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Synthesis of Metal Complexes Fe(II), Co(II), Ni(II) of Monodentate Schiff Bases Derived from Aromatic Aldehyde

Rawand Alsabra
Master student: Department of chemistry–Faculty of Science-Albaath University, Syria

Lena Radwan
Dr. for organometallic chemistry: Department of chemistry, Faculty of Science-Albaath University, Syria

Abstract

A series of Schiff base ligands NPNA and newly NNNA have been synthesized in equimolar reaction of 1-Naphthylamine hydrochloride with or naphthalene-1-carbaldehyde. The synthesized Schiff bases were used for complexation with different metal ions like Fe(II), Co(II) and Ni(II) by using a molar ratio of ligand: metal as 1:1 and 2:1. The characterization of Schiff bases and newly formed complexes was done by UV–VIS, IR, spectral studies and analytical data. On the basis of the spectral studies show that the Schiff bases act as monodentate and an octahedral geometry has been assigned for Fe(II) and Ni(II) complexes and tetrahedral geometry for Co(II) complexes.

Keywords: Schiff bases, Fe(II), Co(II), Ni(II) complexes, spectroscopic studies.

1. Introduction

Schiff bases are named in the owner of Hugo Schiff (1834-1915) [1-2]. Their formula is {HR-C=N-R} R=aryl group and Hugo Schiff prove it in (1864) [1].They are formed by condensation of aldehyde compounds with primary amine compounds in alcoholic medium in the presence of acetic acid as catalyst to make PH ranges between(4.5-5) [3]. Schiff base is called imine, azomethine, aldimine and anil. Schiff base derived from aromatic aldehyde and aromatic amine is more stable because the having effective conjugation and readily synthesized. Schiff bases used as antibacterial [4], antifungi [5], anti-inflammatory [6], analgesic [6], anticancer [7] and corrosion Inhibition [8]. In industry section they are used as antioxidant agents [9], and as primary compound to synthesis new compounds [10]. Metal complexes have wide applications in antibacterial [11-12], antifungal [13], anti-inflammatory [14], anti–leishmanial [15], and binding DNA [16], catalyst in some reactions [17], corrosion inhibition [18], antioxidant [14]. The goal of the study presented here is to synthesize the Fe(II), Co(II) and Ni(II) metal complexes of Schiff bases produced from condensation of 1-Naphthyl amine hydrochloride with benzaldehyde or naphthalene-1-carbaldehyde.

2. Experimental

2.1. Materials and instrumentation

1-Naphthyl amine hydrochloride was supplied from Titan Biotech LTD. Benzaldehyde was supplied from Uni-Chem. naphthalene-1-carbaldehyde, acetonitrile, TLC aluminium sheets was supplied from Merck. $FeCl_2.4H_2O$, EtOH, $CHCl_3$, $(C_2H_5)_2O$, MeOH, $CH_3COOC_2H_5$, DMF, n-Hexan were supplied from Sigma-Aldrich. $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, CH_2Cl_2 Were supplied from Surechem Products LTD. Acetic acid glacial, cyclohexan, nitric acid, silver nitrate were supplied from BDH. Triethylamine was supplied from Panreac Quimica. Potassium chromate was supplied from Medex. IR measurements (KBr pellets) were carried out on Jasco 4100 FT-IR spectrometer. NMR measurements were performed on a Bruker 400 MHz spectrometer. Samples were dissolved in (CD3)2CO with TMS as internal reference. Ultraviolet-Visible spectra were recorded using a Optizen UV 3220 Spectrophotometer in the range of 200–800 nm and DMF is used as a solvent. Elemental analyses (C, N, M, Cl, O) were analyzed on FEI Quanta 200 Scanning Electron Microscopes. Decomposing point of the compounds were recorded using Electro Thermal Melting Point Apparatus (10-370 °C). The chloride content of the complexes was determined using Mohr method.

2.2. General procedure for the synthesis of the ligands NPNA and NNNA

solution of (3mmol, 0.03gr) of Benzaldehyde or (3mmol, 0.47gr) of naphthalene-1-carbaldehyde in (6ml) absolute ethanol added dropwise to a solution of (3mmol,0.55gr) of 1-Naphthylamine hydrochloride in (6ml) absolute ethanol in round bottom flask (50ml), then(1ml) of acetic acid glacial was added to this solution. The mixture was refluxed 23h for NPNA and 21h for NNNA in an oil bath at (77–79°C).The reaction was monitored through TLC. After completion of the reaction (TLC analysis) the flask was cooled on crush ice to afford a yellow solid product. The precipitates obtained were filtered, washed with acetonitrile and ethanol. Then they recrystallization from (CH_2Cl_2:EtOH) in ratio (1:2). Then they dried under vacuum.

I. N-[(E)-Phenylmethylene]Naphthalene-1-Amine **NPNA (L^1):** Yield: 90.82(%). Color (yellow). DP. 183°C. IR (KBr, cm^{-1}): 1636(HC=N). ^{1}HNMR (CD_3COCD_3, δ, ppm) 7.14-7.16 (2,d,Ar), 7.3-7.4 (3,d,Ar), 7.4-7.44 (2,t,Ar), 7.46-7.52 (4,tet,Ar) 7.92-7.98 (2,m, H-C=N, Ar). UV (DMF, nm) 301 (π→π*, CH=N). Anal. Calc. For $C_{17}H_{13}N$ (231.29): C: 88.28; N: 6.06; found: C: 88.18; N: 5.95.

II. N-[(E)-1-Naphthylmethylene]Naphthalene-1-Amine **NNNA (L^2):** Yield: 84.76(%). Color (yellow). DP. 310°C. IR (KBr, cm^{-1}): 1633(HC=N). ^{1}HNMR (CD_3COCD_3, δ, ppm) 7.02-7.03 (2,t,Ar), 7.24-7.33 (2,tet,Ar), 7.48-7.54 (2,t,Ar), 7.59-7.64 (2,t,Ar) 7.79-7.81 (2,d,Ar), 7.92-7.94 (2,d,Ar), 8.01-8.05 (1,d,Ar), 8.12-8.14 (2,m, H-C=N, Ar). UV (DMF, nm) 308 (π→π*, CH=N). Anal. Calc. For $C_{21}H_{15}N$ (281.35): C: 89.65; N: 4.98; found: C: 89.61; N: 4.81.

2.3. General procedure for the synthesis of metal complexes of Schiff base

All the complexes of Schiff base in ratio (ligand: metal)(1:1) were prepared in the same way: A solution of metal salts (0.1mmol) in (6ml) absolute ethanol was added dropwise to a solution of appropriate Schiff base (0.1mmol) in (6ml) absolute ethanol in erlenmeyer flask. then the reaction mixture was added dropwise with to a stirred solution of Triethylamine (0.2mmol,0.02gr) in (9ml) absolute ethanol in round bottom flask (50ml). The final reaction mixture was refluxed for several hours in an oil bath at (60-70°C). The reaction was monitored through TLC. After completion of the reaction (TLC analysis) the flask was cooled on crush ice to afford a solid product. The solid residue was put on filter paper then washed with absolute ethanol and recrystallized from (Methanol:acetonitrile) (3:2) then dried under vacuum.

The same procedure for synthesis complexes of Schiff base in ratio (ligand:metal)(2:1) except the solution of the ligand (0.2mmol) in (12ml) absolute ethanol in erlenmeyer flask.

3. Results and discussion

The Schiff base NPNA (scheme1) was prepared by condensation in ethanol (6ml) an equimolar (3m mol) amount of 1-Naphthyl amine hydrochloride and benzaldehyde. The same method was used for the preparation of the ligand NNNA by condensation of 1-Naphthyl amine hydrochloride and naphthalene-1-carbaldehyde. The structure of Schiff bases thus formed was established by IR, ^{1}HNMR, UV and CN analysis. The synthesized Schiff bases were soluble in DMF, DMSO. The composition of the ligands was consistent with their NMR, IR, and CN data.

The synthesized Schiff bases was further used for the complexation with Fe(II), Co(II) and Ni(II) metal ions in ratio (ligand: metal) (1:1)(2:1) (scheme1), using the following metal salt $FeCl_2.4H_2O$ for complexes 1,5,8, $CoCl_2.6H_2O$ for complexes 2,4,6,9, $NiCl_2.6H_2O$ for complexes 3,7,10. The obtained complexes were established by IR, UV-VIS and CNMOCl analysis. They were completely soluble in DMF, DMSO. The results of the elemental analyses of the complexes, which are recorded in Table 1, are in good agreement with those required by the proposed formulae. All complexes were stable at room temperature. Physical measurements and analytical data of the Schiff bases and their metal complexes 1–10 are given in Table 1.

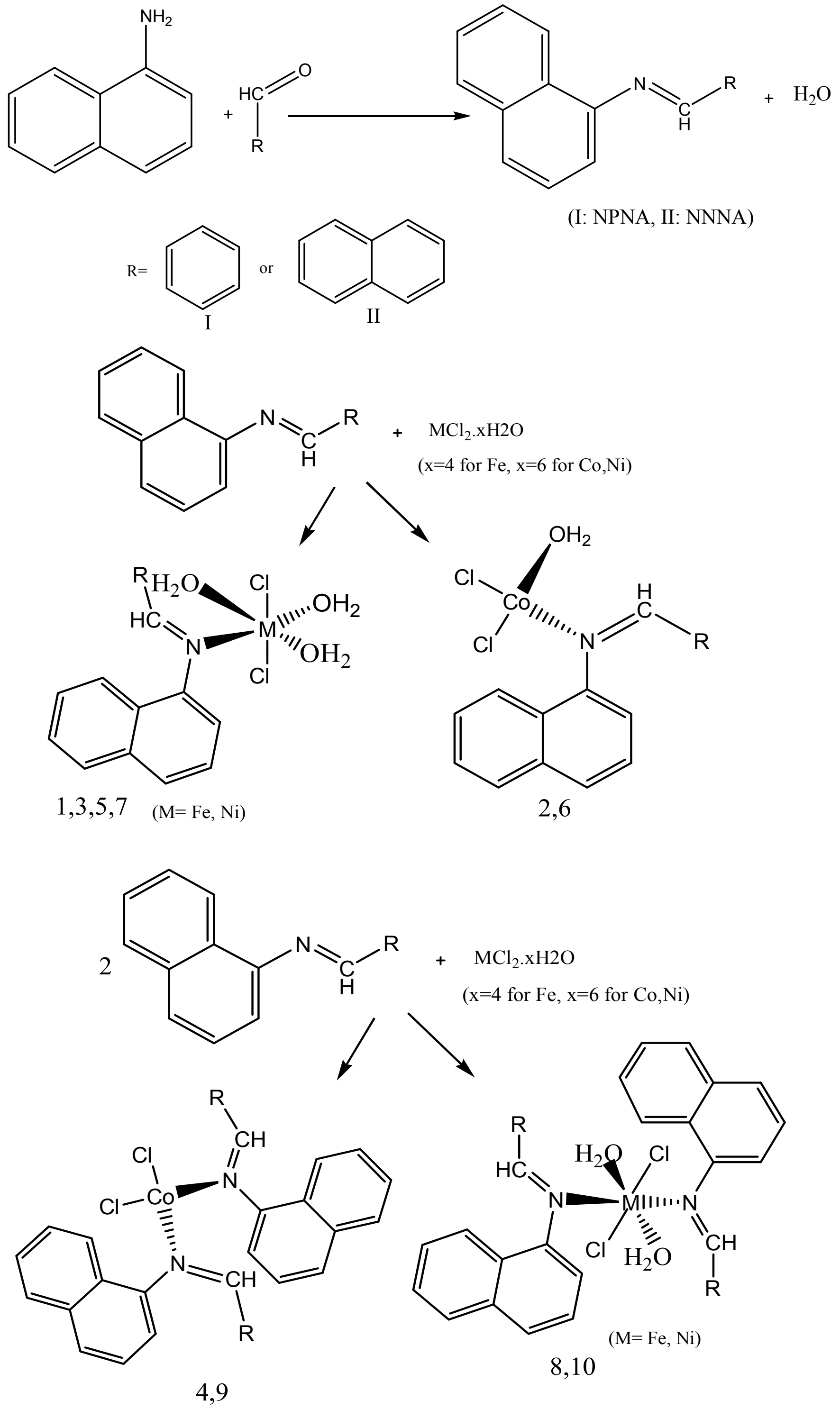
Through TLC we mointred the reaction of Schiff bases and their metal complexes by using (n-hexan: Ethyl acetate) (5:2) as a solvent (Table 1).

3.1. ^{1}HNMR spectra

The ^{1}HNMR spectra have been recorded for ligand L^1 and L^2. The ^{1}HNMR spectra of ligand L^1 (Fig. 1) displayed azomethine (H-C=N) proton as a multiply at 7.92-7.98 ppm [3]. In the ^{1}HNMR spectra of the ligand L^2 (Fig. 2) the azomethine (H-C=N) proton appeared as doublet at 8.12-8.14 ppm [3].

3.2. IR spectra

The characteristic bands of IR spectra of ligands L^1, L^2 and their metal(II) complexes are reported in order to confirm the binding mode of the Schiff base ligands to the corresponding metal ion. Both ligands possessed potential donor site through azomethine (-C=N) which has tendency to coordinate with metal ions (Table 2). Peak corresponding to ν(C=O) stretching vibrations was absent in IR spectra of L^1 and, instead, a new band assigned to azomethine ν(HC=N) linkage appeared at 1636 cm^{-1} confirming the formation of Schiff base [3]. Similarly, the peak at 1633 cm^{-1}in L^2 corresponds to ν(HC=N) linkage [3].The comparison of the IR spectra of Schiff base ligands with corresponding metal complexes gave clue of binding modes of the Schiff base ligand to the corresponding metal ion. The IR band due to azomethine -N shifts to lower frequency (9–69 cm^{-1}) 1562–1624 cm^{-1}, representing the coordination of azomethine -N in the complex formation [19–20].



Scheme 1. Preparation of the ligands and their metal complexes

Table 1

Physical measurements and analytical data of the ligand (L^1, L^2) and metal complexes (1–10).

No	molecular formula	DP	TLC	Yield	Elemental analysis (%) calculate (found)				
		(°C)		(%)	C	N	M	O	Cl
L^1	NPNA (L^1) [$C_{17}H_{13}N$]	183	0.91	90.82	88.28 (88.18)	6.06 (5.95)	---	---	---
L^2	NNNA (L^2) [$C_{21}H_{15}N$]	310	0.83	84.76	89.65 (89.61)	4.98 (4.81)	---	---	---
1	$Fe(NPNA)Cl_2(H_2O)_3$ [$C_{17}H_{19}NFeCl_2O_3$]	125	0.85	82.34	49.55 (49.52)	3.40 (3.38)	13.55 (13.51)	11.65 (11.61)	17.21 (17.18)
2	$Co(NPNA)Cl_2(H_2O)$ [$C_{17}H_{15}NCoCl_2O$]	127	0.78	85.16	53.85 (53.81)	3.69 (3.64)	15.54 (15.50)	4.22 (4.19)	18.70 (18.67)
3	$Ni(NPNA)Cl_2(H_2O)_3$ [$C_{17}H_{19}NNiCl_2O_3$]	120	0.76	89.17	49.21 (49.19)	3.38 (3.35)	14.15 (14.10)	11.57 (11.53)	17.09 (16.87)
4	$Co(NPNA)_2Cl_2$ [$C_{34}H_{26}N_2CoCl_2$]	176	0.69	87.04	68.93 (68.90)	4.73 (4.71)	9.95 (9.91)	---	11.97 (11.94)
5	$Fe(NNNA)Cl_2(H_2O)_3$ [$C_{21}H_{21}NFeCl_2O_3$]	134	0.79	83.24	54.58 (54.52)	3.03 (3.01)	12.08 (12.02)	10.39 (10.33)	15.34 (15.23)
6	$Co(NNNA)Cl_2(H_2O)$ [$C_{21}H_{17}NCoCl_2O$]	137	0.78	81.20	58.77 (58.73)	3.26 (3.24)	13.73 (13.67)	3.73 (3.68)	16.52 (16.51)
7	$Ni(NNNA)Cl_2(H_2O)_3$ [$C_{21}H_{21}NNiCl_2O_3$]	133	0.71	83.54	54.24 (54.22)	3.01 (2.98)	12.62 (12.59)	10.32 (10.28)	15.25 (15.21)
8	$Fe(NNNA)_2Cl_2(H_2O)_2$ [$C_{42}H_{34}N_2FeCl_2O_2$]	148	0.68	91.50	69.53 (69.51)	3.86 (3.87)	7.70 (7.69)	4.41 (4.40)	9.77 (9.79)
9	$Co(NNNA)_2Cl_2$ [$C_{42}H_{30}NCoCl_2$]	149	0.62	91.65	72.84 (72.80)	4.05 (4.02)	8.51 (8.48)	---	10.24 (10.17)
10	$Ni(NNNA)_2Cl_2(H_2O)_2$ [$C_{42}H_{34}N_2NiCl_2O_2$]	153	0.59	91.55	69.26 (69.20)	3.85 (3.82)	8.06 (8.01)	4.39 (4.33)	9.74 (9.70)

3.3. Electronic spectra

The electronic spectra of the ligands and their complexes were recorded in DMF medium at room temperature. All the spectra of the ligands show band in range (301,308 nm) are attributable to the transition ($\pi\rightarrow\pi^*$) of the azomethine corresponding of the ligands (L^1,L^2) respectively [19,21]. In the UV spectra of the complexes of L^1,L^2 the band of transition ($\pi\rightarrow\pi^*$) of (–C=N–) is shifted to longer wavelength (Table 2) indicating the coordinated of the azomethine to the metal ion [19]. The electronic spectrum of Fe(II) complexes generally exhibited one absorption band at range (639-827nm) which is assigned to $^5E_g\rightarrow^5T_{2g}$ transition which may indicate octahedral geometry around Fe(II) ion [22]. The electronic spectrum of Co(II) complexes generally show two absorption bands at range (590-682nm) which are closer and assigned to $^4A_2(F)\rightarrow^4T_1(P)$ transition suggesting tetrahedral geometry [11]. The electronic spectrum of Ni(II) complexes of generally show one absorption bands at range (685nm) which is assigned to $^3A_{2g}(F)\rightarrow^3T_{1g}(F)$ transition indicating distorted octahedral geometry [23]. The IR, UV-VIS spectra data of Schiff bases and their metal complexes are listed in Table 2.

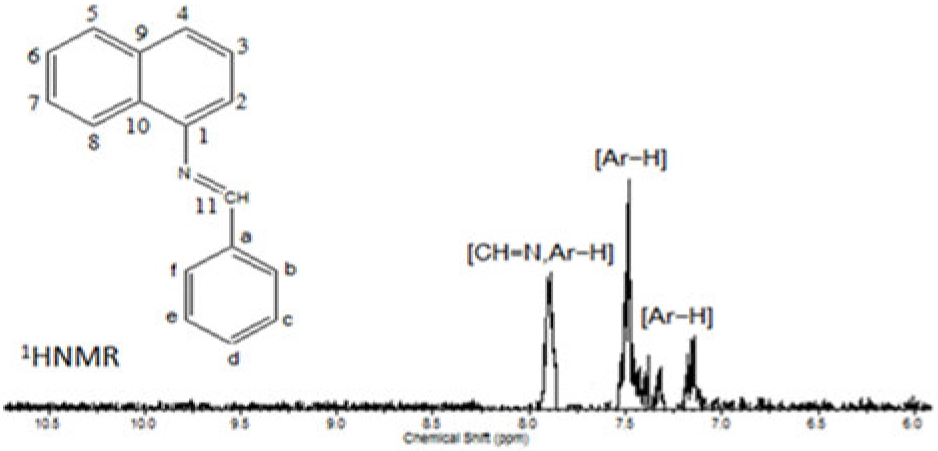


Fig.1. ^{1}HNMR spectrum of L^1 ligand

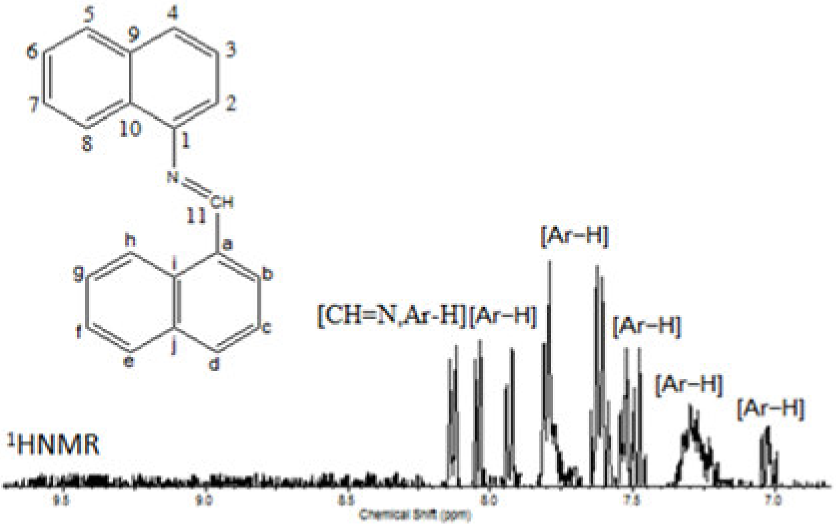


Fig.2. ¹HNMR spectrum of L^2 ligand

By Mohr method we confirmed the presence of chloride ions in metal complexes [24].

Table 2

IR, UV–Vis data of the Schiff bases and their metal chelates

No	**Color**	**IR (cm^{-1})**	**UV-VIS (nm)**			
		ν(CH=N)	π→π*(CH=N)	d–d transition	transition	Geometry
L^1	Yellow	1636	301	---	---	---
L^2	Yellow	1633	308	---	---	---
1	Brown	1626	308	685	${}^5E_g \rightarrow {}^5T_{2g}$	Octahedral
2	Green	1623	323	592-675	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
3	Green	1600	322	674	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	Octahedral
4	Green	1624	315	611-682	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Tetrahedral
5	Brown	1568	315	639	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Octahedral
6	Green	1562	316	590-676	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	Tetrahedral
7	Brown	1565	314	753	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Octahedral
8	Brown	1625	317	827	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Octahedral
9	Green	1618	314	607-678	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	Tetrahedral
10	Brown	1624	315	736	${}^4A_2(F) \rightarrow {}^4T_1(P)$	Octahedral

4. Conclusion

Two Schiff bases mono dentate NPNA, NNNA were synthesized from 1-Naphthylamine hydrochloride with benzaldehyde or naphthalene-1-carbaldehyde. The ligands were confirmed from ¹HNMR,UV–VIS, IR, spectral studies and analytical data. Newly metal complexes of Schiff bases were prepared by reacting NPNA or NNNA with metal salts (Fe, Co, Ni) in ratio (Metal: Ligand)(1:1)(1:2).The complexes were confirmed from UV–VIS, IR, spectral studies and analytical data. The studies show that all Fe, Ni complexes are octahedral whereas Co complexes are tetrahedral.

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