ratio followed by adding few drops of ammonia solution until pH ~ 6-8 were refluxed for 4 hours and the mixtures were left overnight at room temperature, which afforded products. The obtained products were dried in vacuo.

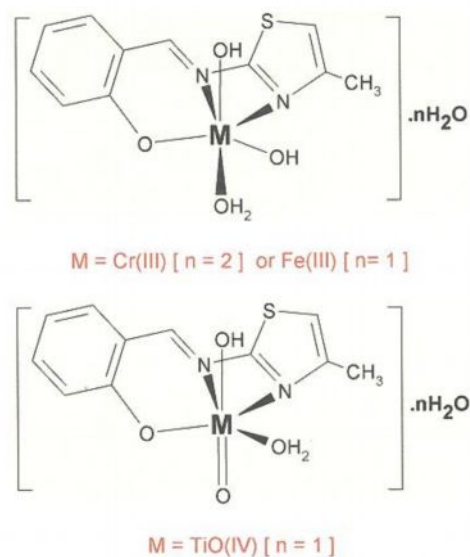
Physical measurements

The prepared Schiff base and its TiO(IV), Cr(III) and Fe(III) chelates were subjected to CHNS elemental analyses using 2400 elemental analyzer. The molar conductance measurements were carried out in DMSO solvent using digital conductivity meter CMD 650. The magnetic moment measurements of the chelates were measured using a Johnson-Mathey-Susceptometer devised by D.F. Evans, USA. The

infrared spectra of the Schiff base and its chelates were obtained by using KBr disc technique on IFS DPUS/IR spectrometer (Bruker) in the range of 4000-400 cm⁻¹. The electronic spectra of the Schiff base and its chelates were measured in DMSO solvent using UV-Vis, NIR 3101 PC.

Conclusion

From the previous results, one can suggest the following chemical structures:



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