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Synthesis and Spectral Studies of Some Transition Metal Complexes of Schiff Base

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The Schiff base has been prepared by condensing 4-[N,N-dimethylamino]benzaldehyde with *o*-aminophenol in ethanolic media, form three new metal complexes of the formulae of $[NiL(OH)(H_2O)]\cdot 5H_2O$ and $[ML(OH)_2(H_2O)_2]\cdot 4H_2O$ in which M represents Cr(III) or Fe(III) ion. These complexes were characterized by elemental analysis, molar conductance measurements, infrared and electronic spectra. The elemental analysis data exhibit the formation of 1 : 1 [M : L] ratio. The molar conductance measurements of the Schiff base complexes reveal the existence of non-electrolytic nature. Infrared spectral data display that the complexation occurs through oxygen atom of the hydroxyl group in the *o*-amino phenol ligand and the nitrogen atom of azomethine group. The electronic spectral data of the complexes suggest a square-planar geometry for Ni(II) complex and an octahedral structure for Cr(III) and Fe(III) complexes.

Key Words: Synthesis, Transition metal complexes, Schiff base.

INTRODUCTION

A series of transition metals, such as Fe(III), Co(II), etc. form complexes with Schiff bases, with theoretical and practical applications of quite varied types. Some of them are capable of reversibly binding molecular oxygen, being consequently employed as models in the study of the reversible fixation of oxygen such as its natural carriers (hemoglobins, hemocyanins, etc.).[1] Day and Ray[2] isolated a manganese(III) complex of the dibasic tridentate Schiff base derived from salicylaldehyde and *o*-amino phenol. Kohli and Bhattacharya[3] synthesized and characterized some transition metal complexes of quinoxaline-2-carboxalidine-2-aminophenol.

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In the present investigation, the synthesis and structural elucidation of Schiff base complexes from the reaction of 4-[N,N-dimethylamino]benzaldehyde with *o*-aminophenol with Cr(III), Fe(III) and Ni(II) metal ions are synthesized and characterized.

EXPERIMENTAL

All chemicals were reagent grade of BDH or Aldrich. All organic solvents used in this investigation were obtained as pure grade materials from BDH and water always used as double distilled.

Preparation of Schiff base and its metal complexes: A solution of 0.1 mol of 4-[N,N-dimethylamino]benzaldehyde in 30 mL ethanol was slowly added to a solution of the same ratio of *o*-aminophenol in the same volume of ethanol. After stirring the reaction mixture for 3 h, the precipitate was collected by filtration. Then, the product was recrystallized from ethanol and dried at room temperature.

The Schiff base metal complexes under investigation were prepared by mixing 0.01 mol (2.40, 2.67 and 2.71 g) of 30 mL of saturated ethanolic solution of the corresponding metal salts ($NiCl_2 \cdot 6H_2O$, $CrCl_3 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$) with the same ratio of 2.39 g of the Schiff base in the same amount of the same solvent. The mixture was refluxed for 2 h. If the complexes did not separate on standing, a few drops of ammonia solution were added slowly with stirring to pH = 6–8. The synthesizes complexes were filtered and washed several times with hot ethanol until the filtrate became colourless. The complexes were then dried in a desiccator over anhydrous calcium chloride (yield 60–70%).

The elemental analysis was performed on the elemental analyzer. Molar conductance measurements were carried out in DMF solvent using conductivity-meter model CMD650 digital. Infrared spectra were obtained by KBr disc technique by using IFS-25DPUS/IR spectrometer (Bruker). The electronic absorption spectra were obtained out by using a Perkin-Elmer lambda-4β spectrophotometer. All the previous analyses were done at Advanced Laboratory of Chemical Analysis, Al-Fateh University, Tripoli, Libya.

RESULTS AND DISCUSSION

The elemental analysis data of the Schiff base and its complexes are given in Table-1. The data show the formation of 1 : 1 [M : L] ratio of the formulae of $[NiL(OH)(H_2O)] \cdot 5H_2O$ and $[ML(OH)_2(H_2O)_2] \cdot 4H_2O$ [$M = Cr^{3+}$ or Fe^{3+}]. The molar conductance values of the complexes in 1×10^{-3} M solution in DMF, shown in Table-1, are in the range of 2.50–6.20 $ohm^{-1}\ cm^2\ mol^{-1}$. These values reveal the presence of a non-electrolytic nature[4].

The infrared spectral data (Table-2) exhibit a band at 1587 cm^{-1}, which is attributed to the appearance of ν(C=N). The lowering of the band as compared to the free Schiff base (1625–1586 cm^{-1}) suggests that the chelation takes place *via* the nitrogen atom of the azomethine group[5, 6]. The Ni(II) complex spectral data show the appearance of a band at 3281 cm^{-1} which is due to the presence of the hydroxyl group (OH) coordinating to the metal ion. But in the other two complexes, this band is not clear because it overlaps with the position of water molecules (3345–3200 cm^{-1})[7]. New bands appear in the range of 500–475 and 625–578 cm^{-1} which are not present in the free ligand due to the ν(M—N) and ν(M—O) vibrations[8].

TABLE-1
ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCES OF THE SCHIFF BASE AND ITS METAL COMPLEXES

Ligand/complexes	m.w.	% Analysis						MC
		C		H		N		
		Calc.	Found	Calc.	Found	Calc.	Found	
LH	239.0	75.31	75.69	6.25	5.65	5.96	5.19	–
$[CrL(OH)_2(H_2O)_2]\cdot 4H_2O$	433.0	41.57	41.40	6.70	5.95	6.50	6.48	2.50
$[FeL(OH)_2(H_2O)_2]\cdot 4H_2O$	437.0	41.20	41.64	6.64	6.00	6.40	5.55	5.70
$[NiL(OH)(H_2O)]\cdot 5H_2O$	422.7	42.58	42.51	6.38	5.83	6.62	6.33	6.20

LH = Free Schiff base
MC = Molar conductivity (ohm^{-1} cm^2 mol^{-1})

The electronic spectra of the Schiff base and its complexes were recorded in DMF and given in Table-2. The Schiff base spectral data exhibit a band in the 302–339 nm (33113–29496 cm^{-1}) range, due to the π–π transition within the azomethine group, affected by the intramolecular charge transfer within the ligand molecule. The electronic spectra of the Schiff base complexes under investigation do not resemble the free Schiff base, which is the supporting evidence for complex formation.

TABLE-2
INFRARED AND ELECTRONIC ABSORPTION SPECTRA OF THE SCHIFF BASE AND COMPLEXES

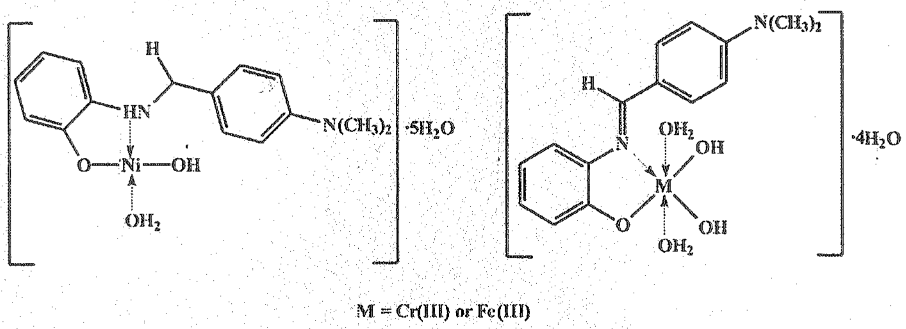
Ligand/complexes	IR (cm^{-1})					UV-Vis nm (cm^{-1})
	ν(C═N)	ν(OH)	ν(OH^W)	ν(M—O)	ν(M—N)	
LH	1625	3500	–	625	500	302 (33113) 339 (29496)
$[CrL(OH)_2(H_2O)_2]\cdot 4H_2O$	1578	–	3200	625	500	380 (26281)
$[FeL(OH)_2(H_2O)_2]\cdot 4H_2O$	1586	–	3345	586	480	395 (25316) 826.5 (12099)
$[NiL(OH)(H_2O)]\cdot 5H_2O$	1587	3250	3312	578	475	410 (24420)

The electronic spectrum of the $[NiL(OH)(H_2O)]\cdot 5H_2O$ complex reveals the appearance of absorption band at 410 nm (24420 cm^{-1}), ascribed to $^2B_{1g} \rightarrow {}^2E_{1g}$ transition, a square-planar geometry has been suggested[9].

For $[CrL(OH)_2(H_2O)_2]\cdot 4H_2O$ complex, the absorption data exhibit a band at 380 nm (26281 cm^{-1}) which is assigned to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition. The intensity of the band is consistent with an octahedral structure[10].

The iron(III) Schiff base complex, $[FeL(OH)_2(H_2O)]\cdot 4H_2O$, displays two bands at 395 nm (25316 cm^{-1}) and 827 nm (12099 cm^{-1}) attributed to the $^2A_{2g}(F) \rightarrow {}^2T_{1g}(F)$ and $^2A_{2g}(F) \rightarrow {}^2T_{2g}(F)$ transitions. Thus, the iron(III) complex data are in agreement with an octahedral geometry.

From the foregoing observations, the suggested chemical structures for the prepared Schiff base complexes under investigation are as follows:



M = Cr(III) or Fe(III)

Fig. 1. Tentative structures of the metal complexes

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