

Preparation and Investigation of some Transition Metal Ions Schiff Base Complexes Derived from Salicylaldehyde and o-Phenylenediamine

M. M. El-ajaily¹, H. F. Bomoraiwaha² and A.A. Maihub³

¹ *Chemistry Department, Faculty of Science, Garyounis University, Benghazi-Libya*

² *Chemistry Department, Al-bayan-1 University, Benghazi-Libya*

³ *Chemistry Department, Faculty of Science, Al-Fatteh University, Tripoli-Libya*

Summary. The preparation and investigation of some Schiff base complexes derived from salicylaldehyde and o-phenylenediamine with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) ions were described. The free Schiff base and its complexes have been investigated on the basis of elemental analysis, the molar conductances and spectral data. The elemental analysis data show the formation of 1:1 [M:L] ratio. The molar conductance measurements of the prepared complexes reveal non-electrolytic nature. The infrared spectral data exhibit the coordination sites of the free Schiff base toward the metal ions under investigation. The electronic spectral data of the Schiff base and its complexes show the existence of $\pi-\pi^*$ and $n-\pi^*$ ($-\text{HC}=\text{N}$) transitions and the expected geometrical structures for all prepared complexes are thus elucidated.

Introduction

Raman et al.⁽¹⁾ prepared Schiff base complexes derived from o-phenylenediamine with acetoacetamide. All prepared complexes have been characterized using different techniques, such as; elemental analysis, infrared, electronic, proton nuclear magnetic resonance spectroscopies. The square planar, octahedral and square pyramidal geometries were suggested.

A novel Schiff base ligand derived from 2,2'-bis (p-methoxyphenylamine) and salicylaldehyde and its transition metal complexes with Mn(II), Co(II) and Cu(II) have been prepared. Their spectral properties and electrochemical behavior were investigated.⁽²⁾

Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes formed from 1-amine-5-benzoyl-4-phenyl-1H-pyrimidine-2-one with salicylaldehyde have been prepared and characterized by using several techniques. The used ligand behaves as a neutral

bidentate (NO) and tridentate (ONO) ligand forming complexes with 1:2 {M:L} ratio and an octahedral geometry was suggested for all complexes.⁽³⁾

El-Zaher,⁽⁴⁾ synthesized Ni(II), Cu(II) and Zn(II) complexes of some tetradentate Schiff bases. The investigation of these complexes is based on some physical techniques, such as; elemental analysis and spectroscopic techniques. Square planar and tetrahedral geometries were suggested for all complexes.

Bensaber et al.⁽⁵⁾ prepared some Schiff base chelates derived from 4-dimethylaminobenzaldehyde and anthranilic acid with Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) ions. The used physical techniques indicate one chelation mode through the nitrogen atom of the azomethine and (COOH) group and an octahedral geometry was suggested for Cr(III) and Fe(III) chelates and square planar for the others.

This study aims to explain the geometrical structures of some prepared transition metal complexes Schiff base ligand derived from o-phenylenediamine and salicylaldehyde.

Experimental

Chemicals

All chemicals used in this investigation were reagent grade BDH/Aldrich including some salt CrCl₃. 6H₂O, MnCl₂. 4H₂O, FeCl₃. 6H₂O, CoCl₂. 6H₂O, NiCl₂. 6H₂O, CuCl₂. 2H₂O, Ethanol, ammonium hydroxide solution, DMF, DMSO, Salicylaldehyde, o-phenylenediamine and doubly distilled water.

Preparation of Schiff base

An ethanolic solution (25 cm³) of o-phenylenediamine (0.01 mole, 1.08 g) was refluxed with the same ratio of salicylaldehyde for 2 hrs. The volume of the solution was reduced to 30% of the original volume. The obtained product (Schiff base) was filtered and recrystallized from ethanol. The purity of the product was performed by TLC technique and yield 70-80%.

Preparation of Schiff base complexes

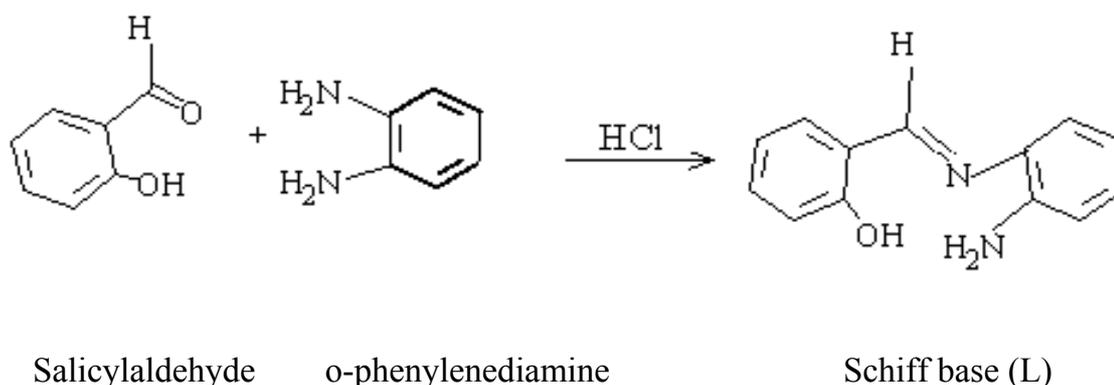
An ethanolic solution (25 cm³) of the Schiff base (0.01 mole, 2.12 g) was added to the same solutions of metal salts of CrCl₃. 6H₂O (2.66g), MnCl₂. 4H₂O (1.98 g), FeCl₃. 6H₂O (2.70 g), CoCl₂. 6H₂O (2.37 g), NiCl₂.6H₂O(2.38 g) and CuCl₂.2H₂O (1.70g). Few drops of ammonium hydroxide solution (1:1) added slowly with stirring to attain pH=8. The obtained products were refluxed for one hour. Then the separated complexes were collected by filtration and washed several times with distilled water and hot ethanol until the mother liquor becomes colorless. The products were dried and stored in a dessicator over anhydrous CaCl₂. Good yields of 75-80% were obtained.

Physical measurements

The prepared Schiff base and its complexes were subjected to the elemental analysis as well as other techniques. The molar conductance measurements were carried out in DMF solvent using conductivity meter model CMD 650 digital meter. The infrared spectra were obtained by using KBr disc technique on IFS-25 DPUS/IR spectrometer (Bruker). The electronic absorption spectra were carried out by using a parkin-Elmer lambda 4B spectrophotometer in 1 cm matched silica cells using DMF solvent. The mass spectra were carried out using Q 1000 EXGC-MS schimadzu spectrometer of 70 e and MA energy using a direct insertion probe at temperature 90-110 °C. The thermogravimetric analysis was achieved using schimadzu thermal analyzer (Japan). The weight losses were measured from ambient temperature up to 1000 °C in rate of 10 °C per minute. The ¹HNMR spectra for the prepared Schiff bases and their complexes were recorded using Varian Gemini 200-200 MHz spectrometer. The solvent used was deuterated DMSO (d⁶-DMSO) and the spectra extended from (0-14 ppm) using TMS as internal standard.

Results and discussion

The chemical reaction of salicylaldehyde and o-phenylenediamine in ethanol (1:1) ratio yields one imine compound. The chemical reaction concerning the formation of the expected compound as follow:



Elemental analysis

The elemental analysis (C, H and N) of the prepared Schiff base and its complexes are listed in table-1. The calculated values are in a good agreement with those obtained from the analysis. The obtained data exhibit the formation of the complexes in 1:1[M:L] ratio. The stoichiometry of the complexes postulate the formula of the type $[ML.2OH.H_2O].nH_2O$, $[ML.OH.2H_2O].nH_2O$ and $[ML.OH].nH_2O$. where L is the Schiff base under investigation, $n = 0, 5/4, 1, 3, 5, 7$ and M represents the metal ions under study (see table-1)

Molar conductance measurements

The molar conductance values of the Schiff base complexes under study determined using DMF solvent (table 1) were in the range of $2.71-7.81 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. These values indicate non-electrolytic nature of the complexes.⁽⁶⁾

Thermogravimetric analysis

The thermogravimetric analysis data of Cr(III) Schiff base complex under investigation display a weight-loss of 27.14% corresponding to loss of seven water molecules of hydration at 180°C and a weight-loss of 5.00% is due to loss of one

505-671 cm^{-1} which may be attributed to $\nu(\text{M-N})$ and $\nu(\text{M-O})$ vibrations.⁽⁹⁾ Supporting the involvement of the nitrogen and oxygen atoms in complexation with metal ions under investigation.

Electronic spectra

The electronic spectra of the free ligand (Schiff base) and its complexes are listed in table 2. The spectra were recorded in DMF solvent. The spectral data of the free ligand display two bands at 333 nm (30030 cm^{-1}) and 550 nm (18182 cm^{-1}) which are due to $\pi-\pi^*$ and $n-\pi^*$ ($-\text{HC}=\text{N}$) transitions.⁽¹⁰⁾ The absorption bands at 404 nm (24752 cm^{-1}) and 493 nm (20284 cm^{-1}) in spectrum of Cr(III) complex are assigned to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ transitions. The intensity of the bands indicates the presence of an octahedral geometry for Cr(III) complex.⁽¹¹⁾ The spectral data of the Mn(II) complex exhibit three bands at 333 nm (30030 cm^{-1}), 319 nm (31348 cm^{-1}) and 293 nm (34130 cm^{-1}). The first and third bands are attributed to the existence of charge transfer transition and the second band is assigned to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ transition. These data support the presence of an octahedral structure. Whereas, the spectrum of Fe(III) complex reveal two bands at 298 nm (25575 cm^{-1}) and 295 nm (33898 cm^{-1}). attributed to charge transfer ($\text{M} \rightarrow \text{L}$) transition and an octahedral geometry was suggested for this complex. The Co(II) complex spectrum shows several bands (table 2) which could be attributed to charge transfer ($\text{M} \rightarrow \text{L}$) transitions. All the observed bands indicates the presence of an octahedral geometry. Meanwhile, the Ni(II) complex spectral data exhibit three bands at 477 nm (20964 cm^{-1}), 377 nm (26525 cm^{-1}) and 290 nm (34483 cm^{-1}) corresponding to charge transfer ($\text{M} \rightarrow \text{L}$) transitions. The data support the existence of a square planar structure.⁽¹²⁾ The absorption spectral data of the Cu(II) complex display two bands at 324 nm (30864 cm^{-1}) and 304 nm (32895 cm^{-1}) which are attributed to the presence of charge transfer ($\text{M} \rightarrow \text{L}$) transitions. A square planar geometry was proposed for Cu complex.

Table (2): Infrared and electronic absorption spectra data of the Schiff base and its complexes

Ligand or Complex	$\nu(\text{C}=\text{N})$	$\nu(-\text{NH}_2)$	$\nu(\text{OH})$ (H_2O)	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$	nm (cm^{-1})
1	1614	3083-3053	-	-	-	550 (18002), 333 (30075)
2	1610	-	3323	498	540	493 (20284), 404 (24753)
3	1602	-	3380	426	517	333 (30030), 319 (31348), 293 (34130).
4	1606	-	3420	447	537	298 (25557), 295 (33898).
5	1606	-	3164	418	541	775 (12903), 409 (24450), 386 (25907), 365 (27397), 311 (32154), 306 (32680), 379 (35842).
6	1609	-	-	458	544	477 (20964), 377 (26525), 290 (34483).
7	1608	-	3443	440	535	324 (23641), 304 (32895).

Proton nuclear magnetic resonance

The ^1H NMR spectra of the free Schiff base and its Ni(II) complex were measured in d^6 -DMSO solvent. The Schiff base spectral data (Table 3) show signals at 6.8-7.5 and 11.2 ppm attributed to C_6H_5 ring and $-\text{OH}$ group, which are present in the prepared Schiff base, respectively. A signal at 8.3 ppm is due to $(-\text{HC}=\text{N})$ group of the azomethine (imine). Also the spectral data show a signal at 9.6 ppm which could be due to $-\text{NH}_2$ group of o-phenylenediamine moiety. The ^1H NMR spectral data of the Ni(II) complex exhibit decrease in $(-\text{HC}=\text{N})$ signal, this indicates the involvement of $(-\text{HC}=\text{N})$ group in chelation with Ni(II) ion. While the $-\text{OH}$ and $-\text{NH}_2$ groups disappeared from their positions, confirming their participation in chelation.

Table(3): Proton nuclear magnetic resonance spectra of the Schiff base complexes

Compound	Arom.(H)	C-O(H)	C(H)=N	-N(H ₂)
L ($\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$)	6.8-7.5 (M,8H)	11.2 (S,H)	8.3 (S,H)	9.6 (S,2H)
(Ni.L.OH)	6.7-7.7 (M,8H)	-	8.2 (S,H)	-

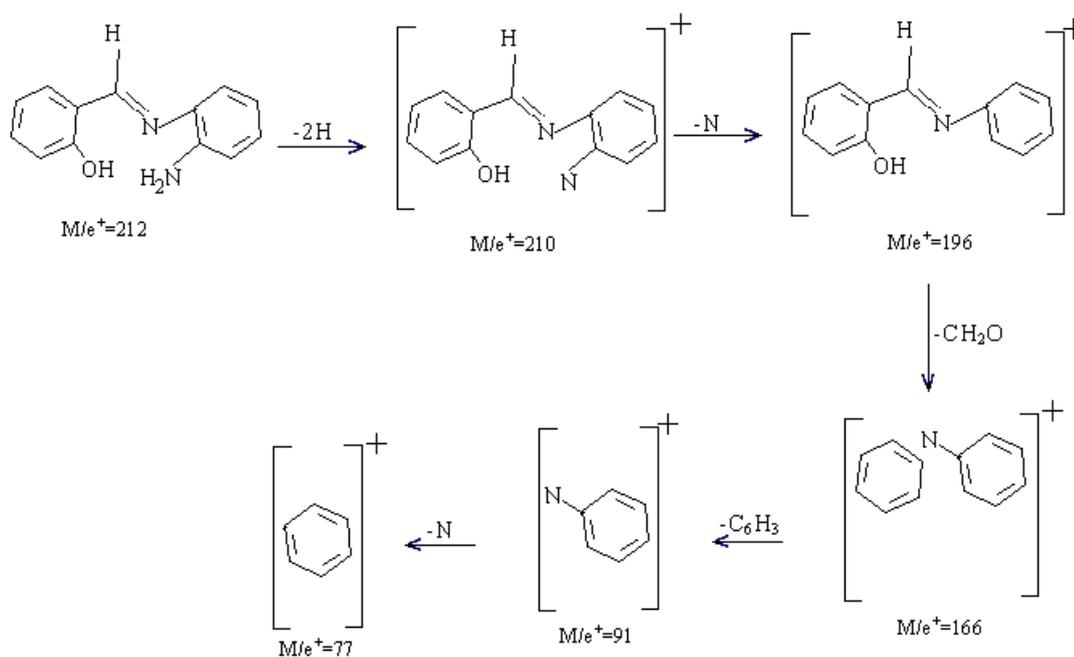
Mass spectra

The mass spectra data of the Fe(III) and Cu(I) Schiff base complexes are shown in table-4 and schemes (1-3). For the free Schiff base, the m/e^+ at 212

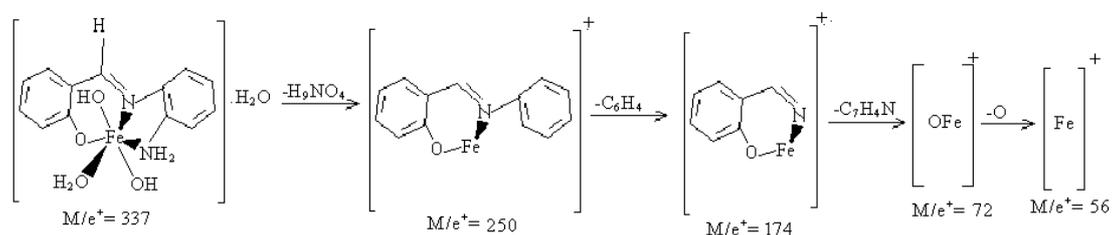
corresponding to the molecular weight of the prepared compound and reach to a stable compound at m/e^+ 77 which is due to the phenyl group. For Cu(II) complex, the base band at m/e^+ 314 corresponds to the exact molecular weight of the prepared complex. Meanwhile, the spectral data of Fe(III) complex display a base peak at m/e^+ 337 analogous to the original molecular weight of the complex. In both complexes, there is a constant weight with raising temperature regarding to the presence of metallic residues (Cu and Fe), respectively.

Table(4): Mass spectra data of the Schiff base and its (Fe-L and Cu-L) complexes

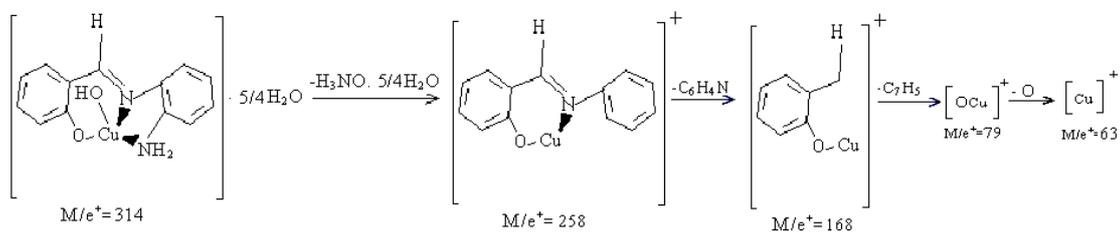
Compound	M/e^+	Fragment
L	212	$M^+(C_{13}H_{12}N_2O)$
	210	$C_{13}H_{10}N_2O)^{+}$
	196	$C_{13}H_{10}NO)^{+}$
	166	$C_{12}H_8N)^{+}$
	91	$C_6H_5N)^{+}$
	77	$C_6H_5)^{+}$
	Fe-L	337
250		$C_{13}H_8NOFe)^{+}$
174		$C_7H_4NOFe)^{+}$
72		$OFe)^{+}$
56		Fe
Cu-L	314	$M^+(C_{13}H_{12}N_2O_2Cu).$
	258	$5/4H_2O$
	168	$C_{13}H_9NOCu)^{+}$
	79	$C_7H_5OCu)^{+}$
	63	$OCu)^{+}$
		Cu



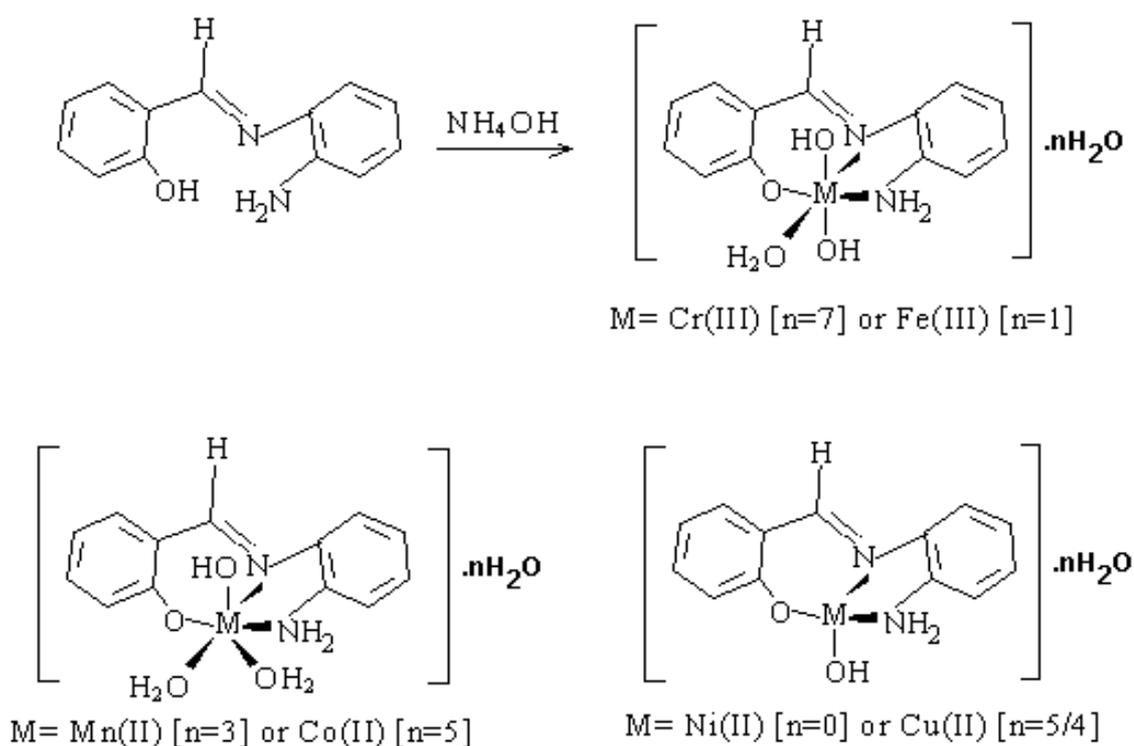
Scheme-1: Mass spectral fragmentation of the free Schiff base



Scheme-2: Mass spectral fragmentation of Fe(III) Schiff base complex.



Scheme-3: Mass spectral fragmentation of Cu(II) Schiff base complex.



The suggested chemical formulae for the Schiff base complexes.

References

1. N. Raman, Y. P. Raja and A. Kulandiasony, Indian Academy of Science., 113 (3), 183 (2001).
2. X. Tai, X. Yin, Q. Chen and N. Tan, Molecules., 8, 439-443 (2003).
3. M. Sonmez and M. Sekercl, Polish. J. Chem., 76, 907-914 (2002).
4. M. M. Abd-Elzaher, J. Chin. Chem. Soc., 48, 153-158 (2001).
5. Ben Saber, A. A. Maihub, S. S. Hundere and M. M. El-ajaily, Microchem. J., 81, 191-194 (2005).
6. W. J. Geary, Coord. Chem. Rev, 7, 81 (1971).
7. A. A. Maihub, M. M. El-ajaily and S. M. Filog., Abhath Al-Yarmonk J., 14(1), 119-128 (2005).
8. H. Keypour, S. Salehzadeh and R.V. Parish, Molecules, 7, 140-144 (2002).

9. H. Keypour, S. Salehzadeh, R. G. Pritchard and R. V. Parish, *Transition Met. Chem.*, 23, 605-607 (1998).
10. P. Bhattacharyya, J. Parr. A. T. Ross and A. M. Z. Slawin, *JChem. Soc. Dalton Trans*; 3149-3150 (1998).
11. A. K. Abdel-hadi, W. M. Hosny, A. H. Basta and H. El-Said, *Polym. Plast. Technol. Eng.* 33, 781 (1994).
12. M. M. El-ajaily, A. A. Maihub and S. S. Hudere, *Asian. J. Chem.*, (in press 2005).