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Research paper

Synthesis and Spectral Studies of Novel Palladium (O) Complex with Ciprofloxacin Antibiotic

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Abstract

New complex of Palladium (0) with ciprofloxacin has been synthesized, The complex was portrayed by different physico - substance systems like essential examination, m.pt. , TLC, molar conductance estimation, attractive helplessness,^{13}C- NMR, ^{1}H-NMR and FT-IR. According to the results obtained, tetrahedral structure suggested for the prepared complex. The neutral ligand act in a Didentate mode, binding through oxygen atom of carbonyl group in pyridonering and oxygen atom of carboxyl ate group.

Keywords: *Spectral studies, palladium complex, ciprofloxacin, elemental analysis.*

1. Introduction

Ciprofloxacin [1 – cyclopro – pyl – 6 – fluoro – 1,4 – dihydro – 4 – oxo – 7 – (1 – piperaz – inil) – 3 – quinolone carboxylic acid] was orchestrated in 1987 for first time.[1].The ligands subordinate from Ciprofloxacin speaks to a class of O,O-benefactor ligands which are essential in coordination science [2].These ligands have incredible capacity to tie metal particles in the unbiased or anionic shape, going about as monodentate or bidentate ligands [3,4]. Metal Ciprofloxacin edifices are of enthusiasm due their bioinorganic applications. As of late research has shown the capacity of Ciprofloxacin ligands and their buildings to be antifungal, antibacterial, antiviral, mitigating and chemotherapeutic operators, possibly helpful for repressing the exercises of tumor cells [5– 7]. The cytotoxicity of these ligands is improved by coordination to metal particles, for example, copper, zinc, platinum and palladium. This movement is clarified not just by the metals' capacity it is valuable for the treatment of an extensive variety of contaminations as antibacterial drug[8,9].

Quinolones are a gathering of engineered antibacterial specialists for more than thirty years additionally ciprofloxacin which is the second era of flouro quinolone is one of the broadly utilized delegates in clinical use[10,11].

The intriguing properties of Ciprofloxacin in organic and synthetic fields by going about as a bidentate ligand through the oxygen iota of carbonyl gathering in pyridonering and the oxygen of carboxylate gathering. The association of Ciprofloxacin and metal particles have been examined and the Writing uncovers that metal particles present in edifices could quicken the medication activity and the adequacy of the natural helpful agents[12].

The pharmacological efficiencies of metal edifices rely upon the idea of the metal particles and the ligands[13]. In this work we report the union and portrayal of progress metal complex of palladium (0) particle with Ciprofloxacin. This ligand framework facilitates with the metal particle in a didentate way through the carbonyl oxygen in pyridone ringand the oxygen of carboxylate gathering.

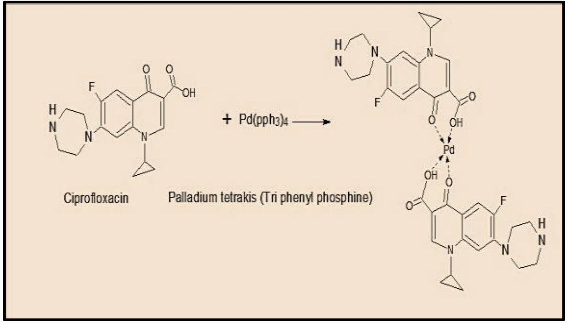
2. Experiment

All synthetic concoctions were obtained from BDH and Fluka IR-spectra were taken ona (Shimadzu , FTIR-8 400 S) Fourier Change Infrared Spectrophotometer (4000-400) cm-1 with tests as circles. Natural investigation (C.H.N) was (EURO3000 Single)), Conductivities were estimated for 10-3M of edifices in DMSO at 25 C utilizing (Digits conductivity meter WTW,720), Metal substance buildings were controlled by nuclear retention (A.A) strategy utilizing aAtomic Ingestion spectrophotometer-5000 ,Perkin-Elmer.1 H NMR and 13C NMR spectra were recorded on Burker [Avance (III)] Burker (300-MHz) in NMR spectrometer utilizing TMS as inside standard and the qualities are communicated in δ ppm .

2.1. Synthesis of novel palladium (0) ion complex with ciprofloxacin

A (250 ml) two – necked flask was equipped with a magnetic stir bar and (0.5gm , 0.001mol)of ciprofloxacin hydro chloride as well as (0.05gm) of [Pd (pph$_3$)$_4$] [Palladium tetrakis (Tri phenyl phosphine)] were added into the flask with 20 ml of absolute ethanol under N_2 gas , The mixture was stirred and heated , after that (0.001 mole) of substituted aryl boronic acid [2-(methyl thio) phenyl boronic acid , 2-methoxy carbonylphenyl boronic acid, 3-formyl phenyl boronic acid , 5- formyl -2- thienylboronic acid, Ferrocene boronic acid] and solution (5% Na_2CO_3) were added in the flask .
The reaction mixture was stirred and heated at 75^{0}Cfor (6-8 h) then followed by TLC and monitor reactions using (n- hexane and ethyl acetate) in 2:3 ratio. The mixture was filtered off [14-17].Washed by ethanol and the solvent was removed, Then cooled ether was added for decantation and dried .yielding brown crystals with 68% yield.

The preparation of palladium (0) ion complexes with Ciprofloxacin is showed in Scheme 1. The physical properties and analytical data for this complex collected in Table.1.



Scheme 1: The preparation of palladium (0) ion complexes with Ciprofloxacin

Table 1: Physical Properties and Analytical Data of Palladium (0) Ion Complexes with Ciprofloxacin

Empirical Formula	Color	Mwt.	Rf	M.P C°	Found (Calc.)%			
					C	H	N	M
$C_{17}H_{17}N_3O_3F$	White	330.34	--	257	61.412 (61.755)	5.120 (5.146)	12.681 (12.714)	—
$[Pd(C_{17}H_{17}N_3O_3F)_2]$	Brawn	767.07	0.72	224	53.06 (53.189)	4.27 (4.432)	10.39 (10.951)	13.50 (13.871)

3. Results and discussion

The metal complex is insoluble in water and soluble in DMSO, DMF, CHCL3, acetone , methanol and ethanol.

3.1. Infrared spectra

The FT-IR spectrum for this complex exhibited absorption band of (COOH) group at 1718cm^{-1}while this group appeared at 1707 cm^{-1} in the ligand(original ciprofloxacin spectrum) , the C=O group in pyridone ring appeared in 1629 cm^{-1} while in ciprofloxacin spectrum exhibited at 1625 cm^{-1} so ,The band of (OH) group appeared at 3437 cm^{-1} in complex spectrum of palladium but exhibited at 3377 cm^{-1} in original ciprofloxacin spectrum These shifting indicated the coordination of the ligand with metal ion .As well as we noticed the band at 1026 cm^{-1} related to (C-F) in the ligand spectrum while exhibited at 1012 cm^{-1} in the complex spectrum .The appearance of a new band at (472and 453) cm^{-1} in IR spectra of the complex due to (M-O) the carbonyl group in pyridone ring and the carboxyl ate group respectively[18,19] . It is concluded that the ligand behaves as a Didentate ligand coordinated to the metal ion via oxygen atom of the carbonyl group in pyridone ring and the oxygen atom of carboxyl ate group. The IR spectral data of Ciprofloxacin ligand and its complex Figures (1 and 2) are presented in Table 2.

Table 2: Characteristic IR Absorption Bands of the Ciprofloxacin Ligand and its Complex with Pd(0) in cm^{-1} Units

Empirical Formula	υ(O-H) of carboxylic group	υ(C=O)of carboxylic group	υ(C=O)of pyridine ring	υ(Pd−O) of carboxylic group	υ(Pd−O) of pyridone ring
$C_{17}H_{17}N_3O_3F$	3377	1707	1625	---	---
$[Pd(C_{17}H_{17}N_3O_3F)_2]$	3437	1718	1629	580.	460

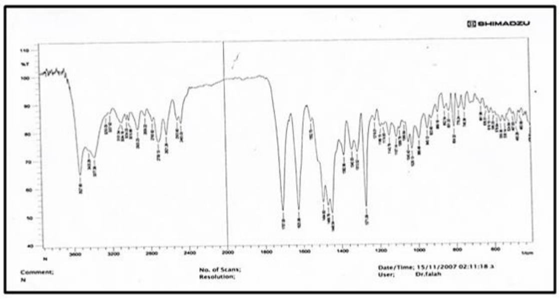


Figure 1: IR spectrum of the ciprofloxacin ligand

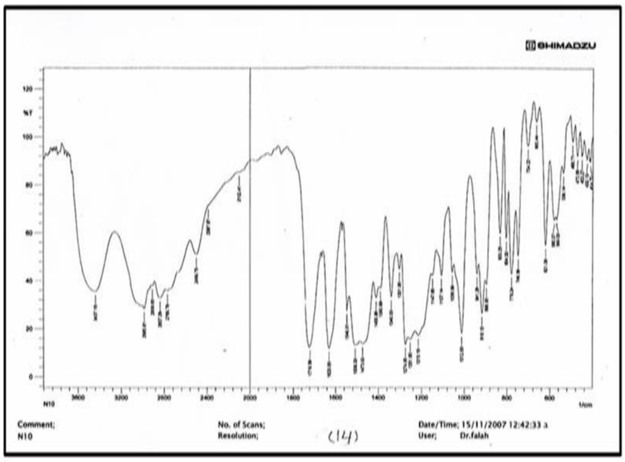


Figure 2: IR spectrum of ion complex of Pd(0) with the Ciprofloxacin ligand

3.2. ^{1}H-NMR spectra

In^1 H-NMR spectrum of this complex showed a triplet signal due to (CH$_2$)group of cyclo propyl ring at (0.8-1.2)ppm and exhibit chemical shift at 2.5 ppm for DMSO solvent , At (3.4-3.8)ppm exhibit multiplet signal due to (-CH$_2$-) for piperazin ringand we noticed at (3.9-4.1) ppm multiplet signal for (-NCH) of cyclo propyl ring as well as in (4.3-4.5) ppm appeared multiplet signal related to (NH) proton of piperazin ring. The spectrum of 1 H-NMR exhibit multiplet signal for protons of aromatic rings at (6.5-7.8)ppm while the proton of hydroxyl group (OH) for carboxylic acid (COOH) exhibited chemical shift at 13.06 ppm. This information indicates the coordination of the metal center to oxygen atom of the carbonyl group in pyridone ring and the oxygen atom of carboxyl ate group[20].

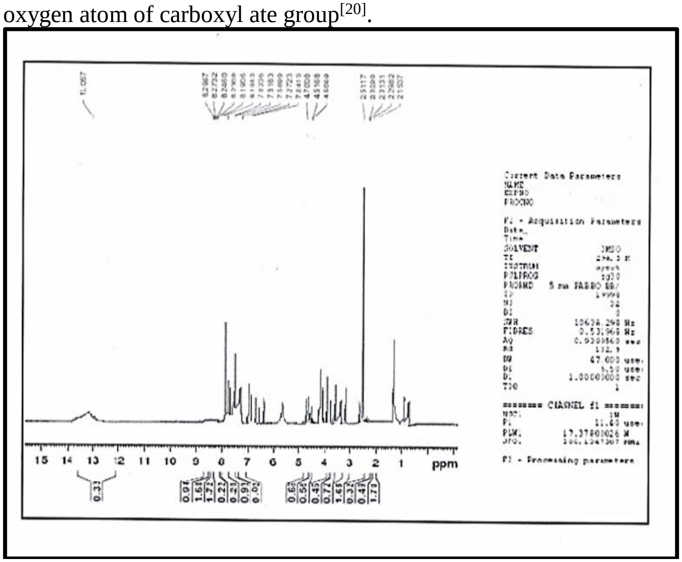


Figure 3: The ^{1} H-NMR spectrum of the complex ion of palladium with ciprofloxacin

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3.3. ^{13}C-NMR spectra

The ^{13}C-NMR spectra for the complex of palladium with ciprofloxacin appeared a clear doublet signal at (200-204) ppm due to carbon of pyridone rings and exhibit doublet signal at (160-162)ppm for carbon of carboxylic group (COOH) as well as appeared bands at (100-138)ppm for carbon of aromatic rings and the complex spectrum exhibit signal band due to DMSO solvent at 40 ppm so the spectrum appeared quartet signal at (32-38) ppm due to carbon of piperazin rings .I n (16-18) ppm exhibit doublet signal related to the carbon of (NCH) in cyclo propyl ring while appeared a clear doublet signal between (10-12) ppm for carbon of cyclopropyl ring (CH_2)[20].

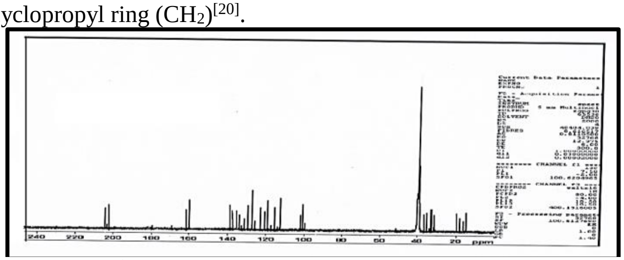

Figure 4: The^{13} C-NMR spectrum of the complex ion of palladium with ciprofloxacin

3.4. Molar conductance and magnetic moment

The molar conductance esteem for the combined complex was indicated molar conductivity esteem at (27.10) S.cm2. mol-1 and controlled by utilizing 1x10-3M DMSO arrangement, as appeared in Table 3. Molar conductivity estimation led on the palladium(0) complex uncovered the non-conductivity nature of the arrangement at room temperature demonstrating the nonattendance of any electrolytes [20] . This esteem demonstrate that there is no particles existing in the external circle coordination of the complex. Not surprisingly, the attractive helplessness estimation demonstrated diamagnetic conduct reflected in the zero powerful attractive minute, µeff = 0, in the complex steady with the 0 unpaired electrons of Pd(0) d10species having tetrahedral geometry .

Table 3: Molar Conductivity and Magnetic Moment (µeff.) of the Complex of Palladium with Ciprofloxacin

Complex	Molar Conductivity S.cm^2.mol^{-1}	µeff. B.M
[Pd ($C_{17}H_{17}N_3O_3F$)$_2$]	27.10	Dia.

3.5. Suggested structure

On the basis of elemental microanalysis, molar Conductivity, magnetic moment and spectroscopic studies for the palladium complex ion with ciprofloxacin ligand, we suggest that the ligand behaves as Didentate on Complexation with metal ionvia oxygen atom of the carbonyl group in pyridone ring and the oxygen atom of carboxylate group. All we found that the Mole ratio M:L was 1:2 . According to these results, the complex has tetrahedral geometry around metal ion.

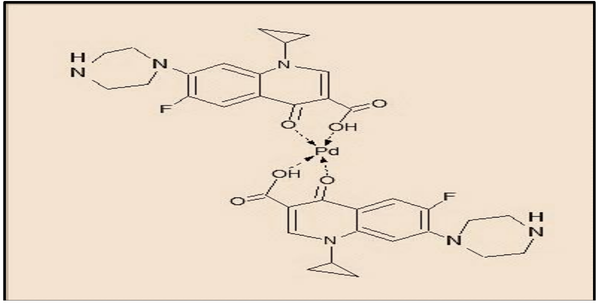

Figure 5: The suggested structural of Pd (0) complex ion with ciprofloxacin ligand

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