

SYNTHESIS, CHARACTERIZATION AND *IN VITRO* ANTIMICROBIAL STUDIES OF MANGANESE(II) AND IRON(II) COMPLEXES OF (2)-*N*-PHENYL-2-[1-(PYRIDIN-2-YL)ETHYLIDENE]HYDRAZINE-1-CARBOTHIOAMIDE SCHIFF BASE *¹Isyaku S., ²Atiku I., ³Jabbi A. M. and ¹Uba S.

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ABSTRACT

(2)-N-phenyl-2-[1-(pyridin-2-yl)ethylidene]hydrazine-1-carbothioamide (AP-PTSC) Schiff base derived from 2-acetylpyridine, with 4-phenylthiosemicarbazide were synthesized and complexed with Mn(II) and Fe(II) ions. The Schiff base and the metal(II) complexes were characterized based on melting point/decomposition temperature solubility, magnetic susceptibility, infra red (IR) spectra, molar conductance measurements and elemental analyses. The Schiff base was yellow in colour, with a melting point of 170 °C and a yield of 86%. Decomposition temperatures of the complexes indicated their moderate stability. The compounds were soluble in some common organic solvents. The effective magnetic moment of the metal(II) complexes were 5.8BM and 5.5BM, which indicated their paramagnetic nature and high spin octahedral geometry. The infra red spectral data of the Schiff base and its metal(II) complexes assignable to v(C=N) vibration were at 1648cm⁻¹, 1638cm⁻¹ and 1627cm⁻¹ ¹, respectively. This indicates coordination of the Schiff base to the metal(II) ion via azomethine nitrogen. Molar conductance measurements of the complexes showed that they are electrolytes. The results of the elemental analysis of the ligand and its complexes were in agreement with the calculated values, suggesting a 1:2 (metal-ligand) ratio. Antimicrobial screenings of the ligands and the complexes were carried out against gram-positive (Staphylococcus aureus,), gram-negative (Salmonella typhii, and Escherichia coli) pathogenic bacteria and three fungi mainly (Candida albicans, Mucus indicus and Aspergillus flavus). The results showed that both the ligands and the complexes were active against the pathogens.

Keywords: 4-phenylthiosemicarbazide, elemental analysis, ligand, magnetic susceptibility, molar conductivity, Schiff base, 2-acetylpyridine

INTRODUCTION

Schiff base is a compound containing >C=NR group that is formed by condensation of either an aldehyde or a ketone with a primary amine and was first reported by Hugo Schiff in 1864[1]. Thus a Schiff base is a nitrogen analogue of an aldehyde or a ketone in which the O in the C=O group is replaced by an N-R group where R may be an alkyl or aryl substituent [2]. Schiff base chelates to active site of metal ion through N, O and S donor atoms [3]. Schiff bases of transition metal complexes have been reported and found to be important for their biological activity [4]. They have been used as analytical reagent, polymer-coating, ink, pigment, fluorescent materials and catalytic reagent [5].

Thiosemicarbazones are well established as a special class of sulphur (S) donor Schiff bases that are particularly useful for transition metals due to their metal complexing ability [6]. They are found to be potentially useful as anti-bacterial, antifungal, antitumor, antiviral, radio protective and anti-inflammatory activities [7]. A large number of thiosemicarbazone complexes have been studied for a considerable period and known to have high tendency to exhibit square planar and octahedral geometry [8]. Thiosemicarbazones were reported to show activity against tumor, tuberculosis and leprosy [9]. Clinical and experimental studies on the effect of thiosemicarbazones and were found to be active against leukemia [10].

Pyridine is an important electron-acceptor group, due to its high electron affinity [11]. Poly (2, 5-pyridinediyl) (PPY) was described as an efficient electron transport bilayer polymeric light emitting diodes (LEDs), [11]. The LEDs with a PPY layer exhibited external quantum efficiency 60-times greater than that of similar devices without a PPY layer. Complexes of pyridine carboxyaldehyde thiosemicarbazone were active against leukemia cells [12] and Pd(II) complexes of N-4-alkyl-2-acetylpyridine thiosemicarbazones show *in vitro* inhibitory activity of DNA syntheses in cell cultures [13]. Platinum(II) complexes of N-4-ethyl 2-formyl and 2-acetylpyridine thiosemicarbazones of cells [14].

Although, many structures of thiosemicarbazone have been reported, there are only few for the complexes of the precursor compounds. Therefore, this research concentrated on the synthesis, characterization of a Schiff base derived from 2-acetylpyridine with 4phenylthiosemicarbazide and its Mn(II) and Fe(II) complexes and carrying out an *in vitro*

antimicrobial studies of the prepared Schiff base and the metal(II) complexes against Gram-positive (*Staphylococcus aureus*) and two Gram-negative (*Salmonella typhii and Escherichia coli*) bacteria isolates and three fungi isolates (*Candida albicans, Mucus indicus* and *Aspergillus flavus*).

MATERIALS AND METHOD

All the chemicals used in this work were of Analar Grade and were used without further purification. The main chemicals; 4-phenylthiosemicarbazide and 2-aceltylpyridine, were all purchased from Sigma Aldrich U. K.

All weighing were carried out using Electrical Meter Balance AB 54. Magnetic susceptibility measurements of the complexes were determined using Sherwood Scientific MSB MK1 Magnetic Susceptibility Balance. Melting point/Decomposition temperatures were determined using a digital WRS-IB Microprocessor Melting Point Apparatus. Infrared spectral analyses were recorded using Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer in the range 4500-250cm⁻¹. Molar conductivity measurements were carried out using George Kent model 5003 conductivity metre. Metal and Elemental Analysis of C, H and N were carried out at Robertson Microlit Laboratories, New Jersey (U.S.A).

The microorganisms used in this research were obtained from the Department of Medical Microbiology, Aminu Kano Teaching Hospital Kano. Identification and antimicrobial screening against the microbial strains (*Staphylococcus aureus, Salmonella typhii, Escherichia coli, Candida albicans, Mucus indicus and Aspergillus flavus*) were conducted in the Department of Microbiology, Bayero University Kano. Ciprofloxacin was used as standard drugs for antibacterial screening and Ketoconozole for antifungal test. Mueller Hinton agar and Potato dextrose were used as growth media for the microbes

Preparation of Schiff base derived from 2-acetylpyridine and 4-phenylthiosemicarbazide (AP-PTSC)

A solution of 2-acetylpyridine (0.01mol, 1.12cm³), was added drop wise to a hot solution of 4phenylthiosemicarbazone (1.67g, 0.01mol) in 70cm³ ethanol, followed by three drops of acetic acid. The mixture was refluxed at a temperature of 70°C with constant stirring for 3 hours. The

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solution was cooled at 5°C for 24 hours in the refrigerator. The precipitate obtained was filtered off, washed several times with ether and dried over P_2O_5 in a desiccators for three days [15].

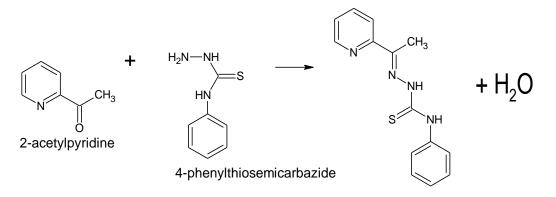


Fig. 1: Procedure for the Preparation of Thiosemicarbazone

Procedure for the Preparation of the Schiff base metal (II) complexes

Mn(II) and Fe(II) complexes for the Schiff base derived from 2-acetylpyridine with 4-phenyl thiosemicarbazide (AP-PTSC), were prepared by the addition of the solution of the Schiff base (0.002 mol) in 20 cm³ ethanol to the solution of each of the metal (II) salts (0.001 mol) in 10 cm³ ethanol. The mixtures were each refluxed for 3 hours with stirring. On cooling, the precipitate of each of the complexes was filtered off, washed with ethanol, diethyl ether and dried over P_2O_5 in a dessicator for three days [15].

Determination of Melting point/ Decomposition Temperature

The melting point of the Schiff base and the decomposition temperature of the metal(II) complexes were determined using microprocessor melting point apparatus (WRS-IB) and Gallenkamp melting point apparatus [16]. The results obtained are shown in Table 1.

Solubility Test

The solubility of the Schiff base and each of its metal(II) complexes was tested using common organic solvents and distilled water. About 20 mg of each compound was tested in 5 cm³ of each of the corresponding solvent in a test tube, shaken thoroughly [17]. The results obtained are shown in Table 2.

Magnetic Susceptibility Measurement

The magnetic susceptibility (χ_g) of complexes was determined using magnetic susceptibility balance MKI Sherwood science Ltd via equation 1[18]. The results obtained are shown in Table.3.

$$\chi_g = \frac{CL (R_1 - R_0)}{m \times 10^9} \ \dots \dots (1)$$

Where; m= sample mass (g) = $W_1 - W_0$, W_0 = weight of empty capillary tube, W_1 = weight of the capillary tube and the complex, R_0 = initial reading from the balance for empty capillary tube, R_1 = reading from the balance for the loaded capillary tube, L = length of the complex in the capillary tube (cm). C = balance calibration constant (C = 1).

Infrared Measurements

Shimadzu FTIR-8400S Fourier Transform Infrared Spectrophotometer in the range 250-4500cm⁻¹ was used. A small amount of powder sample (about 1-2% of KBr amount) was taken and mixed with KBr powder and then analyzed using infrared analyzer. The results obtained are shown in Table 4.

Molar Conductance Measurement

Molar conductivity measurements were carried out on 1×10^{-3} moldm⁻³(0.001 M) solution of each of the metal complexes in Dimethyl Formamide (DMF) at 25°C [19]. The molar conductance is calculated using equation 4,.

$$\Lambda_{\rm M} = \frac{1000 \rm L}{\rm C} \dots \dots (4)$$

Where Λ_M = molar conductance, L = specific conductance and C = concentration of the complex. The results are presented in Table 5.

Elemental Analysis

The analysis was carried out using Perkin-Elmer CHN 2400 Elemental Analyzer based on the classical Pregl-Dumas method. About 20 mg of each of the samples for analysis was encapsulated in an aluminium vial and inserted automatically into the combustion zone of the analyser using a single-sample auto injector. In the presence of excess oxygen and combustion reagents, the

samples were combusted completely and reduced to the elemental gases CO_2 , H_2O and N_2 . All the results were computed automatically and were given as percent weight of each element. The results are shown in Table 6.

Antimicrobial Test

The *In vitro* antimicrobial activity of the ligand (AP-PTSC) and its complexes were tested against Gram-positive (*Staphylococcus aureus*,) and two Gram-negative (*Salmonella typhii, and Escherichia coli*) pathogenic bacteria. Also three fungi mainly (*Candida albicans, Mucus indicus* and *Aspergillus flavus*) were used. Muller Hilton Agar media for bacteria while Potato Dextrose Agar (PDA) for fungi were used and were prepared in distilled water. The ligands and the complexes were dissolved separately in Dimethyl Sulphoxide (DMSO) to obtain three different concentrations (15 µg/ml, 30 µg/ml and 60 µg/ml), which were used to check the antimicrobial activities by well diffusion method. The discs were saturated with the dissolved compounds in Dimethylsulfoxide (DMSO) and then placed in petridishes containing the culture media. The petridishes were incubated at 37°C and the inhibition zone was measured after 24 hours for bacteria and Ketoconozole for fungi), [14] as shown in Tables 7 and 8.

RESULTS AND DISCUSSION

The results of the colours, percentage yields, melting points of the Schiff bases, decomposition temperatures, solubility test, molar conductance magnectic susceptibility, infrared and elemental analysis of the transition metal(II) complexes are presented below:

Table 1: Some physica	l Properties of	(AP-PTSC) Sc	hiff base and its meta	al (II) comple	xes
Ligand Complex,	Colour	Melting point (°C)	Decomposition Temperature (°C)	Percentage Yield	(%)
AP-PTSC	Yellow	170	_	86.8	
[Mn(AP-PTSC)2]Cl2	Pale green	-	256	80.0	
[Fe(AP-PTSC)2]Cl2	Deep green	-	258	80.7	
AP PTSC = Schiff box	a darived from	agotulouriding	and 1 phonylthiosom	icorbozido	

AP-PTSC = Schiff base derived from 2-acetylpyridine and 4-phenylthiosemicarbazide.[M(AP-PTSC)₂]Cl₂ = Metal (II) complex for the Schiff base derived from 2-acetylpyridine and 4-phenylthiosemicarbazide, where M = Mn or Fe(II) ion.

Table 2: Solubility Data of (AP-PTSC) Schiff base and its metal (II) complexes

Ligand/Complex	Water	Methanol	Ethanol	N-	Ether	Acetone	Dichloro	Chloroform	DMSO
				hexane			Methane		
AP-PTSC	IS	IS	IS	IS	IS	S	S	S	S
[Mn(AP-PTSC)2]Cl2	IS	SS	SS	IS	IS	S	S	SS	S
[Fe(AP-PTSC) ₂]Cl ₂	SS	S	S	IS	IS	S	S	S	S

S=> Soluble, SS=> Slightly soluble while IS=>Insoluble

Table 3: Magnetic Susceptibility Values of AP-PTSC Metal(II) Complexes

Complex	Gram susceptibility (Xg)10 ⁻⁶	Molar Magnetic Susceptibility (Xm)10 ⁻³	Magnetic Moment µ _{eff} (B.M)	Magnetic Property
[Mn(AP-PTSC)2]Cl2	21.0	0.14	5.8	Paramagnetic
[Fe(AP-PTSC)2]Cl2	19.0	0.13	5.5	Paramagnetic

AP-PTSC=> Schiff base derived from 2-acetylpyridine and 4- phenylthiosemecarbazide, [M(AP- PTSC)₂]Cl₂,=>Its Metal (II) complexes where M= Mn(II) or Fe(II) ion.

Table 4: Infrared Spectra Data of AP-PTSC and its Metal(II) Complexes

Compounds	υ (C=N) (cm ⁻¹)	υ (N-H) (cm ⁻¹)	υ (C=S) (cm ⁻¹)	υ(M-N) (cm ⁻¹)	v(M-S) (cm ⁻¹)
AP-PTSC	1648	3296	766	-	-
[Mn(AP-PTSC) ₂]Cl ₂	1638	3299	758	541	378
[Fe(AP-PTSC)2]Cl2	1627	3304	755	461	394

Table 5: Molar Conductance Measurement for AP-PTSC Metal(II) Complexes

$[Mn(AP-PTSC)_2]Cl_2 1.5 1.87 124.64 [Fe(AP-PTSC)_2]Cl_2 2.40 100 000 000 000 000 000 000 000 000 0$	Compound	Conc. Moldm ⁻³ x 10 ⁻³	Specific Conductance x 10 ⁻⁴ SΩ ⁻¹	Molar Conductance Ω^{-1} 1 cm ² mol ⁻¹
	[Mn(AP-PTSC) ₂]Cl ₂	1.5	1.87	124.64
	[Fe(AP-PTSC) ₂]Cl ₂	2.40	3.32	138.50

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Table 6: Elemental Analysis o	f AP-PTSC and it	s Metal (II) comp	lexes	
Ligand/Complex	%C	%H	%N	%M
	(Calc) Found	(Calc) Found	(Calc) Found	(Calc) Found
A AP-PTSC	(62.20)	(5.22)	(20.72)	
	62.40	5.70	20.80	
[Mn (AP-PTSC) ₂]Cl ₂	(50.45) 50.70	(4.23) 4.60	(16.18) 16.30	(8.24) 8.27
[Fe (AP-PTSC) ₂]Cl ₂	(50.39) 50.50	(4.23) 4.00	(16.79) 16.20	(8.37) 8.20

 $AP-PTSC => Schiff base derived from 2-acetylpyridine and 4-phenylthiosemecarbazide, [M(AP-PTSC)_2]Cl_2,=>Its Metal (II) complexes where M= Mn or Fe (II) ion$

Isolate	-	iylococ is (µg/		Esche (µg/d	erichia isc)	coli		<i>ionella</i> disc)	typhirium
Compd/conc.	15	30	60	15	30	60	15	30	60
AP-PTSC	~	0	11	7	0	11	6	0	10
Mac(AD DTSC) 1C1	6	8	11	7	9	11	6	8	10
[Mn(AP-PTSC) ₂]Cl ₂	9	13	14	9	11	13	6	10	14
[Fe(AP-PTSC) ₂]Cl ₂	ĺ	15	14	ĺ	11	15	0	10	14
	7	10	13	9	10	14	7	12	14
Ciprofloxacin(at all con)									
_		34			40			43	

PTSC=> Schiff base derived from 2-acetylpyridine and 4-phenylthiosemecarbazide, [M(AP-PTSC)₂]Cl₂,=>Its Metal (II) complexes where M= Mn or Fe(II) ion.

AP-

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Isolate	Mucus specie)	· · ·	ndicus sc)	Asper (µg/d		flavus	<i>Candic</i> (µg/dis		Albican
Compd/conc.	15	30	60	15	30	60	15	30	60
AP-PTSC	7	8	11	6	6	6	7	10	13
[Mn(AP-PTSC) ₂]Cl ₂	9	11	13	8	10	14	9	11	14
[Fe(AP-PTSC) ₂]Cl ₂	7	9	12	9	11	12	10	13	16
Ketoconozole (At all conc.)		27			32			38	

Table 8: Zone of inhibition (mm) for Antifungal of AP-PTSC and its metal (II) complexes

Interaction between 4-phenylthiosemicarbazide with 2-acetylpyridine in (1:1 molar ratio) in ethanol produced a Schiff base; (2)-*N*-phenyl-2-[1-(pyridin-2-yl)ethylidene]hydrazine-1-carbothioamide (2-acetylpyridine-4-phenylthiosemicarbazone) (AP-PTSC). Reaction of the Schiff base with Co(II) and Ni(II) metal salts in (2:1 molar ratio) in ethanol produced Schiff base complexes; [Mn(AP-PTSC)₂]Cl₂ and [Fe(AP-PTSC)₂]Cl₂. The Schiff base AP-PTSC and its Mn(II) and Fe(II) complexes were characterized based on melting point/decomposition temperature, solubility, magnetic susceptibility, infrared (IR) spectra, molar conductance measurements, elemental and gravimetric analyses.

Physico-Chemical Properties of the Schiff Base and its Metal(II) Complexes.

The Schiff base is yellow powder with a yield of 86.8% and a melting point of 170°C. The complexes [Mn(AP-PTSC)₂]Cl₂ and[Fe(AP-PTSC)₂]Cl₂ are pale green and deep green with decomposition temperature of 256°C and 258°C, a yield of 80.0% and 80.7% (Table 1). The variation in colour of the Schiff base with its corresponding complexes is attributed to'd-d' orbital transition of electron between one energy level to another, by their magnitude of splitting, which in turn depends on the geometry of the complex, the nature of the ligand and charge transfer [21]. The decomposition temperatures of the complexes are relatively high, indicating good thermal stability of the complexes.

The Schiff base and its complexes are soluble in acetone, dichloromethane, and DMSO.

However, [Fe(AP-PTSC)₂]Cl₂ is still soluble in methanol, ethanol and chloroform, but slightly soluble in water. [Mn(AP-PTSC)₂]Cl₂ is slightly soluble methanol and ethanol but insoluble in water (Tables 2). The solubility of the Schiff bases and their metal(II) complexes in the common solvents indicated their low polarity which can be used in order to determine the suitable solvents that could be utilized for subsequent spectroscopic measurements [22].

The magnetic susceptibility of [Mn(AP-PTSC)₂]Cl₂ and[Fe(AP-PTSC)₂]Cl₂ are 5.8BM and 5.5.BM as presented in Tables 3. This indicates high spin octahedral geometry [23].

The infrared spectra of the Schiff base shows a broad band at 1648cm^{-1} , that is attributable to v(C=N) stretching vibration, shifted to a lower frequency at 1638cm^{-1} and 1627cm^{-1} in the spectra of the complexes. This indicates coordination of the Schiff base to the metal ions via azomethine nitrogen. The frequency in the spectra of the Schiff base at 3296cm^{-1} , is assignable to v(N-H) stretching vibration makes an upward shift at 3299cm^{-1} and 3304cm^{-1} in the spectra of the complexes also support coordination of the Schiff base to the metal(II) ion. The IR bands in the spectra of the complexes assignable to v(M-N) at 541cm^{-1} and 461cm^{-1} , and that assignable to v(M-S) at 378cm^{-1} and 394cm^{-1} respectively. This confirmed coordination of the Schiff base to the metal (II) ion through sulphur and nitrogen atoms respectively [24, 25], (Tables 4).

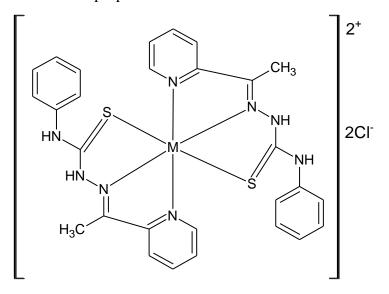
The molar conductivities of 10^{-3} M solutions of $[Mn(AP-PTSC)_2]Cl_2$ and $[Fe(AP-PTSC)_2]Cl_2$ in DMF are 124.64 Ω^{-1} cm²mol⁻¹ and 138.50 Ω^{-1} cm²mol⁻¹ as shown in (Table 5). These values indicate that the solutions of the complexes are electrolyte, [19, 23].

The results of the elemental analysis (C, H and N) of the Schiff base and its respective metal(II) complexes are presented in Table 6. The values are in agreement with the proposed formula of the ligand and its corresponding metal complexes, since the values for the theoretically calculated percentage compositions of carbon, hydrogen and nitrogen in the respective compounds are in agreement to the values of the elements experimentally found, suggesting 1:2 metal-ligand ratio.

Antimicrobial test of the AP-PTSC Schiff base and its metal(II) complexes were carried out against three bacteria isolates; Gram-positive (*Staphylococcus aureus*,), Gram-negative (*Salmonella typhii, and Escherichia coli*) and three fungi (*Candida albicans, Mucus indicus and Aspergillus flavus*). Concentrations of 15, 30 and 60(µg/disc) were used, standard drugs

ciproflaxacin and ketoconozole for bacteria and fungi, served as controls, (Tables 7-8). The results of the tests indicated moderate antimicrobial activity against the tested microorganisms when compared with the standards, and this activity increases by increasing concentration. Also the metal complexes showed higher activity than free ligand, which can be explained on the basis of chelation theory, which states that; the chelation tends to make the complex acts as a more powerful and potent bactericidal or bacteriostatic agent than the ligand [26].

From the results of analysis of the complexes and the available literature data, the general molecular structure below is proposed:



Where M= Mn or Fe

Fig 2: Proposed Structure of Metal(II) complex

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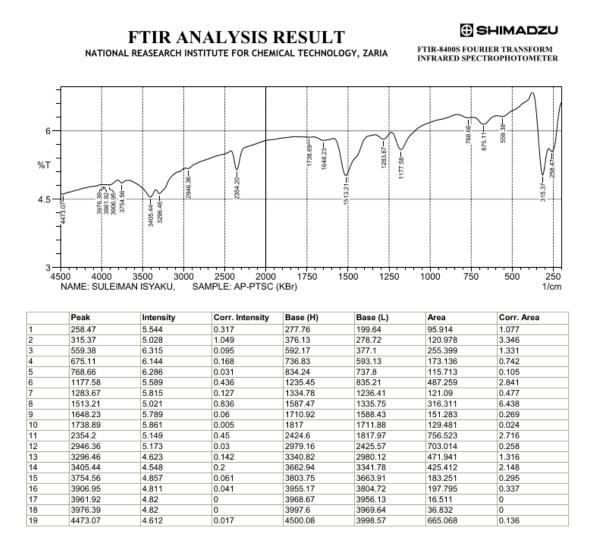
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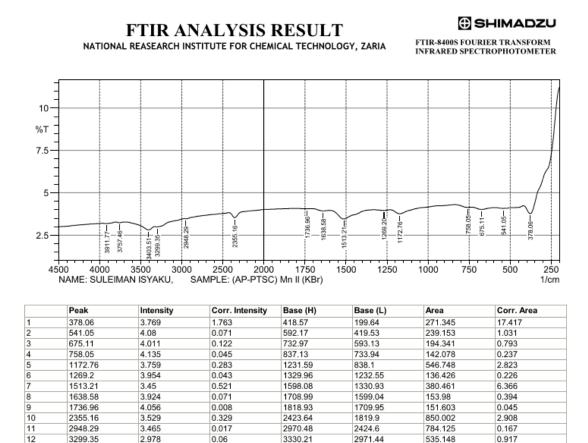


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Apodization; Happ-Genzel

Resolution; 2.0



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3803.75

3969.64

No. of Scans; 10

Date/Time; 1/12/2016 2:07:39 PM

562.264

149.244

246.319

4.017

0.289

0.487

Apodization; Happ-Genzel

3331.18

3703.45

3804.72

Resolution; 2.0

13

14

15

3403.51

3757.46

3911.77

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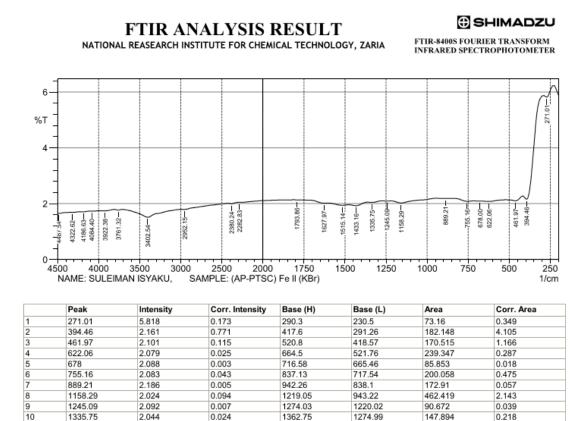
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3.187

0.246

0.046

0.033



1477.52

1605.79

1785.18

1815.08

2307.9

2425.57

2973.37

3711.17

3808.57

3967.71

4107.55

4228.1

4346.73

4500.08

1363.72

1478.49

1606.76

1786.14

1816.04

2308.87

2426.53

2974.33

3712.13

3809.54

3968.67

4108.51

4229.07

4347.7

194.007

217.049

299.742

48.316

825.94

197.869

940.028

1306.399

168.716

277.524

244.46

211.122

208.331

270.728

0.818

0.496

0.151

0.001

0.192

0.311

0.138

20.036

0.27

0.343

0.046

0.162

0.099

0.036

No. of Scans; 10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

1433.16

1515.14

1627.97

1793.86

2282.83

2380.24

2952.15

3402.54

3761.32

3922.38

4186.63

4322.62

4487.54

4084.4

1.928

1.942

2.018

2.138

2.043

1.997

1.797

1.512

1.769

1.743

1.731

1.707

1.685

1.655

0.068

0.035

0.017

0.007

0.027

0.009

0.283

0.023

0.015

0.003

0.011

0.006

0.003

0