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Template Synthesis and Spectroscopic Characterization of Some Schiff Base Complexes of Transition Metal Ions

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Schiff bases having biological activities are used as ligands have been synthesized and analyzed. The synthesis of a Schiff base by condensing benzoin with 4-aminophenazone in an ethanolic medium on the addition of divalent and trivalent transition metal ions was investigated. All the metal Schiff base chelates of the formulae $[ML(OH)_x(H_2O)_w]\cdot nH_2O$, in which M represents the divalent transition metal ions of Mn, Ni and Cu and trivalent transition metal ions of Cr and Fe; x = 1 or 2, w = 0, 1 or 2 and n = 0, 5, 6 or 7 have been isolated. These chelates were characterized by elemental analysis, molar conductance measurements, infrared and electronic absorption spectra.

Key Words: Template synthesis, Spectroscopic, Metal complexes, Schiff base.

INTRODUCTION

Schiff base metal complexes play a vital role in several biological activities[1]. The synthesis and characterization of nickel and copper ion complexes of unsymmetrical tetradentate Schiff bases have been carried out by using common tools of investigation[2]. The unsymmetrical ligand environment and the nature of complexes of biological importance have also been investigated[3,4]. The growing interest in the formation of Schiff base ligand chelates involving divalent and trivalent metal ions seems to be of extra importance in understanding the chemistry, the nature, the behaviour of the Schiff base as polydentate ligand and the effect of the coordination on the biological activity of this ligand.

In spite of the fact that the amino group can interact with the carbonyl group of the benzoin to form an imino moiety, in the case of the complexes, the transition element can function as a catalyst leading to the formation of Schiff base chelates[5]. Our study in this paper aims to elucidate the preparation and the geometrical structures of some metal Schiff base chelates.

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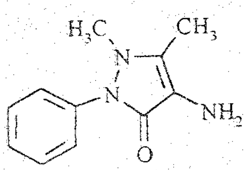
The synthesized ligands are bidentate and have applications in chemistry and pharmaceuticals. Benzoin is an ideal additive in powder coating and extended to new fields to overcome the defects of raw material and useful in the determination of the metal content in its chelates[6].

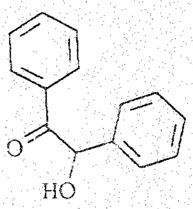
Complexes of benzointhiosemicarbazone with divalent metal ions have been studied and characterized by using different techniques[7]. The divalent metal ions of Co(II), Ni(II) or Zn(II) have the formulae of ML_2X_2 and ML_2 in their complexes, in which L represents benzointhiosemicarbazone and X represents halide or nitrate ions.

EXPERIMENTAL

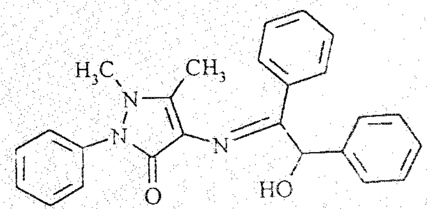
All chemicals used were reagent grade of BDH or Aldrich including $CrCl_3{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $FeCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$, 4-aminophenazone, benzoin, C_2H_5OH, DMF and $CHCl_3$ or purified by recommended methods[8]. All chemicals used in this investigation are of AnalaR grade and some were redistilled and water was used as doubly distilled.



4-Aminophenazone



Benzoin



The Schiff base

Preparation of the Schiff base chelates: The chelates of the Schiff base under investigation were synthesized by stepwise techniques.

$$M \xrightarrow{L} ML \xrightarrow{L'} M(L\text{-}L') \qquad (a)$$

L = Benzocane; L′ = 4-Aminophenazone.

Hot saturated ethanolic solution (30 mL) of the respective metal salt (0.01 mol) was mixed with an equal amount of saturated ethanolic solution (30 mL) of the first ligand (Benzoin, 2.12 g, 0.01 mol). The mixture was refluxed for 1 h and then the second ligand (4-aminophenazone, 2.03 g, 0.01 mol) in the same amount of the same solvent was added. The mixture was then refluxed for 5–6 h.

The synthesized chelates were filtered and washed several times with hot ethanol until the filtrate became colourless. The chelates were dried in desiccators over anhydrous $CaCl_2$. The yields of products were in the range of 65–82%. The infrared spectra were obtained by the KBr disc technique by using IFS-25 DPUS/IR spectrometer (Bruker) 1998Y. Molar conductivity measurements were carried out in DMF solutions using a conductivity bridge model CMD 650 digital. Electronic absorption spectra of the chelates were measured in chloroform ($CHCl_3$) solvent using a Perkin-Elmer Lambda 4B spectrophotometer with 1 cm matched silica cells. The elemental analysis and spectroscopic studies were carried out at the Advanced Laboratory of Chemical Analysis, Al-Fateh University, Tripoli, Libya.

RESULTS AND DISCUSSION

The ratio concluded in Table-1 agreed with other analyses that corresponded with the proposed chemical structures.

TABLE-1
RATIO OF THE CHELATE CONTENTS

Chelates	Metal ions	x	w	n
$[ML(OH)_x(H_2O)_w]\cdot nH_2O$	Cr(III)	2	1	7
	Mn(II)	1	2	0
	Fe(III)	2	1	5
	Ni(II)	1	0	5
	Cu(II)	1	0	6

The Schiff base metal chelates prepared in 1 : 1 ratio which separated out were in good yield and purity as indicated by acceptable satisfactory results of elemental analysis data (Table-2). The obtained elemental analysis data are in good agreement with calculated data proposed the formula $[ML(OH)_x(H_2O)_w]\cdot nH_2O$, where M represents Cr(III), Mn(II), Fe(III), Ni(II) or Cu(II) ions, L represents the Schiff base, x = 1 for Mn, Ni and Cu chelates or x = 2 for Cr and Fe chelates, w = 0 for Ni and Cu chelates, w = 1 for Cr and Fe chelates and w = 2 for Mn chelate and n = 0 (for Mn chelate), n = 5 for Fe and Ni chelates, n = 6 for Cu chelate and n = 7 for Cr chelate.

TABLE-2
ELEMENTAL ANALYSIS AND MOLAR CONDUCTANCES
OF THE SCHIFF BASE CHELATES

Chelates	% Elemental analysis						MC
	C		H		N		
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
$[CrL(OH)_2(H_2O)]\cdot 7H_2O$	40.64	40.37	5.19	6.35	7.85	8.07	6.00
$[MnL(OH)(H_2O)_2]$	54.60	54.68	4.99	4.81	11.08	10.63	2.50
$[FeL(OH)_2(H_2O)]\cdot 5H_2O$	42.94	42.94	5.47	5.96	8.79	8.35	6.50
$[NiL(OH)]\cdot 5H_2O$	45.81	45.88	4.90	5.73	8.86	8.92	4.20
$[CuL(OH)]\cdot 6H_2O$	43.64	43.76	4.61	5.87	8.75	8.51	3.70

L = Schiff base; MC = Molar Conductivity ($ohm^{-1}\ cm^2\ mol^{-1}$)

The infrared band assignments of the Schiff base chelates of Cr(III), Mn(II), Fe(III), Ni(II) or Cu(II) ions are listed in Table-3. The spectra of the $[ML(OH)_x(H_2O)_w]\cdot nH_2O$ chelate exhibiting two bands at 1601 and 1594 cm^{-1} are attributed to the presence of $\nu(C{=}N)$. The lowering of these two bands compared to the free ligand (1630 cm^{-1}) indicates a coordination of the azomethine to the metal ions through nitrogen atom[9]. The infrared spectral data of all chelates show a broad band in the range of 1625–1610 cm^{-1} which is attributed to the presence of the carbonyl group (C=O) of the 4-aminophenazone part coordinated with the metal ions resulting from the shifting in the band to lower frequency to its position in the free ligand (1650 cm^{-1})[10].

TABLE-3
INFRARED AND ELECTRONIC ABSORPTION SPECTRA OF THE SCHIFF BASE CHELATES

Chelates	IR (cm^{-1})				UV-Vis (cm^{-1})
	ν(C═N)	ν(C═O)	ν(OH^{w})	ν(M—O) ν(M—N)	
$[CrL(OH)_2(H_2O)]\cdot 7H_2O$	1570	1616	3375	547, 443	36166, 29673, 23121
$[MnL(OH)(H_2O)_2]$	1578	1610	3385	560, 450	36697, 31348, 28695
$[FeL(OH)_2(H_2O)]\cdot 5H_2O$	1562	1610	3383	593, 423	37736, 28860
$[NiL(OH)]\cdot 5H_2O$	1578	1610	3391	578, 457	37453, 23529, 16000
$[CuL(OH)]\cdot 6H_2O$	1571	1600	3390	609, 457	29027, 23753, 18382

w = water

The spectral data of all the chelates show a broad band in the range of 3390–3375 cm^{-1}; this could be assigned to ν(OH) of water molecules associated with chelate formation. The disappearance of ν(OH) of the hydroxyl group was confirmed by the absence of ν(C—OH) and δ(OH) groups[11] and the appearance of new bands in the range of 609–547 and 457–423 cm^{-1} which are attributed to ν(M—O) and ν(M—N) vibrations, respectively, existing in the chelates satisying the involvement of oxygen atom of hydroxyl group and nitrogen atom of azomethine in the complexation[12, 13].

The electronic spectral absorption bands of the chelates which are recorded in chloroform are listed in Table-3. For Cr(III) chelate, the absorption spectral data exhibit three bands at 36166, 29674 and 23121 cm^{-1}. The first band suggests the existence of $\pi \rightarrow \pi^*$ transition within azomethine (C═N) and the other two bands are assigned to ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ and ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ transitions. These transitions support the octahedral geometry[14].

The electronic spectral absorption data of Fe(III) chelate, displays two bands at 37736 and 28860 cm^{-1}. The first band suggests the existence of $\pi \rightarrow \pi^*$ transition within azomethine (C═N) and the other band is assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ transition. These data support the octahedral geometry[15]. The electronic spectral absorption data of Mn(II) chelate exhibit three bands at 36697, 31348 and 28695 cm^{-1}. The first two bands suggest the existence of $\pi \rightarrow \pi^*$ transition within azomethine (C═N) and the third band is assigned to ${}^2T_{2g} \rightarrow {}^2E_g$ transitions. These transitions also support the existence of octahedral geometry[16].

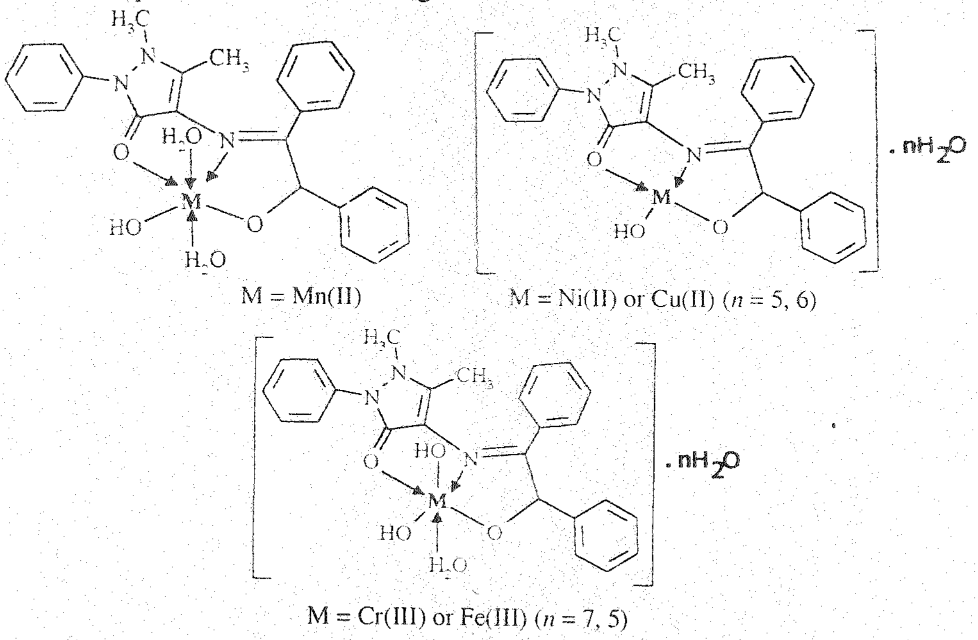
The electronic spectral absorption data of Ni(II) chelate exhibit three bands at 37453, 23529 and 16000 cm^{-1}. The first band suggests the existence of $\pi \rightarrow \pi^*$ transition within azomethine (C═N) and the other two bands are assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1A_{1g}$ transitions which are consistent with a square-planar geometry[17].

Finally, the electronic spectral absorption data of Cu(II) chelate reveal three bands at 29028, 23753 and 18382 cm^{-1}. The first band suggests the existence of $\pi \rightarrow \pi^*$ transition within azomethine (C═N) and the other two bands are assigned to $^2B_{1g} \rightarrow {}^2E_g$ and $^2A_{1g} \rightarrow {}^2B_{1g}$ transitions which support a square-planar geometry[18].

The molar conductance measurements of the Schiff base chelates of M : L (1 : 1) in 1×10^{-3}M solution in DMF solvent (Table-2) are in the range of 2.5–6.0 ohm^{-1} cm^2 mol^{-1}. These values display the presence of a non-electrolytic nature of these chelates[19].

Conclusion

From the previous analysis, we can conclude that the chelates have the general formula $[ML(OH)_x(H_2O)_w]\cdot nH_2O$ and the suggested geometrical structures of the chelates complexes are shown in Fig. 1.



M = Mn(II)

M = Ni(II) or Cu(II) (n = 5, 6)

M = Cr(III) or Fe(III) (n = 7, 5)

Fig. 1. The proposed structures of the metal chelates

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