Spectrophotometric Study for Determination of Cobalt (II) by the Reagent [2-(4-Methoxyphenyl) Azo (4, 5-Dipheny Imidazole)](MPAI)

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ABSTRACT

A new Spectrophotometric method has been established for the determination of cobalt (II) ion in formulations. The method based on formation of stable red complex with [2-(4-methoxyphenyl) azo (4, 5-dipheny imidazole)] (MPAI) reagent at (pH = 9).The complex absorption was at λ =491 nm. Linearity was in the range (3.00 – 50.00) µg/ml with molar absorptivity (0.2703 x 10^4) L mol^{-1} cm^{-1} and Sandell's sensitivity (0.0021) µg.cm^{-2}. Limit of detection (LOD) and limit of quantification (LOQ) were (2.083 and 6.309) µg/mL, respectively. Job`s method of continuous variations was used to investigate the stoichiometry of complex which indicates the confirmed ratio of reagent to Metal was (1:2). Different parameters were studied for optimize this method such as effects of pH, concentration of reagent, time, sequence of addition, Oxidation-Reduction agent and foreign ion.

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INTRODUCTION

Cobalt is one of the component keys for human bodies. Diminishing of this fundamental component can cause some diseases while it is unsafe and unfortunate for overwhelmed [1]. Toxicological impacts of a lot of cobalt incorporate vasodilatation, flushing and cardiomyopathy in human and creatures [2].

Cobalt is grayish lustrous, brittle and hard metal. Atomic number of cobalt is 27, Number of natural occurring isotopes 1, atomic weight 85.993, electronegativity 1.7, m.p/^{0}C 1459, b.p /^{0}C2927, Thermal conductivity / Wm^{-1} k^{-1} 100. Density (20 ^{0}C)/ g cm^{-3} 8.9, electrical resistivity (20 ^{0}C)/μΩ cm 6 [3] . Cobalt was not found as the free metal. The multiplicity of cobalt in the outside of earth was 30 ppm.

The investigation strategies for cobalt grew rapidly and got to be intrigued for its wide utilize and trace content in environment sample which incorporate spectrophotometry [4], AAS [5], flow injection [6], polarography [7], chemiluminescence [8], HPLC [9], ICP-AES [10], ICP-MS[11].

The azo dyes of heterocyclic compounds are concerned highly active towards most of the metal ions. There is more than one active group in the azo dye and this makes it able to form chelatic coordinational complexes with metal ions which distinct by their color and ability to dissolve in various solvents. The complexes of metal ions are important in the biological field because they contain atoms make them make them able to connect with different metal ions. Numerous Reagents of high selectivity and affectability have arranged, these includes heterocyclic azo dye [12], porphyrin reagent [13], fluorescent ketone reagent [14], triazene reagent [15]. The spectrophotometric determination of cobalt is commonly forego by a reaction with Reagents such as 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline[16], bis (2,4,4-trimethyl penthyl)phosphinic acid [17], 2-amino-cyclopentene-1-dithiocarboxylic acid[18] , 2-(2-benzothiazolylazo)-2-*p*-cresol[19], ammonium 2-amino-1-cyclohexane-1-dithiocarbamate[20] , 2-(2-thiazolylazo) -5- [(N,N-dicarboxymethyl)amino]benzoic acid[21], penicillamine and carbocisteine[22].

In recent work, azo derivative [2-(4-methoxyphenyl) azo (4, 5-dipheny imidazole)](MPAI) which synthesized by (Noor M. Mahdi et al., 2008) has been tried as a conceivable chromogenic reagent for the spectrophotometric determination of cobalt. It was

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experimentally observed that (MPAI) forms coloured complexes with cobalt (II). This coloured reaction is utilized in analyzing spectrophotometrically trace amount of this metal.

MATERIALS AND METHODS

Experimental:

Apparatus:

Spectrophotometric measurements were made with double Beam UV-Visible Spectrophotometer − 1800, Shimadzu, (Japan) , by using cell of 10 nm path length .pH values were measured with digital pH-mv-Temp. Mode of pH − meter was -WTW- 720 inolap (Germany). Digital water path shaker model- BS-11 JEIO TECH (Korea) was used.

Reagents:

Ultra-high-purity grade reagents were used for the dilution, preparation and analysis of samples so as to avoid contamination at trace element levels.

- Stock solution of Cobalt (II) (1mg/ml), 1.697×10^{-2} M was prepared by dissolving 0.403 gm of $CoCl_2.2H_2O$ in 100 ml distilled water.

- MPAI reagent with concentration 2.825×10^{-3} M was prepared by dissolving 0.100 gm of reagent in 100 mL distilled water.

- Solution of 0.1 M HCl and NaOH were used for adjusting pH.

RESULTS AND DISCUSSION

Absorption spectra

UV-visible absorption spectra of (MPAI) reagent, and Co (II) - (MPAI) complex solutions are appeared in fig. (1and 2). Maximum absorptions were 415 nm, 510 nm, and 491 nm for reagent, cobalt ion, and the complex, respectively.

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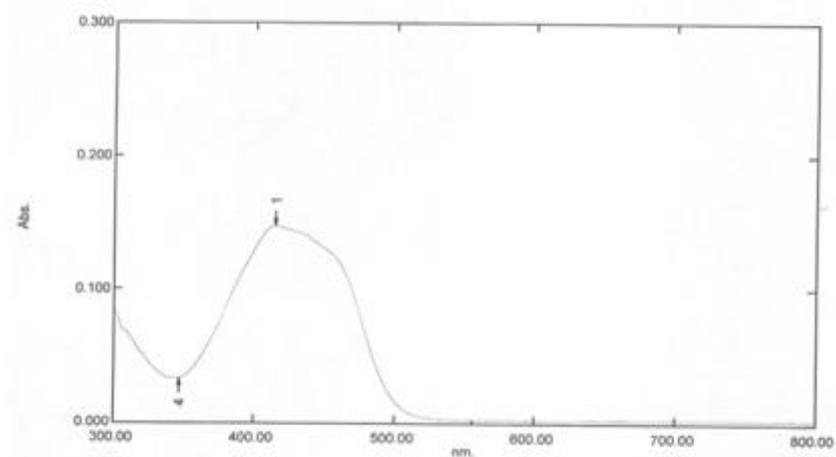
Fig.(1) UV-Visible spectrum for reagent
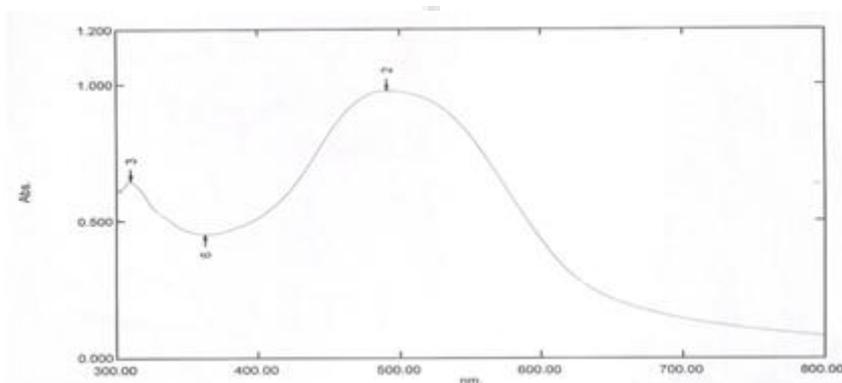
Fig.(2) UV-Visible spectrum for cobalt(II) complex

Effect of pH

Standard solutions of copper (II) and (MPAI) were buffered at varying pH-value ranged from (1.0 -10.0) and the absorbance measured at (491) nm. Absorbance was plotting against pH as shown in figure (3) which demonstrated that the absorbance increment up to pH 9.0 and diminished over pH 9.0. For this, pH was utilized further for all analyses. Increasing in the (MAPI) complex solution under these conditions might be because of increasing the sensitivity of the reagent at this value of pH towards copper (II).

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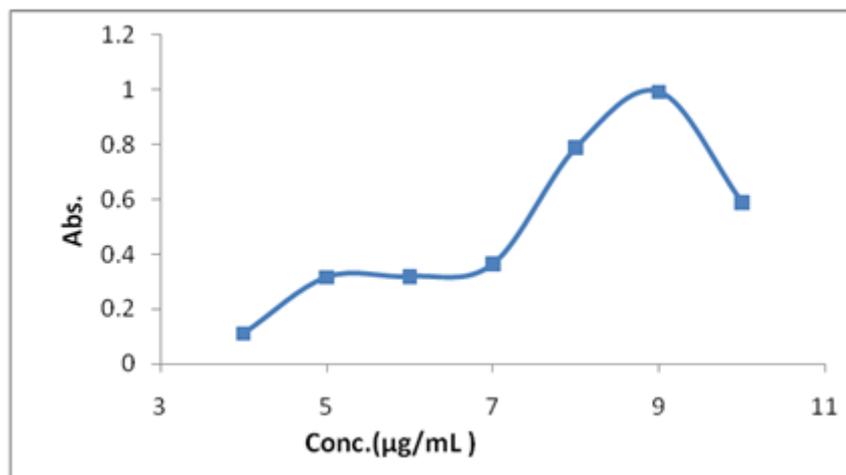
Fig. (3) Effect of pH on absorbance measured

Effect of Reagent concentration

The impact of overabundance concentration on the absorbance of complex is appeared in figure (4), where the absorbance of (50 μg/mL) cobalt (II) solution at (pH=9.0) was plotted against reagent concentration in the range (10.0-90.0 μg/mL). It was found that the absorbance increase with increasing reagent concentration and (50 μg/mL) metal ion concentration were chosen for 10 mL sample volume.
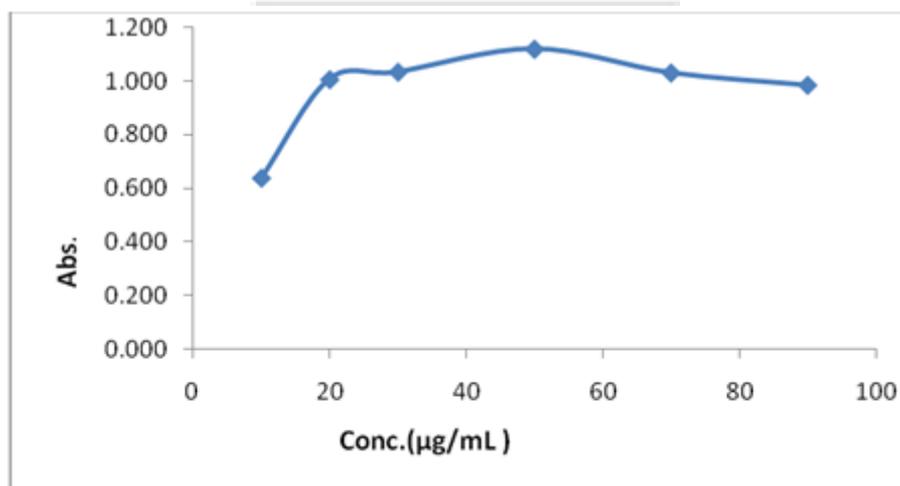
Fig.(4) Effect of reagent concentration on absorbance measured

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Effect of Time

The stability of absorbance of complex was studied from (0-60) min at different time of intervals. Fig.(5) showed the maximum absorbance reached at 10 min, after that the absorbance remains stable till 24 h.
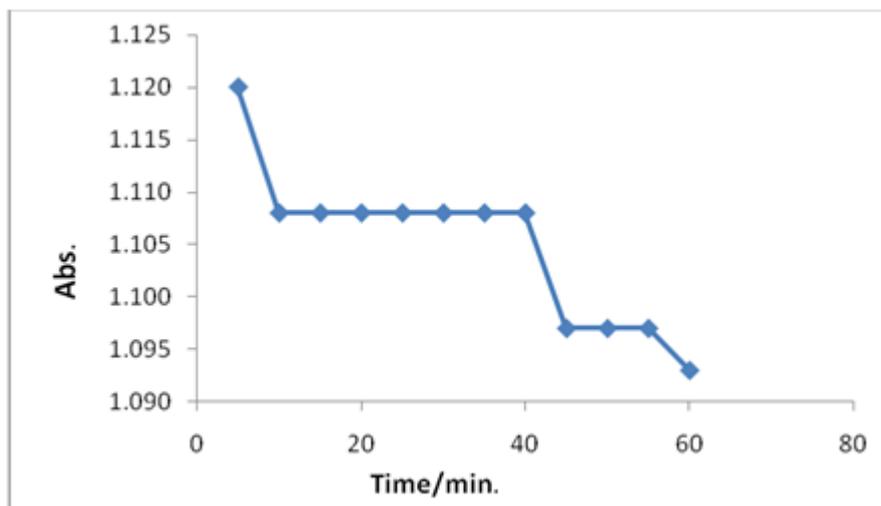
Fig.(5) Effect of time on absorbance measured

Effect of Temperature

The effect of temperature on the absorbance of complex was examined. The study was performed at temperature between 10-60 ^{0}C .Figure (6) demonstrated that the maximum absorbance obtained at temperature 20^{0}C which was viewed as an appropriate temperature of complex formation. At temperatures higher than 50^{0}C the absorbance decreases due to dissociation of complex gradually.

Fig.(6) Effect of time on absorbance measured

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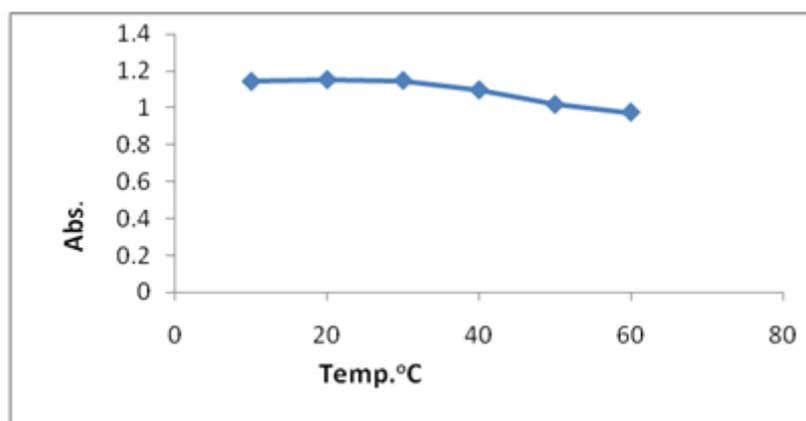
Effect of sequence of addition

To determine the order of addition on the absorption of complex, three methods have been adopted for addition as illustrated in table (1).

Table (1): Effect of sequence of addition

Sequence of number	Sequence of addition	Absorption of Cobalt (II) complex
1	M+L+pH	1.120
2	L+M+pH	0.931
3	L+pH+M	0.929

Where M=Metal , L=Ligand

From table (1) absorptions of complex were decreased at second and third order addition, this may be due to interference of acidic and basic ions to coordinate with metal, thereby the first order was recommended to estimate the cobalt ion in this method.

Calibration curve

Linearity for calibration curve was obtained by plotting absorption corresponding to concentration ranged from (3.00 – 50.00) μg/ml. Calibration curve and analytical values of the statistical treatment of the calibration curve were illustrated in figure (7) and table (2).

$y = 0.0176x + 0.1085$
$R^2 = 0.9989$
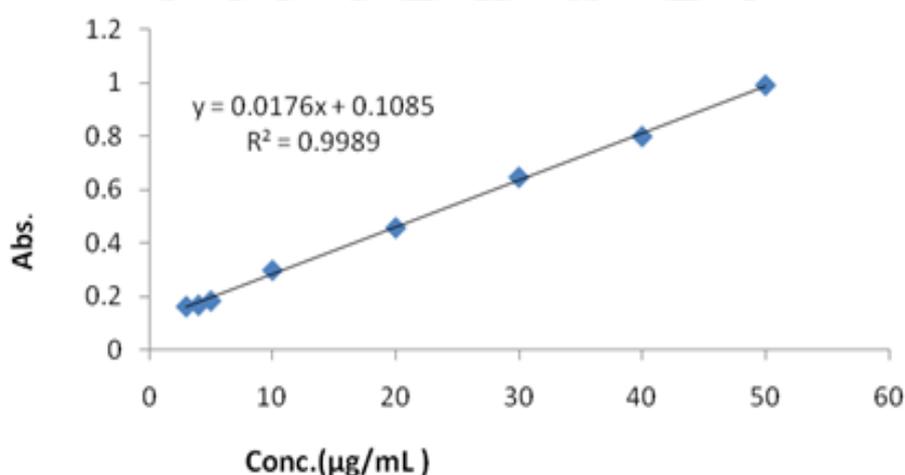
Fig.(7) : Calibration curve or cobalt(II) complex

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Table (2): Analytical values of the statistical treatment of the calibration curve

Characteristics	Results
Molar Absorpitivity ($L.mol^{-1}.cm^{-1}$)	0.2703×10^4
Slope	0.0176
Concentration limit (µg/mL)	(3.00 – 50.00) µg/mL
Linear regression equation	Y=0.0176x + 0.1085
Sandell's sensitivity ($µg.cm^{-2}$)	0.0021
LOD (µg/mL)	2.083
LOQ (µg/mL)	6.309
correlation coefficient	0.9989

Effect of foreign ions

The effect of diverse ions on the cobalt (II) determination was studied, in presence of a definite amount of a foreign ion. Various cations and anions were investigated in order to find the tolerance limit of these foreign ions in the extraction of cobalt (II) (Table 3).

Table (3): Effect of foreign ion on the determination of cobalt

Foreign ions	Formula structure of ions	50µg/mL		100µg/mL	
		Absorbance after addition of ions	E%	Absorbance after addition of ions	E%
		1.120		0.875	
Ni^{+2}	$NiCl_2.6H_2O$	0.026	-97.678	0.003	-99.657
Cr^{+3}	$CrCl_3.6H_2O$	0.009	-99.196	0.051	-94.171
Cd^{+2}	$CdCL_2.2.5H_2O$	0.004	-99.642	0.041	-95.314
K^{+1}	KCL	0.021	-98.125	0.031	-96.457

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Foreign ions	Formula structure of ions	50µg/mL		100µg/mL	
		Absorbance after addition of ions	E%	Absorbance after addition of ions	E%
		1.120		0.875	
NO_3^{-1}	KNO_3	0.003	-99.732	0.029	-96.685
MnO_4^{-2}	$KMnO_4$	0.013	-98.839	0.031	-96.457
Br^{-1}	KBr	0.121	-89.196	0.193	-77.942
I^{-1}	KI	0.039	-96.517	0.030	-96.571

Effect of Oxidation-Reduction agent on the determination of Cobalt

The influence of oxidation-reduction on the absorption of complex formation was studied by adding (1ml) from (1M) H_2O_2 solution as oxidant agent and (1mL) from (1M) $SnCl_2.2H_2O$ solution as reductant. Result was illustrated in table (4).

Table (4): The effect of oxidation-reduction on the absorption of complex formation

Oxidation - Reduction agent	Abs.	E%
In absence of oxidation - Reduction agent	1.120	
In presence of Oxidant agent H_2O_2 solution	0.455	-59.375
In presence of Reducing agent $SnCl_2.2H_2O$ solution	0.012	-98.928

Determination of stoichiometry and formation constant

Job`s method of continuous variations was chosen to study the ratio of metal to reagent, results illustrated in figure (8). The method indicated that the ratio of metal ion to reagent molecules (M:L) was (1:2) at pH=9.0. The formation constant computed by applied procedure was observed to be $(1.4x10^7)$ $L^2.mol^{-2}$.

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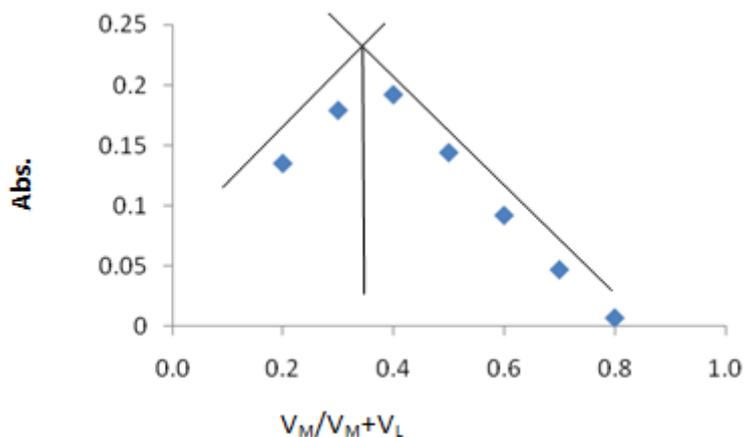
Fig.(8) Job`s method of continuous variations

Study of FT-IR spectra for ligand and complex

FT-IR spectra for organic ligand and its complex with cobalt (II) was recorded in the range from (4000-200cm^{-1}) as explained in figures (9 and 10), respectively. There is a noticeable change in the spectra of the complex from that of free ligand in term of position, shapes and intensities of peaks in addition to that, new peaks appeared because of the coordination between ligand and metal under study. All typical FT-IR absorption frequencies for ligand and complex were illustrated in table (5).
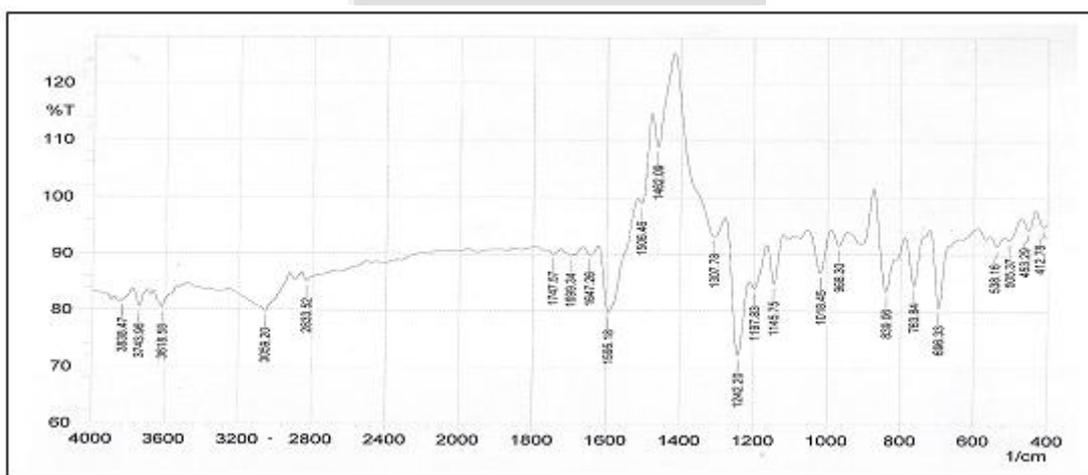
Fig.(9) FT-IR spectrum of ligand (MPAI)
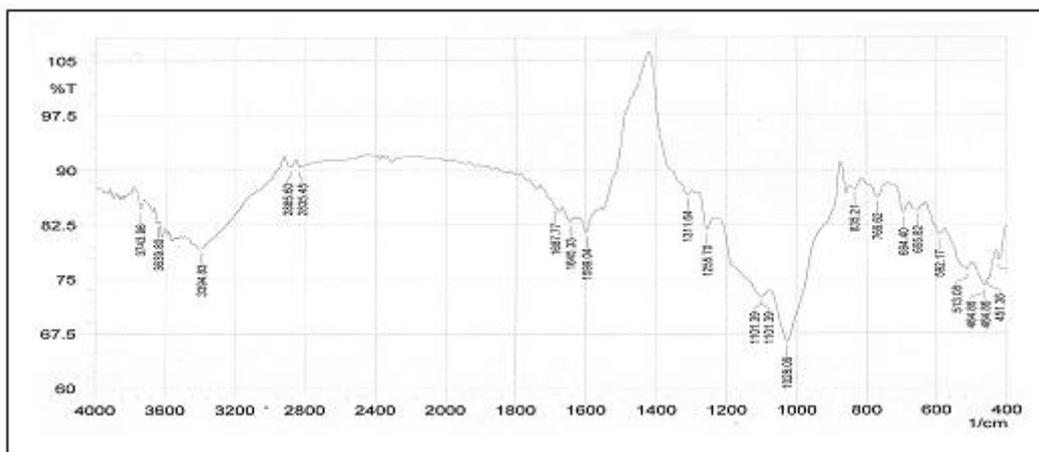
Fig.(10) FT-IR spectrum of complex[Co(MPAI)₂]

Table (5): typical FT-IR absorption frequencies for ligand and complex

Compounds	(MPAI)	[Co(MPAI)2]
U(N-H)	3618 w	3639 b
U(C-H) Ar	3059 m	3394 m
U(N=N)	1462 m	1311 m
U(C=C)	1506 m	1520 m
U(C=N)	1595 m	1599 m
(M-O)	---------	464
(M-N)	----------	592

Where: m=medium, w = weak, b = broad

Electrical conductivity

The molar conductivity for complex with $(1 \times 10^{-3} M)$ of ligand in room temperate by using ethanol as solvent was studied. Results in table (6) indicate that there are no ionic properties for complex of cobalt (II) with ligand.

Table (6): molar conductivity for solution of solid cobalt(II)complex

Complex	Λ_m (µs/cm)
	In ethanol
[Co(MPAI)₂(NO₃)₂]	19.9

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The suggested figure for complex

From the results of this study, the stoichiometry of complex (M: L) was found to be (1:2). The suggested figure for complex explained in figure (11).
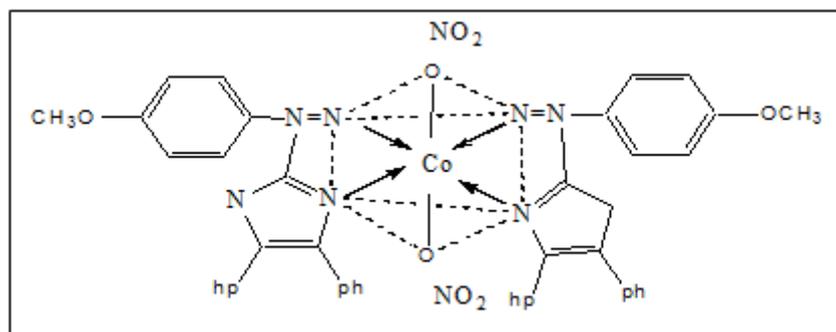
Fig.(11) The suggested figure for complex

CONCLUSION

The new reagent [2-(4-methoxyphenyl) azo (4, 5-dipheny imidazole)] was successfully used to determine Co(II) ion under optimum condition obtained with ratio of 1:2 (M:L).The results above explained that the method was sensitive, furthermore the method was simple, rapid and accurate with low cost. The formation of sharp red color for the complex makes the method suitable for Spectrophotometric analysis.

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