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SYNTHESIS AND CHARACTERIZATION OF Cu(II), Ni(II) METAL COMPLEXES OF SOME BIS SCHIFF BASES

BY

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Abstract. This paper presents the synthesis of bis Schiff bases by condensation of the β-hydroxy-α-naphthalic aldehyde with aromatic diamines, in acid catalysis, the molar ratio 2:1, major compounds in the coordinative chemistry. Bis Schiff bases have been converted to chelated metal complexes (Cu^{+2}, Ni^{+2}). Characterization of bis Schiff bases and metal complexes was achieved by FT-IR, UV-VIS spectroscopy, and thermogravimetric analysis.

Key words: bis Schiff bases, metal complexes, Cu(II), Ni(II).

1. Introduction

Metal complexes of azomethines (Schiff bases) have attracted researchers' interest and energies towards the synthesis of new mono-and bis Schiff bases, complexing with many metals, complete characterization of those and thorough investigation of what properties are applied in various fields.

In recent years, the metal complexes of Schiff bases have attracted considerable attention by their remarkable antifungal properties, antibacterial, antitumour [1],…,[3], potent anticancer activity [4], antimicrobial [5].

The literature cites complexes with Ni(II) and Cu(II) Schiff bases of some bis Schiff bases having the properties of liquid crystals [6], fluorescence and fluorometry applications [7].

Metal complexes with Co(II) bis of some Schiff bases have been tested for catalytic activity in oxidation reactions [8], cyclic voltammetry on metal complexes of Co, Fe, Cu, Ni showing a quasi-reversible behavior or slowly reversible [9].

2. Experimental

2.1. Materials

Were purified by recrystallization of 1,4-diaminobenzene (from water), 4,4'-diaminodifenil (from water), β-hydroxy-2-naphthalic aldehyde (from ethanol). Acid p-toluene (AcPTS), used as a catalyst in the synthesis of Schiff bases, was a product of Merck (min. 99%).

Metal salts - acetates of Cu, Ni were Merck products.

Benzene, dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$) and other solvents were dried and purified by distillation before use.

2.2. Physical Measurements

Melting points of synthesized metal complexes and Schiff bases were determined on a microscope Boetzius.

FT-IR spectra were recorded in KBr pellet on a spectrophotometer DIGILAB FTS 2000, region 4000-400 cm^{-1}, resolution 4 cm^{-1}.

Electronic spectra were recorded with a spectrophotometer SPECORD M 42, Carl Zeiss Yena, in acetonitrile as solvent.

^{1}H-NMR spectra were performed on a JEOL 60 MHz device in CDCl3 as solvent and TMS as a standard.

Thermogravimetric investigations were performed on a MOM-BUDAPEST device, a temperature range of 20-1000°C, with a heating speed of 10°C/min and air carrier gas. Processing of the thermograms was done by Freeman-Carroll method.

2.3. Chemical Synthesis

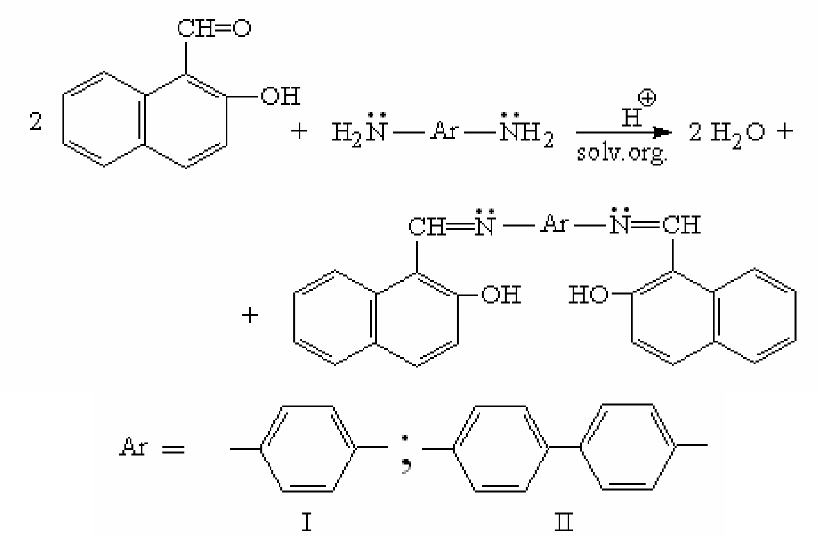
Bis Schiff Bases Synthesis

The aromatic amines react with carbonyl derivatives via an addition-elimination mechanism leading to imines substituted or azomethines called Schiff bases, the reaction occurs in acid catalysis. Bis Schiff bases were prepared according to reaction Scheme 1.

They adopted two variants of synthesis.

Option 1

In a round bottom flask were placed 50 cm^3 of benzene, 0.02 moles aromatic diamine, 0.04 moles β-hydroxy-α–naphthalic aldehyde and p-toluene acid (AcPTS) in catalytic amounts. The reaction mixture was heated, stirring, distilling an azeotropic mixture of benzene-water and fresh benzene entering the flask. Distillation was continued until the reaction water was removed. By cooling the reaction mass crystallized azomethine, which filtered and purified.



I = N, N’- Bis-(2-hydroxynaftilidene)-1,4-diaminobenzene
II = N, N’- Bis-(2-hydroxynaftilidene)-4,4’-diaminobifenil

Scheme 1

Option 2

In a round bottom were placed 0.04 moles β-hydroxy-α–naphthalic aldehyde, ethanol as solvent, 0.02 moles diamine soluble in ethanol and 5-6 drops of glacial acetic acid as a catalyst. Bis Schiff base was precipitated from the system then filtered and purified.

Purification was achieved by column chromatography, Al_2O_3 fillers with eluents CH_2Cl_2 for compound I and $CHCl_3$ for compound II.

Metal complexes synthesis

To prepare metal complexes was done as follows: organic ligand (Schiff base bis I and II), dissolved in a solvent, is treated with a metal acetate (Cu^{+2}, Ni^{+2}) solution, the reaction mixture was under reflux, magnetic stirring, for 1-3 h. It is immediately apparent darkening reaction mass and separation of a precipitate under hot conditions, which is filtered, washed with water, then with hot ethanol to remove acetate and unreacted azomethine respectively.

3. Results and Discussions

As shown in Table 1 it can be said that by both synthesis were obtained the same products.

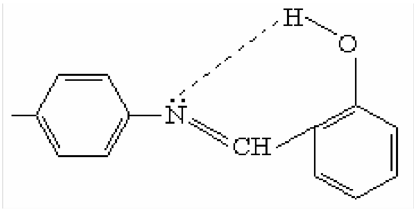
Table 1

Data Obtained for Synthesis of Bis Schiff Bases

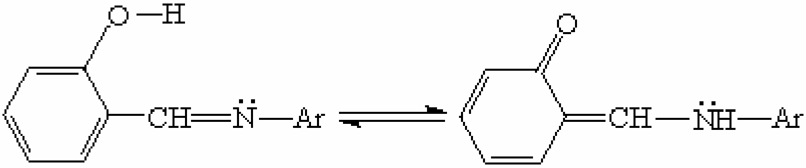
Bis Schiff base	Yield, [%]		Melting point, [ºC]		Color	Solubility
	Catalyst AcPTS	Catalyst CH_3COOH	Catalyst AcPTS	Catalyst CH_3COOH		
I	89	87	308	309	red	Cold solution: CH_2Cl_2, $CHCl_3$ CH_3COCH_3, dioxan
II	78	88	329	326	oranj	Cold solution: $CHCl_3$, dioxan partially solubility in cold solution: CH_2Cl_2, CH_3COCH_3,

Being extended conjugated molecules with highly delocalized electrons, azomethines have high melting points.

An important characteristic of these compounds is the presence of -OH phenolic group in ortho-position to azomethine group, which allows establish of intramolecular hydrogen bond with non-participating electron pair of nitrogen atom.



The presence of -OH phenolic group in ortho to azomethine group characterized by prototropic rearrangement, establishing a equilibrium between the forms tautomers enolimine and ketoenamine:



The tautomers proportion depends on the nature of substitute constituent, solvent polarity and intermolecculare interactions through hydrogen bonds.

The chemical structure of azomethines was confirmed by FT-IR and UV-VIS spectroscopic methods (Table 2).

FT-IR spectra of Schiff bases presents a major band at 3420 cm^{-1} assigned δ_{OH} vibration, a peak at 1622 cm^{-1} characteristic $\nu_{C=N}$ vibration and typical bands of aromatic ring.

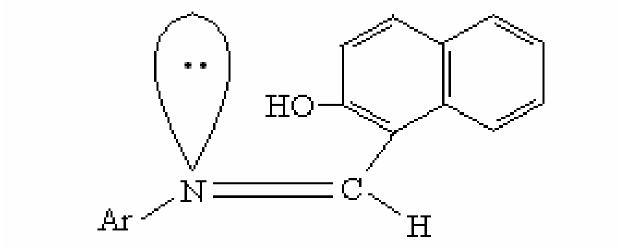
Electronic spectra of Schiff bases, recorded in acetonitrile, show strong absorption bands in UV-VIS region (200-400 nm) assigned of transitions σ - σ*, π - π* and n - π*.

Table 2

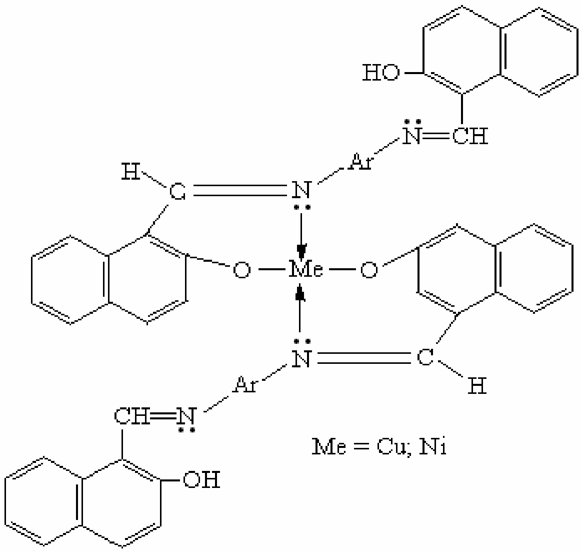
The FT-IR and UV-VIS Characteristics of Bis Schiff I, II Bases

Bis Schiff base	I.R. absorption, [cm^{-1}]	UV-VIS characteristics λ, [nm]; log ε, [l.mol^{-1}.cm^{-1}]
I	$-OH_{phenolic}$ 3422 $-HC=N-$ 1622 Aromatic ring	λ_1=274 (3.31) λ_2=209.5 (4.00)
II	$-OH_{phenolic}$ 3420 $-HC=N-$ 1622 Aromatic ring	λ_1=399 (3.01) λ_2=272.5 (3.39) λ_3=209.5 (3.86)

The azomethine molecule adopts an E configuration at $-N=CH-$ group, which explains the subsequent possibility of complexation with metal salts.



The general structure proposed for metal complexes of azomethines, when working at a molar ratio azomethine: metal acetate = 2:1, is shown below:



Characterization of metal complexes Cu(II) and Ni(II) of bis Schiff bases I and II are presented in Table 3.

Table 3

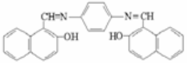
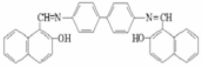
Characteristics of Metal Complexes Cu(II) and Ni(II) of Bis Schiff Bases I and II

Metal complex	Yield [%]	Melting point, [ºC]	Color	I.R. absorption [cm^{-1}]
I_{Cu}	72	>350	Dark brown	$-OH_{phenolic}$ 3433 -HC=N- 1614 Aromatic ring
I_{Ni}	30	>350	Reddish brown	$OH_{phenolic}$ 3451 -HC=N- 1616 Aromatic ring
II_{Cu}	37	>350	Reddish brown	$OH_{phenolic}$ flatted 3433 -HC=N- 1614 Aromatic ring
II_{Ni}	25	>350	Reddish brown	$OH_{phenolic}$ flatted 3468 -HC=N- 1618 Aromatic ring

Differential thermal and thermogravimetric analysis of metal complexes was performed on a MOM-BUDAPEST device, a temperature range of 20-1000°C, with a heating speed of 10°C/min. and air carrier gas. Thermograms processing was done by Freeman-Carroll method. The data confirmed retention of metal in their structure and the data are presented in Table 4.

Table 4

The parameters of thermal analysis of Schiff bases and those of metal complexes

No.	Sample	Thermogravimetry Data							Differential thermal Data				
		Peak no	T_{onset}, °C	T_{peak}, °C	T_{offset}, °C	Reaction order	$E_{a\,MAX}$ J/g	Mass loss, %	Peak no	T_{onset}, °C	T_{peak}, °C	E_{ap}, J/g	Area, u.a.
1.	N,N'-Bis-(2-hydroxy-naftiliden)-1,4-diamino- benzen (I) 	1	326.5	353.0	375.0	0.33	43643.19	16.1	1	299.2	370.6	53.3 EXO	43029
2.	I-complex Cu	1	329.1	350.8	375.4	0.26	15448.86	12.5	1	247.3	394.5	470.3 EXO	236469
3.	N,N'-Bis-(2-hydroxy-naftiliden)-4,4'-diamino-Bifenil (II) 	1	318.6	369.9	425	0.31	8376.27	26.3	1	304	433.7	97.8 EXO	44989
4.	II – Complex Cu	1	-	-	-	-	-	-	1	271.2	352.0	120.1 EXO	66240
5.	II – Complex Ni	1	-	-	-	-	-	-	1	-	-	ENDO	-

$E_{a\,max}$ – maximum activation energie; E_{ap} – activation energie of sample; A_p – total area; A_e – area of standard; $E_{ap} = E_e \bullet \frac{A_p}{A}$

3. Conclusions

It was synthesized (by two different methods) and fully characterized two original Schiff: N, N'-Bis-(2-hydroxynaftiliden) -1,4-diaminobenzene and N, N'-Bis-(2-hydroxynaftiliden) -4,4'-diaminobifenil.

Were obtained and fully characterized by FT-IR, UV-VIS spectroscopy, and thermogravimetric analysis of original azomethine metal complexes with Ni(II) and Cu(II).

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REFERENCES

1. Usha A.K., Chandra S., Synth. React. Inorg. Met. – Org. Chem. **2**, 1565 (1992).
2. Garg B.S., Lapur L., Inorg. Chem. Acta. **173**, 223 (1990).
3. Chohan Z.N., Kansar S., Chem. Pharm. Bull. (Japan). **41**, 951 (1993).
4. Zishan W., Zhiping L., Zheunhuan Y., Trans. Met. Chem., **18**, 291 (1993).
5. Raman N., Muthuraj V., Ravichandran S., Kulandaisamy A., Proc. Indian Sci. (Chem. Sci.) **115**, *3*, 161−167 (2003).
6. Zolfaghar Rezvani, Leili Rahimi Ahar, Kamelia Nejati, Seyed Masoud Seyedahmanian, *Acta Chim. Slov*., **51**, 675-686 (2004).
7. Zvjezdana Cimerman, Snezana Miljanic, Nives Galić, Croatica Chem. Acta, **73**, *1*, 81−95 (2000).
8. Pui A., Berdan I., Morgenstern-Bădărău I., Gref A., Perrée-Fauvert M., Inorg. Chim. Acta, **320**, 167−171 (2001).
9. Pui A., Cecal Al., Drochioiu G., Pui M., Rev. Roum. Chim., **48**, *6*, 439−443 (2003).

SINTEZA ŞI CARACTERIZAREA COMPLECŞILOR METALICI AI Cu(II), Ni(II) CU UNELE BIS BAZE SCHIFF

(Rezumat)

Lucrarea prezintă sinteza unor bis baze Schiff prin condensarea, în cataliză acidă, a aldehidei β-hidroxi-α-naftoică cu diamine aromatice, raport molar 2:1, compuşi importanţi în chimia coordinativă. Bis bazele Schiff au fost transformate în complecşi chelatici metalici (Cu^{+2}, Ni^{+2}). Caracterizarea bis bazelor Schiff şi a complecşilor metalici s-a realizat prin spectroscopie FT-IR, UV-VIS, analiză termogravimetrică şi termodiferenţială.