

Synthesis and Characterization of Zn(II), Cu(II), Ni(II) and Co(II) Biphenyl Schiff base Complexes

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ABSTRACT: The Biphenyl Schiff base ligand and its divalent metal complexes have been prepared. Solubility, melting point decomposition temperature and elemental analysis, magnetic susceptibility, molar conductance measurement, infrared (IR) and UV-Visible spectrophotometric studies were used in characterizing the complex compounds. The melting point of the Schiff base is 185.03°C, and the decomposition temperatures of the Schiff base Zinc(II), Copper(II), Nickel(II), and Cobalt(II) complex compounds were found to be 323°C, 304°C, 317°C and 311°C respectively. The molar conductance values determined for the complexes are within the range 20–26 ohm⁻¹cm²mol⁻¹. The spectrophotometric analysis of the complex compounds revealed 1:1 (Schiff base: metal ion) stoichiometry.

Keywords: Molar conductance, Schiff base, azomethine, spectrophotometry, Jobs mono variation method and stoichiometry.

INTRODUCTION

Biphenyl schiff bases are those compounds containing the azomethine group, -R-C=N-, Hobday and Smith (1972) and Holm et al. (1966)[1-6]. They are usually obtained by the condensation of a primary amine with an aldehyde or a ketone. It has been known that a variety of metal ions on interaction with schiff bases yield chelates complexes, for example; Holm et al. (1966) reported the synthesis and magnetic studies on schiff base complexes of copper (II)[7-8]. Recently, Xishi *et al.*[16] (2003) reported the synthesis and characterization of Mn (II), Co(II) and Cu(II) complexes with a novel schiff base ligand derived from 2,2'-bis(p-methoxyphenylamine) and salicylic aldehyde. Schiff bases are used as rubber accelerators, dyes, reaction intermediates and also as liquid crystals in electronic display systems, Peter (1990) [9-15]. Transition metal schiff base complexes have been found to play a vital role in medicine, biological systems and industries. The field of medicine has witnessed an increase in the number of complexes with therapeutic value, for example, cobalt (III) schiff base complexes are

potential antiviral agents, cisdichlorodiamineplatinum (II) is an anti-cancer agent and copper (II) schiff base complex is an antitubercular agent, Bleomink and Reedi (1996) and Lippard (1994). The use of atom transfer radical cyclisation mediated by copper (II) schiff base complexes to furnish nitrogen heterocyclic, most of which are biologically active molecules, and also the use of copper schiff base catalyst in carbon based radical cyclisation reactions were recently investigated (Clerk and Jones, 1989; Clerk *et al.*, 1998 and Clerk *et al.*, 1999). The synthesis and characterization of the complex compound [Co(sal₂-DAB)] from the interaction of the schiff base (sal₂-DAB) and cobalt(II) chloride has been reported (Zacharias, 1984) [17]. The same synthetic procedure was adopted for the synthesis of four new complex compounds; [Zn₂(NDADPB)₂], [Cu₂(NDADPB)₂], [Ni(NADPB)], and [Co₂(NDADPB)₂]. This paper reports the synthesis and characterization of the complex compounds above.

MATERIALS AND METHODS

The solvents and chemicals used in this work were of Analar grade. All the glass wares used were washed thoroughly with distilled water and dried

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in an oven. Weighing was carried out on electric microbalance balance, Sartorius MC 5. Melting point, decomposition temperature and coordinated water were determined using DSC-TQ10 apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer; using TMS as an internal reference at room temperature operating at 400 MHz. Infrared absorption spectra ($4000\text{-}400\text{cm}^{-1}$) were obtained from a JASCO FT/IR-5300 spectrometer. Mass spectra (ES⁺-MS) were determined on Perkin Elmer (SCIEX API-2000, ESI) at 12.5 eV. Carbon, nitrogen and hydrogen elemental analyses were performed on a LECO CHNS-932 analyzer. Melting points were determined on DSC Model: Q 10 TA Instruments. Thermal analyses of these samples were performed on a Thermal Advantage DSC Q2000 V9.8 Build 296 (TA Instrument, USA) module which was calibrated for temperature and cell constants using indium and sapphire. Electrochemical instrumental model: CHI660C. The magnetization studies were carried out at temperatures ranging from 5 to 300 K, in applied fields of up to 10 kOe with a Quantum Design Physical Properties Measurement System. A JEOL JES PE 3X model spectrometer was used for running the ESR spectra. Electrical conductivity measurements were carried out using conductivity meter model 4010, while UV-visible spectral measurements were done on a SHEMIDEZ UVPC-1601 UV-visible spectrophotometer.

Preparation of the Schiff Base (NDADPB)

To a 500 ml beaker containing 100 ml methanol was added 1.84g (0.01mol) 4, 4'-diaminobiphenyl and 2.442 cm³ (0.02mol) 2-hydroxy-1-naphthylaldehyde, and the mixture was stirring for 20 minutes. The flask and its contents were cooled in an ice-bath to precipitate pale orange crystals, which were suction filtered, washed with cold water, dried and then recrystallized from hot methanol, Holm *et al.*, (1966).

Preparation of the Complexes [$\text{M}_2(\text{NDADPB})_2$]

Into a 250 cm³ beaker containing methanolic solution of 0.01mol metal (II) acetate was added a solution of 0.01mol Schiff base solution in chloroform drop wise with stirring. The mixture was precipitated the pale orange product, which was suction filtered, washed with ethanol and ether before recrystallized from acetone and

dichloromethane mixture (70:30 ratio), Zacharias *et al.* (1984).

Determination of Dissociation Constant of the Schiff Base (NDADPB)

Into a 500 cm³ beaker containing a bar magnetic stirrer were poured 90 cm³ water, 10 cm³ 0.1M nitric acid, 100 cm³ 0.2M potassium nitrate and 10 cm³ of 0.4M Schiff base, and the initial pH of the solution recorded. A 10 cm³ 0.48M NaOH solution was added at intervals into the mixture, stirred and the corresponding pH recorded. The dissociation constant of the Schiff base was calculated from the pH values obtained as reported by Angelici, (1971).

Determination of Metal to Ligand Ratio in the Schiff Base Metal (II) Complexes [$\text{M}_2(\text{NDADPB})_2$]

Into a 500 cm³ beaker containing a bar magnetic stirrer were poured 90cm³ water, 10 cm³ 0.1M nitric acid, 100 cm³ 0.2M KNO₃ and one millimole of metal (II) acetate. The initial pH of the solution was recorded and 10 cm³ of 0.4M sodium salt of the Schiff base was added into the mixture with stirring at intervals and the corresponding pH recorded. The metal-ligand ratio was calculated for each complex as reported by Angelici, (1971).

RESULTS AND DISCUSSIONS

The Schiff base was prepared as reported; it is a pale yellow product that melts at 195°C Zacharias *et al.* (1984). The metal (II) Schiff base complexes; [$\text{Zn}_2(\text{NDADPB})_2$], [$\text{Cu}_2(\text{NDADPB})_2$], [$\text{Ni}_2(\text{NDADPB})_2$], and [$\text{Co}_2(\text{NDADPB})_2$], have been prepared using the adopted synthetic procedure reported by Zacharias *et al.* (1984). The decomposition temperatures (Table 1) of the complexes are 259 °C, 253 °C, 248 °C and 270 °C, respectively, which present fairly stable compounds. The complex compounds are insoluble (Table 2) in water and common organic solvents, but are readily soluble in nitromethane, nitrobenzene, diethylether and dimethyl formamide. The molar conductance measurement (Table 3) of the complex compounds in $1 \times 10^{-3}\text{M}$ dimethyl formamide solution are within the range 12-19 ohm⁻¹ cm² mol⁻¹, suggesting their non-electrolytic nature (Geary, 1971). The IR spectrum (Table 4) of the free Schiff base shows a band at 1600 cm⁻¹ which is assigned to $\nu(\text{C}=\text{N})$ stretching

Table 1
Physical, Analytical and Magnetic data of the Biphenyl Bridged Schiff base M(II) Complexes

Compound	Color	M. P decomposition temp (°C)	Elemental analysis Calculated (found)				% Yield	Magnetic Susceptibility μ_{eff} B. M
			% C	% H	% N	% M		
NDADPB	Orange	185.03	82.91 (82.50)	4.91 (4.15)	5.69 (5.91)	-	90	-
[Zn ₂ (NDADPB) ₂]	Yellow	323.67	69.04 (68.35)	4.35 (3.92)	4.74 (5.04)	11.06 (11.01)	82	-
[Cu ₂ (NDADPB) ₂]	Brown	304.71	69.20 (69.36)	4.44 (2.59)	4.75 (4.65)	10.77 (10.69)	85	1.76
[Ni ₂ (NDADPB) ₂]	Green	317.87	74.35 (75.75)	4.04 (2.04)	5.10 (5.11)	10.69 (10.65)	87	2.89
[Co ₂ (NDADPB) ₂]	Brown	311.25	74.32 (74.10)	4.04 (4.10)	5.10 (5.08)	10.73 (10.53)	75	3.72

Table 2
**The Solubility test of the Complexes in water and
Some Common Organic Solvents**

Solvent	Zn	Cu	Ni	Co
Water	IS	IS	IS	IS
Methanol	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS
Tetrachloromethane	SS	SS	SS	SS
Dichloromethane	SS	SS	SS	SS
Nitromethane	S	S	S	S
Nitrobenzene	S	S	S	S
Acetonitrile	S	S	S	S
n-Hexane	SS	SS	SS	SS
Cyclohexane	SS	SS	SS	SS
Acetone	SS	SS	SS	SS
Acetylchloride	SS	SS	SS	SS
Ethylacetate	SS	SS	SS	SS
Glacial acetic acid	SS	SS	SS	SS
Diethyl ether	S	S	S	S
Diethylformamide	S	S	S	S
Benzene	SS	SS	SS	SS
Toluene	SS	SS	SS	SS
Xylene	SS	SS	SS	SS

Where S means soluble, SS slightly soluble and IS means insoluble

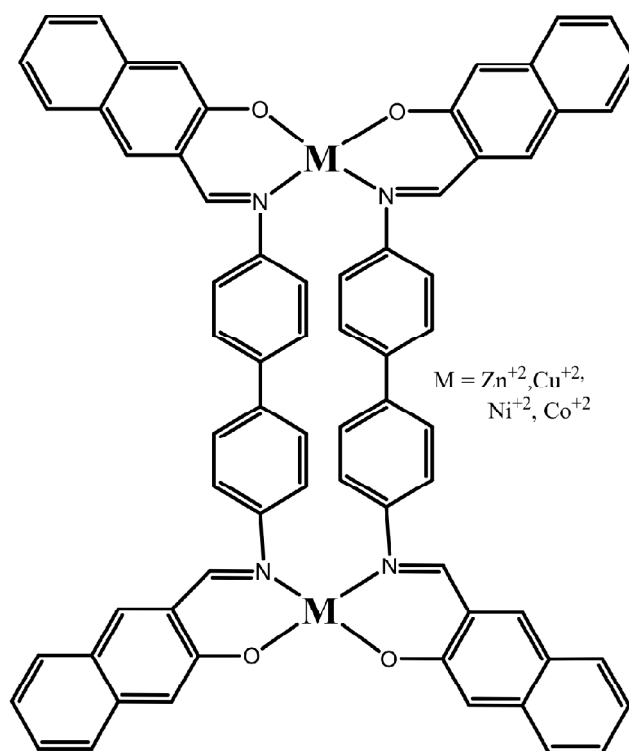

Scheme : The general molecular structure of the Schiff base metal (II) complex compounds, where M is Zn(II), Cu(II), Ni(II) and Co(II)

Table 3
The Conductivity Measurement of the Complexes in 1 x 10⁻³M Dimethylformamide Solution

S. No	Compound	Specific conductivity (k)	Molar conductivity (ohm ⁻¹ cm ² mol ⁻¹)
1	[Zn ₂ (NDADPB) ₂]	3.5 x 10 ⁻⁵	35
2	[Cu ₂ (NDADPB) ₂]	2.7 x 10 ⁻⁵	27
3	[Ni ₂ (NDADPB) ₂]	2.8 x 10 ⁻⁵	28
4	[Co ₂ (NDADPB) ₂]	2.7 x 10 ⁻⁵	27

Table 4
The Infrared Spectral Data of the Schiff Base and its Metal (II) Complex Compounds (cm⁻¹)

Complex	IR spectral data (cm ⁻¹)					
	$\nu(\text{C-H})$	$\nu(\text{C=N})$	$\nu(\text{C-O})$	$\nu(\text{M-N})$	$\nu(\text{O-H})$	$\nu(\text{M-O})$
NDADPB	1510	1620	1541	-	3515	-
[Zn ₂ (NDADPB) ₂]	3040	1612	1211	489	-	550
[Cu ₂ (NDADPB) ₂]	3030	1616	1215	561	-	462
[Ni ₂ (NDADPB) ₂]	3034	1616	1211	565	-	424
[Co ₂ (NDADPB) ₂]	3038	1618	1211	520	-	489

Table 5
The Number of Coordinated Schiff Base with Varying pH in the Complex Compounds

[Zn ₂ (NDADPB) ₂]		[Cu ₂ (NDADPB) ₂]		[Ni ₂ (NDADPB) ₂]		[Co ₂ (NDADPB) ₂]	
pH	Number of coordinated NDADPB	pH	Number of coordinated NDADPB	pH	Number of coordinated NDADPB	pH	Number of coordinated NDADPB
6.44	0.28	7.5	0.14	6.08	0.24	6.14	0.2
6.51	0.36	7.58	0.2	6.1	0.28	6.13	0.27
6.57	0.44	7.67	0.28	6.11	0.4	6.13	0.35
6.58	0.52	7.78	0.36	6.12	0.42	6.14	0.43
6.59	0.59	7.89	0.43	6.12	0.51	6.14	0.51
6.61	0.68	8.02	0.51	6.13	0.59	6.15	0.59
6.61	0.76	8.14	0.59	6.14	0.67	6.16	0.67
6.61	0.84	8.12	0.68	6.15	0.75	6.16	0.75
6.63	0.91	8.36	0.76	6.15	0.83	6.17	0.83
6.64	1	8.42	0.84	6.16	0.91	6.18	0.91
6.62	1.08	8.5	0.91	6.16	0.99	6.18	0.99
6.62	1.16	8.57	0.99	6.17	1.02	6.19	1.07
6.62	1.24	8.61	1.08	6.18	1.15	6.2	1.15
6.58	1.32	8.65	1.16	6.18	1.23	6.21	1.23
6.59	1.4	8.68	1.22	6.19	1.31	6.2	1.31
6.59	1.48	8.71	1.32	6.19	1.39	6.21	1.39
6.58	1.56	8.73	1.38	6.2	1.47	6.2	1.48
6.58	1.64	8.7	1.46	6.21	1.53	6.19	1.53
6.57	1.72	8.65	1.55	6.21	1.63	6.19	1.58
6.59	1.4	8.68	1.24	6.19	1.31	6.2	1.31
6.59	1.48	8.71	1.32	6.19	1.39	6.21	1.39
6.58	1.56	8.73	1.39	6.2	1.47	6.2	1.47
6.58	1.64	8.7	1.46	6.21	1.53	6.19	1.53
6.57	1.72	8.65	1.55	6.21	1.63	6.19	1.58
6.58	1.64	8.7	1.46	6.21	1.53	6.19	1.53
6.57	1.74	8.64	1.53	6.22	1.63	6.20	1.57
	$\bar{n} = 1$		$\bar{n} = 1$		$\bar{n} = 1$		$\bar{n} = 1$

vibrational mode, which is a fundamental feature of azomethine group (Boutcher and Day, 1977). The bands in the regions 1510-1300 cm⁻¹, 1180—925cm⁻¹ and 890—800cm⁻¹ correspond to $\nu(\text{C-H})$ bending vibrational mode, $\nu(\text{C-N})$ stretching

vibration, and $\nu(\text{C-C})$ stretching mode, respectively. The bands within 484—565cm⁻¹ and 424—562cm⁻¹ are assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching vibrations respectively Nakomato (1963), Silverstein and Bassler (1967), Koji (1977),

Patel and Agwara (1990) and Koji (1977). These bands confirmed the coordination of the Schiff base to the respective divalent metal ions. The dissociation constant of the Schiff base is 11.85, but could not be confirmed as there was no available literature. The potentiometric analysis (Table 5) of the complexes prepared in this work revealed 1:1 (meta: ligand) stoichiometry (Chanage and Jahagirdar, 1983) and the general molecular structure of the complexes proposed below is quite consistent with the structure of the Schiff base cobalt (II) complex compound earlier reported by Zacharias (1984).

References

- [1] Angelici, R. J., Synthesis and Techniques in Inorganic Chemistry, W. B. Saunders Company, New York, 2nd Edition, 115-125, **1971**.
- [2] M. J., and Reedi, J. K., "Metal Ions in Biological Systems", 3rd Edition, MerceL Dekker Inc. New York, pp. 641-644, **1996**.
- [3] Medicated Atom Transfer Radical Cyclization Reactions, Tetrahedron Letters, 1, 3807-3812.
- [4] Clerk, A. J., Filik, R. P., Thomas, G. H., and Wongtap, H. Generation and Cyclization of Homogeneous and Solid Supported Copper (II) Schiff Base Complexes, *Journal American Chemical Society*, 1, 216, 743, **1998**.
- [5] Geary, W. J. The Use of Conductivity Measurement in Organic Solvents for the Characterization of Coordination Compounds, *Coordination Chemistry Review*, 7: 82-110, **1971**.
- [6] Hobday, M. D. and Smith, T. D. N, N'-ethylene bis(salicylideneiminato) Transition Metal ion Chelates, *Coordination Chemistry Review*, 9: 311-337, **1972**.
- [7] Holm, R. H., Everett, J. R., and Chakravorty, R. S, Metal Complexes of Schiff Bases and β -ketoimines, *Inorganic Chemistry*, 7: 83-214, Koji N. **1966**.
- [8] *Infrared Absorption Spectroscopy*, 2nd Edition, Holden-Day Inc, Sanfrancisco, 20-49 Lippard, S. J, **1994**. Bioinorganic Chemistry, 2nd Edition, University Science Books.
- [9] Chanage P. S., and Jahagirdar D. V., Potentiometric and Spectrophotometric Studies of Iron (III) Salicylic Acid Formaldehyde Polymer Complexes, *Indian Journal of Chemistry*, 22A; 624-625., **1983**.
- [10] Clerk, A. J. and Jones, K., Evidence onthe Nature of Cobalt-mediated Arylradical Cyclization, *Tetrahedral Letters*, 30: 5485-5489., **1989**.
- [11] Clerk A. J., Duncalf R. P., Filik R. P., Thomas G. H., and Wongtap H., (N-Alkyl-2-pyridylmethanimines as Tuneable Alternatives to Bipyridine Ligan in Copper Millvalley, pp. 505-508. Nakomato, K., **1963**.
- [12] *Infrared Spectra of Inorganic and Coordination Compounds*", Willey, New York, pp. 234-241., **1999**.
- [13] Patel, K. S. and Agwara, M. O. Hexamethylenetetramine Complexes of Divalent Metal Nitrates, *Nigerian Journal of Science*, 24: 107., **1990**.
- [14] Peter M. B. W. Academic Press Dictionary of Science and Technology, 3rd Edition, U. K. Academic Press Limited, 125-129 Silverstein, **1990**.
- [15] S. M. and Bassler, G. C. Spectrophotometric Identification of Organic Compounds, Willey, New York, pp. 12-23., **1967**.
- [16] Xishi, T., Xian, H. Y., Qiang, C. and Minyu, T., Synthesis of Some Transition Metal Complexes of a Novel Schiff Base Ligand Derived from 2, 2' - Bis(p- Methoxy Phenylamine) and Salicylic Aldehyde, *Molecules*, 8: 439-443., **2003**.
- [17] Zacharias P. S. Binuclear Cobalt (II) Complexes of Tetradentate Schiff Base Ligand, *Indian Journal of Chemistry*, 23A: 26-2., **1984**.

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