

Synthesis and Characterization of Cr(III) & Fe(II) Bis(2-Methoxybenzylidene)Biphenyl-4,4'-Diamine Complexes

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Abstract

Bis(2-methoxybenzylidene)biphenyl-4,4'-diamine Schiff base was prepared by the reaction of benzidine and O-methoxy benzaldehyde 1:2 reaction. Two complexes of this ligand with Cr(III) and Fe(II) were prepared. All prepared compounds were analysed using elemental analysis, IR, ¹H NMR and mass spectroscopy. The formation of proposed structures, including the free ligand and complexes were confirmed.

Keywords

Schiff Base, Complexes, Spectroscopy, Bis(2-Methoxybenzylidene)Biphenyl-4,4'-Diamine

1. Introduction

The chemistry of coordination compounds is well known and widely studied, yet many new developments are continuously taking place in this area of inorganic chemistry. The preparative work of Jorgenson, Werner and many others during the turn of the century opened up new vistas in the coordination chemistry of transition metals. It was Alfred Werner¹ who systematized the subject coordination chemistry, by propounding theory in 1893, for which he awarded Nobel Prize in 1913. These ideas have considerably enriched the understanding of the nature of metal-ligand bonds, structure, and chemistry of metal complexes, their stabilities and liabilities and other properties. It is now the need of time that new ligands of specified design should be synthesized, which could lead to metal complexes with special desired and possible predictable properties. The steady improvement in synthetic methodology allows us to foresee coordinating che-

mistry entering a phase of creative chemistry [1]. Schiff base complexes with transition metal have played a central role in the development of coordination chemistry. Because Schiff base ligands are capable of forming stable complexes with metal ions. Metal complexes play an important role in agriculture, pharmaceutical and industrial chemistry [2]. It is well known that azomethine of the general formula ($-C=N-$) has a great attention as precursor in huge organic synthesis and biological applications such as cycloaddition reaction [3] [4], optoelectronic properties [5], dyes and pharmaceuticals, antimicrobial activity [6], liquid membrane technology [7], anti-inflammatory [8], anticonvulsant [9], anti-tumour [10], antihypertensive activity [10] and anti-HIV activities [11]. Moreover, the reactions of azomethine throughout ring-closing to generation a wide range of five, six and seven members ring of heterocyclic organic molecules such as 4-thiazolidinone derivatives [12], 1,2-Dihydro-1-arylnaphtho[1,2-e][1,3] oxazine-3-one derivatives [6] [13] and [14] and 1,3-oxazepinediones [15]. All of these derivatives of heterocyclic compounds have importance as pharmaceutical drugs, active substances in biological systems [3] [14] [16] and liquid-crystalline compounds [15]. Therefore the synthesis of these kinds of organic compounds has become interesting.

Benzidine (4,4'-diaminobiphenyl), other names for benzidine are [1,1'-Biphenyl]-4,4'-diamine, 4,4'-diamino-biphenyl, 4,4'-bianiline, 4,4'-diphenyldi-amine is a greyish-red, yellowish, or white-coloured, very toxic, crystalline aromatic amine that darkens when exposed to air and light. Benzidine has been widely used for the detection of blood. A reagent in the manufacture of dyes. Ingestion of benzidine causes cyanosis, headache, mental confusion, nausea and vomiting. The azo dyes derived from benzidine are important because they are unlike simpler classes of azo dyes, they become strongly fixed to cotton without a mordant [17] [18]. Its use is now limited because of the strong association between exposure to benzidine and an increased risk of bladder cancer in humans [19]. The chemical or enzymatic oxidation of benzidine proceeds via a radical cation detectable by electron spin resonance. Peroxidase-catalyzed oxidation of benzidine generates reactive electrophiles which readily form adducts with phenol and thiol compounds. The structures of these novel metabolites are described. Peroxidases, including prostaglandin synthase, catalyze benzidine binding to protein and nucleic acid; the nature of the resulting adducts is unknown. The relevance of these processes to benzidine carcinogenesis *in vivo* is the subject of research and debate [20]. Benzidine is prepared in a two-step process from nitrobenzene. First, the nitrobenzene is converted to 1,2-diphenylhydrazine, usually using iron powder as the reducing agent. Treatment of this hydrazine with mineral acids induces a rearrangement reaction to 4,4'-benzidine. Smaller amounts of other isomers are also formed. The benzidine rearrangement, which proceeds intramolecularly, is a classic mechanistic puzzle in organic chemistry. Benzidine, the trivial name for 4,4'-diaminobiphenyl, is the solid organic compound with the formula $(C_6H_4NH_2)_2$. This aromatic amine is a component of a test for cyanide

and also in the production of dyes. Benzidine has been linked to bladder and pancreatic cancer. Since August 2010 benzidine dyes are included in the EPA's List of Chemicals of Concern [21]. Benzidine is no longer produced in the United States, although benzidine-based dyes may be imported into this country. No information is available on the acute (short-term) effects of benzidine in humans by inhalation exposure, but benzidine is considered to be very acutely toxic to humans by ingestion. Chronic (long-term) exposure to benzidine in humans may result in injury to the bladder. Epidemiological studies have shown occupational exposure to benzidine to result in an increased risk of bladder cancer. Animal studies have reported various tumour types at multiple sites from benzidine exposure via oral, inhalation, and injection exposure. EPA has classified benzidine as a Group A, known human carcinogen [21] [22].

Benzidine has been used since the 1850s as the reagent base for the production of a large number of dyes, particularly azo dyes for wool, cotton, and leather. However, because benzidine was found in the 1970s to be carcinogenic to humans, there has been a considerable decline in the use of the benzidine dyes. Benzidine is used for the quantitative determination of sulfuric acid and the detection and determination of numerous anions and metal ions. The reaction of benzidine with pyridine in the presence of elemental chlorine is suitable for detecting traces of free chlorine or pyridine in drinking-water. The green to blue colouration that occurs when benzidine reacts with hydrogen peroxide in the presence of peroxidases can be used to detect blood. Benzidine still plays a role in many chemical syntheses [23]. In the past, benzidine also has been used as a rubber compounding agent, in the manufacture of plastic films, for detection of hydrogen peroxide in milk, and quantitative determination of nicotine. Most of these uses have been discontinued, although some dyes that may contain benzidine as an impurity are still used as stains for microscopy and similar laboratory applications [24]. Archana *et al.* [25] synthesised and investigated four Schiff base chelates of Cu(II), Co(II), Ni(II) and Zn(II) formed from the reaction of 2-hydroxy benzaldehyde and benzidine. Metal complexes are reported and characterized using several analytical and spectroscopic techniques; the reaction is shown in **Figure 1**.

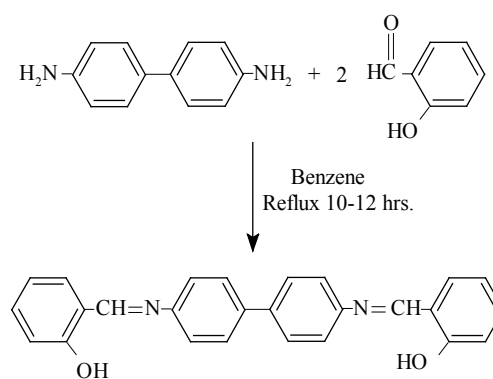


Figure 1. Preparation of Bis (2-Hydroxy Benzylidene) benzidine.

In present work, The complexes of Cr(III) and Fe(II) ions with the Schiff bases derived from the condensation of 2-methoxy benzaldehyde and benzidine were synthesised and characterised by different techniques, in particular, elemental analysis and molar conductance measurements as well as IR and electronic spectroscopy.

2. Materials and Methods

2.1. Materials

All chemicals and reagents used in this work were laboratory pure (BDH or Aldrich) and used without further purification, these include, benzidine, 2-methoxybenzaldehyde, $\text{Cr}(\text{NO}_3)_3$, FeCl_2 , NaOH , CH_3OH , THF and distilled water. Melting points were determined on a Gallenkamp melting point apparatus. The ^1H NMR spectra were recorded on a Bruker Avance II 500 MHz spectrometer. The chemical shifts were reported in ppm relative to tetramethylsilane (TMS).

2.2. Synthesis of Schiff Base

Schiff base under investigation is synthesised by dissolving 0.01 mol (1.842 g) of Benzidine in 25 ml methanol, 0.02 mol (2.723 g) of 2-methoxy benzylidene is added to this solution with reflux for 2 - 3 h. The formed yellow precipitate was filtered, washed with hot methanol until the filtrate becomes clear and finally dried in excellent yield. The chemical reaction is represented in **Figure 1**. Yield: 87%, 1.65 g M.P. 210°C .

2.3. Synthesis of Metal Complexes

Bis(o-methoxy benzaldehyde) benzidine (2.14 g, 0.005 mol) was dissolved in hot THF (50 mL), and a solution of 0.01 mol of metal salt in methanol $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ is slowly added to this solution, and the reaction mixture was refluxed at 60°C for 5 - 6 hours. The coloured crystalline product obtained after filtration was washed with hot THF several times and finally with diethyl ether. Yield: 75%, 1.60 g.

3. Results and Discussion

3.1. Elemental Analysis

The structures of the synthesised compounds were identified by (C.H.N.) elemental analysis, IR, ^1H NMR and mass spectral measurements and were in good agreement with the proposed structures (**Table 1**). C.H.N. elemental analysis was carried out for the free ligand and its complexes with Cr^{3+} and Fe^{2+} and found in good agreement with the calculated values, as shown in **Table 1**.

3.2. Infrared Spectroscopy and Magnetic Moment

The IR spectrum of the Schiff base bis(2-methoxybenzylidene)biphenyl-4,4'-diamine showed the band at 1620 cm^{-1} which was due to $\text{C}=\text{N}$ confirms the formation of

Table 1. Elemental analysis and magnetic moment of the Schiff base and its metal complexes.

Schiff Base/Metal Complexes	M.wt. (g/mol)	Elemental Analysis (Calc.)			μ_{eff} (BM)
		C%	H%	N%	
$\text{C}_{28}\text{H}_{32}\text{O}_2\text{N}_2$	428.31	78.991 (78.513)	5.834 (7.471)	6.606 (6.542)	-
$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_6 \text{Cl}_2 \text{Fe}_2$	746	47.874 (45.079)	4.825 (4.298)	4.408 (3.753)	5.08
$\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_{14} \text{Cr}_2$	756	47.448 (47.619)	4.234 (4.761)	6.389 (7.407)	4.40

the Schiff base. This stretching frequency at 1620 cm^{-1} C=N bond in the ligand is shifted to 1612 cm^{-1} and 1616 cm^{-1} in Fe^{2+} and Cr^{3+} complexes, indicating coordination of azomethine group through nitrogen atom with metal ion [26] [27] [28]. The low stretching frequency to 524 cm^{-1} and 516 cm^{-1} indicates the formation of new Fe-N and Cr-N bonds, respectively [29] [30]. Aromatic C-H and aromatic C=C vibrations are seen at $3001, 1593 \text{ cm}^{-1}$, respectively, these data are in good agreement with [31] [32]. In the Schiff base FT-IR spectra the broad, active absorption bands at 817 cm^{-1} and 759 cm^{-1} due to the $\delta(\text{C-H})$ aromatic of benzene ring out of the plane.

The magnetic susceptibility measurements for Cr^{3+} and Fe^{2+} complexes were done using Sherwood Scientific Magnetic Balance, Cambridge Science Park, Cambridge, England. Model number MSBI/230/95/6801. The magnetic susceptibility measurements (Table 2) showed that the complexes $[(\text{Cr(III)})_2 \text{L}]$ and $[(\text{Fe(II)})_2 \text{L}]$ were paramagnetic. The greenish-grey paramagnetic chromium complex gave a magnetic moment of 4.40 B.M corresponding to three unpaired electrons and the light brown (beige) paramagnetic Iron complex gave a magnetic moment of 5.08 B.M corresponding to four unpaired electrons [30] [33] [34].

3.3. $^1\text{H-NMR}$ and Mass Spectral Studies

The $^1\text{H-NMR}$ spectra confirmed the formation of Schiff base ligand. $^1\text{H-NMR}$ spectra of the ligand were taken in $\text{DMSO } d_6$ solvent as shown in Figure 2. The aromatic region was a set of multiples in the range 6.5 - 7.3 ppm for the Schiff base ligand, while the azomethine protons were observed in the range 8.6 ppm. $^1\text{H-NMR}$ in $\text{DMSO-}d_6$ showed $\delta = 2.497$ ppm for solvent (s, 2H, azomethane) deshielded at $\delta = 8.920$ ppm, (dd, 14H) aromatic groups = 8.085 - 7.050 ppm and (s, 3H) for methoxy group in ortho position at $\delta = 3.834$ ppm.

Mass spectra of chromium (III) complex with Schiff's base $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_{14} \text{Cr}_2 \cdot \text{H}_2\text{O}$ was recorded and was agreed with its stoichiometry. The molecular ion peak was observed at 674.38 for having complex molecular formula $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_{14} \text{Cr}_2 \cdot \text{H}_2\text{O}$ (Figure 3). From the analysis carried out on free ligand and compared with complexes, the proposed structures of complexes which confirmed by these analyses will be as follows as shown in Figure 4.

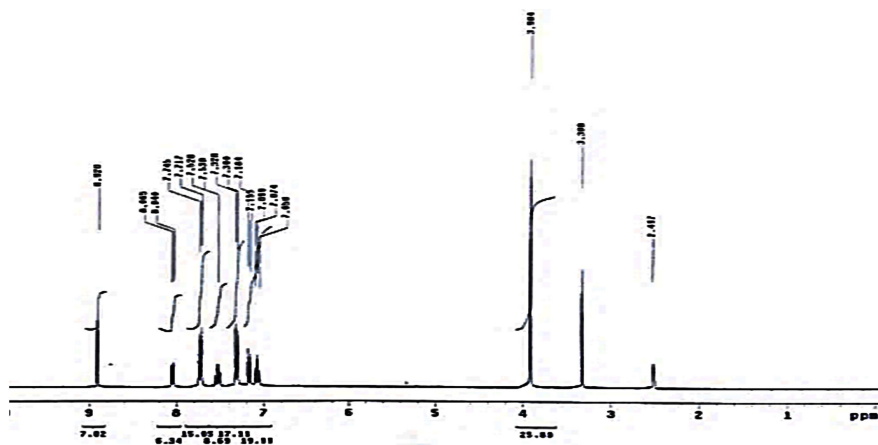


Figure 2. $^1\text{H-NMR}$ spectra of bis(2-methoxybenzylidene)biphenyl-4,4'-diamine.

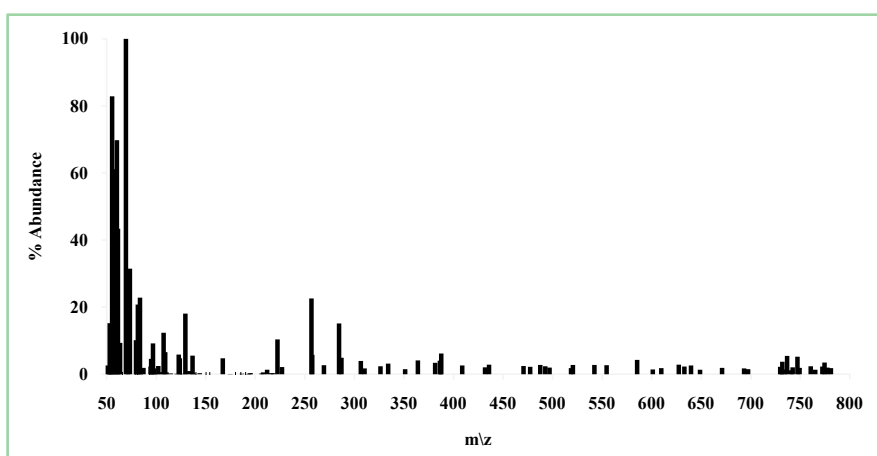


Figure 3. Mass spectra of $\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_{14}\text{Cr}_2$ complex.

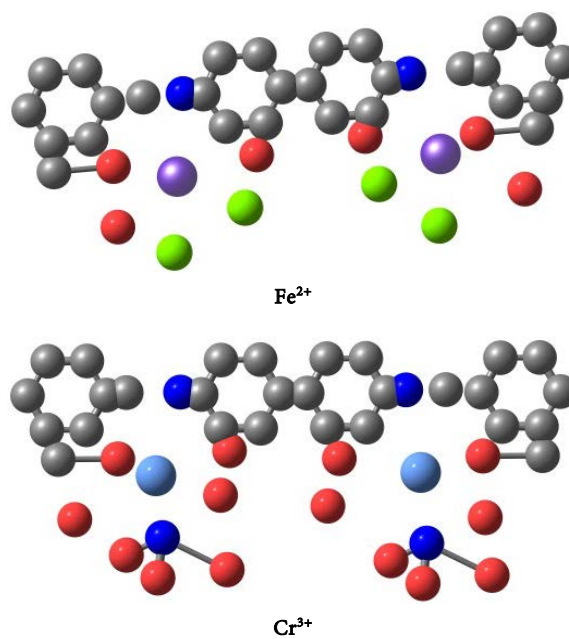


Figure 4. The proposed structures of Fe^{2+} and Cr^{3+} complexes.

Table 2. The IR spectral data of the Schiff base and of the complexes.

Schiff Base/Chelates	IR bands cm^{-1}					
	$\nu(\text{OH})$ Water	$\nu(\text{C-H})$	$\delta(\text{C-H})$	$\nu(\text{C=C})$	$\nu(\text{HC=N})$	$\nu(\text{M-N})$
$\text{C}_{28}\text{H}_{32}\text{O}_2\text{N}_2$	3444	3001	817,759	1593	1620	-
$\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_6 \text{Cl}_8 \text{Fe}_2$	3421	2835	818,756	1593	1617	524
$\text{C}_{28}\text{H}_{36}\text{N}_4\text{O}_{14} \text{Cr}_2$	3416	3267	814,760	1496	1616	516

4. Conclusion

In the present work, appropriate aldehyde derivatives were reacted with benzidine to give the corresponding Schiff base which confirmed by several analysis methods, and two coordination compounds of Cr(III) and Fe(II) with this Schiff base were prepared and confirmed with several analysis methods. This area of research is an open area, and other coordination compounds can be prepared using this Schiff base which we think it is a new Schiff base and aldehydes derivatives can also be used.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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