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Synthesis, Characterization and Spectral Studies of Cobalt(II) with a Novel Azo-Azomethine reagent Derived From Thiosemicarbazone

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A B S T R A C T

By employing a novel organic reagent, 5-[{3-[(2-carbamothioylhydrazinylidene)methyl]-4-hydroxyphenyl}diazenyl]-2-hydroxybenzoic acid (CMHPHB), the prepared reagent and complex were characterized using UV-Vis spectroscopy. Additionally, FT-IR and 1H NMR spectra were obtained for the new reagent. Cobalt (II) was determined utilizing a rapid and sensitive spectrophotometric method. The cobalt compound exhibits a molar absorptivity of 4.24×10^4 $L.mo1^{-1}.cm^{-1}$, a Sandell sensitivity of 1.389×10^{-3} $\mu g.cm^{-2}$, and a maximum absorbance at 410 nm. The limit of detection is 0.0209 µg/mL, and the limit of quantitation is 0.0697 µg/mL. The metal concentration adheres to Beer's law within the range of 0.0589 – 2.946 µg/mL, with a correlation coefficient value of 0.9953, indicating the linearity of the standard cobalt titration. In the complex, the molar ratio of metal to reagent is (1:2). The results suggest that the complex possesses a high stability constant of 1.9693×10^8 $mol.L^{-1}$.

NOMENCLATURE			
At.wt	Atomic weight	As	Absorbance at the equivalence point
xi	Reading for every absorption	Am	Absorbance when the ratio of metal to reagent (1:4)
x’	mean	N	Number of readings
λ	Wave length	α	Degree of dissociation
M	Metal	Kst	Stability Constant
R	Reagent	Kinst	Instability Constant
ε	Molar absorptivity	ΔG°	Gibbs free energy
S	Sandell’s sensitivity	ΔH°	Enthalpy
L.O.D	Limit of detection	ΔS°	Entropy
L.O.Q	Limit of quantitation	%T	Transmittance
A	Absorbance	b	Path length cell (1cm)
C	Molar concentration	S.D	Standard deviation

1. INTRODUCTION

Schiff bases are compounds containing an azomethine group (-CH=N-) [1, 2] that have the general formula (R_1R_2C=N-R_3), where R_3 represents alkyl or phenyl groups, making them stable imines. Schiff bases can be prepared by a condensation reaction of carbonyl compounds (aldehydes or ketones) with a primary amine, in which the carbonyl group is replaced by a group (C=N-R) [3, 4]. Schiff base compounds are among the most widely used compounds in the field of coordination chemistry due to their structural flexibility and application in various fields [5]. A large number of Schiff bases and their complexes have been studied for their important biological properties such as antidiabetic, antioxidative, antimicrobial, antifungal, anticancer activities, and their complexing activity against some toxic metals [6-8]. Polyimines known as Schiff bases or polyazomethenes have received much attention in recent years because of their wide applications and other important properties [9]. Oligophenol derivatives containing imine groups (CH=N) have been used in a few fields such as active catalysts, refractory and semiconductor compounds, formation of new metal-polymeric complexes, for analytical purposes, and to prevent environmental pollution [10-12]. Schiff bases are widely used as analytical reactants because they allow simple and inexpensive quantification of many

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organic and inorganic substances [13]. These compounds are often used as chelating ligands in the field of coordination chemistry, and their metal complexes have received great interest for many years [14]. There are many applications for Schiff bases in the dye, food, and fungicide industries. Schiff bases exhibit anti-germ, anti-ulcer, and anti-cancer activities depending on the transition metal ions present in Schiff bases [15]. The aim of this study is to prepare a new organic reagent and then use it to determine small quantities of cobalt metal and study the optimum conditions for it.

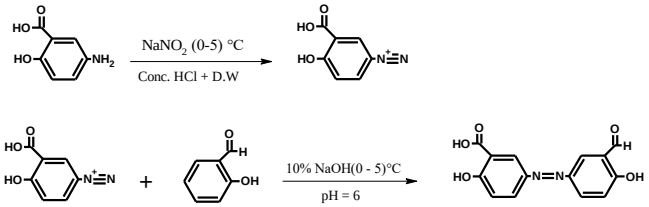
2. MATERIALS

All solvents and solid chemicals used are of high purity from C.D.H., Thomas Baker, and Meark.

3. EXPERMANTALS

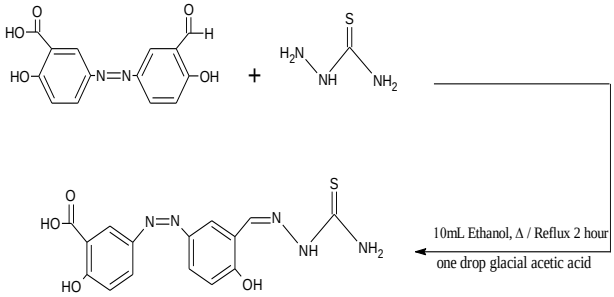
3.1 Synthesis of the ligand

In the first step, 1.685 grams (0.011 moles) of 5-aminosalicylic acid (mesalazine) was dissolved in 5 mL of concentrated HCl and 20 mL of water in an ice bath at 0-5°C. Then, 6 mL of sodium nitrite solution (0.9 grams, 0.011 moles) was gradually added to the above solution with constant stirring to produce the diazonium salt. The mixture was left to stabilize and complete the diazotization process for 30 minutes. Next, 1.353 grams (0.011 moles) of salicylic aldehyde, dissolved in 15 mL of a basic medium solution (10% NaOH), was added to produce the azo compound. Drops of $NaHCO_3$ solution were added to adjust the pH to 9 and complete the reaction. The solution was then left for 15 minutes before adjusting the pH again to pH 6 by adding drops of HCl acid solution. Afterward, the solution was filtered and washed thoroughly with distilled water, and left to dry at room temperature for 24 hours. The product yield was 76.87% (**Scheme 1**) [16].



Scheme 1. The first step to preparation of reagent

The second step involves reacting 1 gram (0.0035 moles) of the azo compound with 0.319 grams (0.0035 moles) of thiosemicarbazide (TSC) in 10 mL of ethanol under reflux for 2 hours at 100°C. One drop of glacial acetic acid was added as a catalyst. The reaction progress was monitored by thin-layer chromatography (TLC) using a mixture of solvents (ethyl acetate:n-hexane) in a ratio of 3:1 to confirm the formation of the product. The mixture was then left to dry at room temperature overnight. The yield was 70%, and the melting point was measured to be 80–82°C (**Scheme 2**) [17].



Scheme 2. The second step to preparation of reagent

4. RESULTS AND DISCUSSION

4.1. Study of UV-Vis. spectra

A spectroscopic survey of the cobalt complex was conducted in the ultraviolet-visible region of the spectrum, within the range of 200-750 nm. The electronic absorption spectra of the new reagent and complex were measured in absolute ethanol solution at a concentration of 1×10-4 M.

In Figure 1, the electronic spectrum of the very light orange reagent showed three bands at λ = 234 nm, λ = 269.5 nm, and λ = 305 nm. In Figure 2, the Co(II) complex showed four absorption bands at λ = 226 nm, λ = 263 nm, λ = 297 nm, and λ = 410 nm [18].

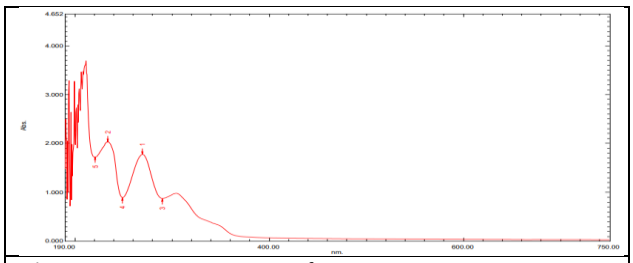


Figure 1. UV-Vis spectrum of reagent

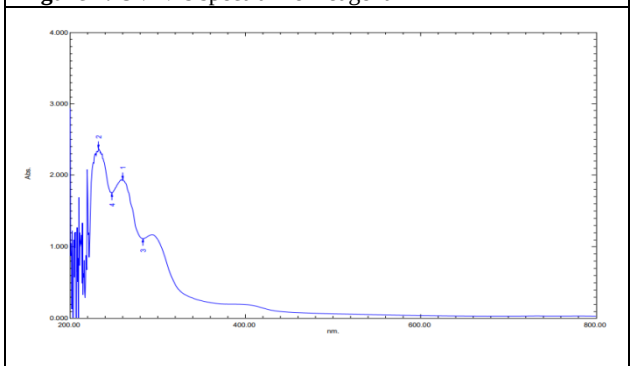


Figure 2. Th e UV-Vis spectrum of complex.

4.2. Study the optimum condition for the cobalt (II) complex

4.2.1. Effect of pH

A wide range of buffer solutions ranging from pH 4 to 9 were chosen. The absorption at the maximum absorption wavelength was measured at a concentration of 1 $x10^{-4}$ M of the cobalt complex. It was observed that the absorption increased at pH 8, as depicted in Figure 3 [19].

4.2.2. Effect of reagent concentration

A 10 mL volumetric flask was used, into which 1 mL of the metal ion solution with a concentration of 1×10^{-3} M was added. Various volumes of the reagent solution with concentrations ranging from 0.5×10^{-3} M to 5×10^{-3} M were then added. The volume was made up with buffer solution at pH 8 to obtain a wide range of concentrations (0.5×10^{-4} M to 5×10^{-4} M). The absorbance of all solutions was measured at λmax = 410 nm. Figure 4 illustrates the study of the effect of the reagent, indicating that the optimal concentration of the reagent is 4×10^{-4} M [20].

4.2.3. Time's impact on stability of cobalt complex

Monitoring the interaction of the reagent with cobalt over time periods ranging from 2-90 minutes, it was shown that the complex formed directly when the reagent solution was added to the metal ion solution. This indicates the persistence and high stability of cobalt, as shown in Figure 5 [21].

4.2.4. Effect of temperature in stability of cobalt complex

We note from Figure 6 that the absorbance values of the complex reach their peak and give the best color intensity at temperatures between 10-25°C. Subsequently, the absorbance of the complex decreases with increasing temperature. This is due to the low stability of the complex or its dissociation at high temperatures [22].

4.2.5. Study the effect of the order of addition for cobalt complex

The purpose of this study is to determine the best addition order to form the cobalt complex under optimal conditions. The first case was chosen as the best addition because it yields the highest absorption, as shown in Table 1 [23].

TABLE 1. Effect of order of addition on cobalt complex formation.

NO.	Sequence of addition	Abs. of Co(II) complex
1	M + R + pH	0.532
2	R + M + pH	0.527
3	M + pH + R	0.523
4	R + pH + M	0.525

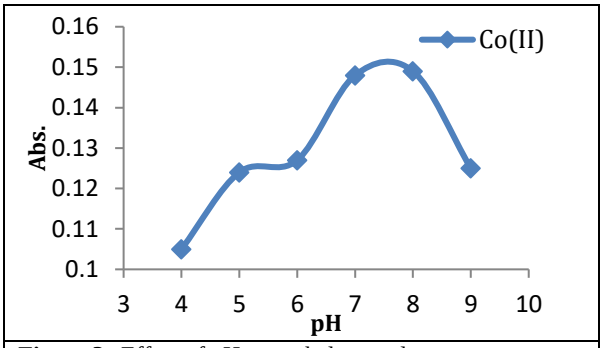


Figure 3. Effect of pH on cobalt complex

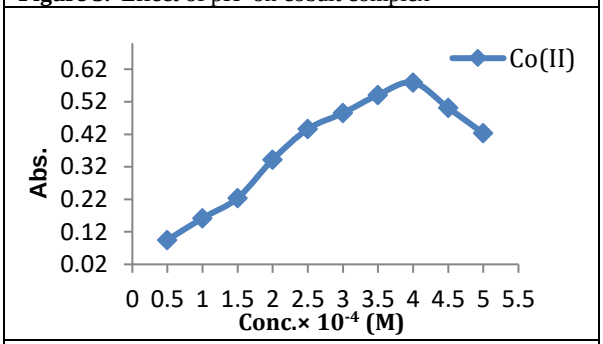


Figure 4. Reagent concentration's impact.

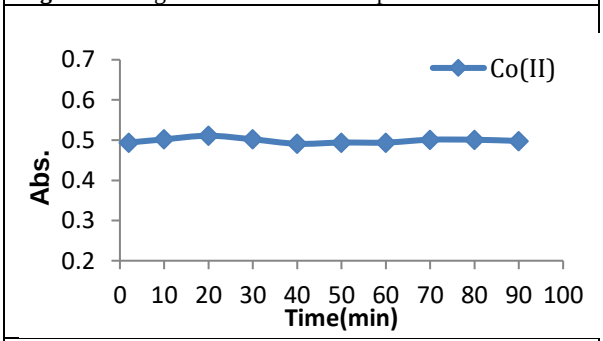


Figure 5. Time's impact on stability of Cobalt complex.

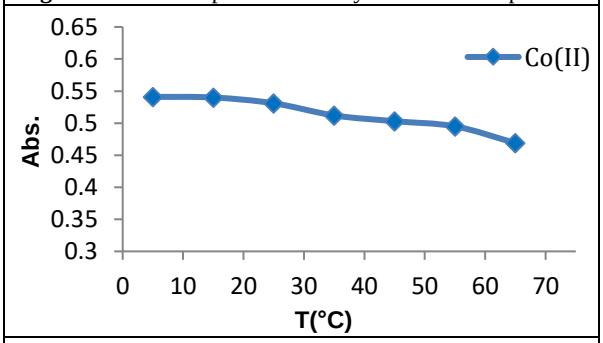


Figure 6. Effect of temperature in stability of Cobalt comple

4.2.6. Study of explanation of the calibration curve for cobalt complex

The concentrations adhering to the Beer-Lambert law were determined for the cobalt complex by constructing a calibration curve. Several concentrations were excluded due to their deviation from the Beer-Lambert law and the appearance of absorption peaks outside the measurement limits. Therefore, the concentrations conforming to the Beer-Lambert law are within the range of (0.0589 – 2.946) µg/mL, as depicted in Figure 7. Table 2 presents some characteristics of the calibration curve for the cobalt complex, extracted using equations (1-5) [24].

$A = \varepsilon bc$	(1)
$S = \frac{At.wt}{\varepsilon}$	(2)
$L.O.Q = \frac{10\ S.D}{Slope}$	(3)
$S.D = \sqrt{\frac{\sum(xi - x')^2}{N-1}}$	(4)
$X' = \sqrt{\frac{\sum xi}{N}}$	(5)

4.2.7. Study the stoichiometry composition of cobalt complex

Two methods were used to determine the ratio of metal to ligand: the molar ratio method and the continuous variation method.

In the molar ratio method, solutions were prepared in a set of 10 mL volumetric bottles containing a fixed concentration of copper solution with a variable concentration of ligand solution. The volumes were adjusted to the optimal pH value of 6, and then the absorbance was measured at the maximum wavelength. The results of the study showed that the ratio is (1:2) (metal:ligand).

In the continuous variation method, different volumes of the metal ion solution (0.5-4.5 mL) were mixed with different volumes of the ligand solution (4.5-0.5 mL), and the results indicated that the ratio between metal and ligand is (1:2) [25], as shown in Figure 8 and Figure 9.

4.2.8. Calculation of the stabilization constant for complexes

The stability of the cobalt complex with the reagent was studied by calculating the degree of dissociation and the stability constant based on the absorption values obtained. As shown in Table 3, the results, which were obtained using equations (6-8), indicate that the complexes have a high degree of stability, enhancing the possibility of using the detector in the spectral estimation of these elements [26].

$kst. = \frac{(1-\alpha)}{4(\alpha^3 C^2)}$	(6)
$kinst. = \frac{1}{Kst.}$	(7)
$\alpha = \frac{Am - As}{Am}$	(8)

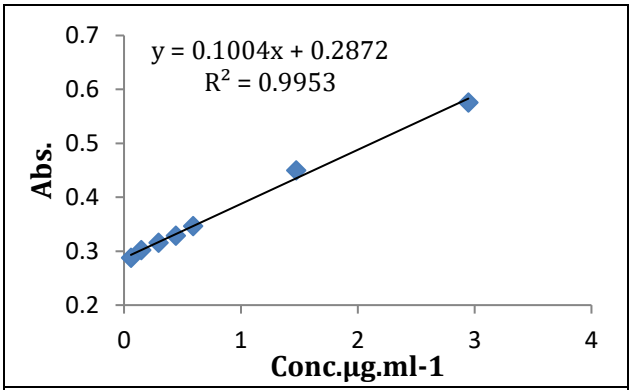


Figure 7. calibrate curve for cobalt complex.

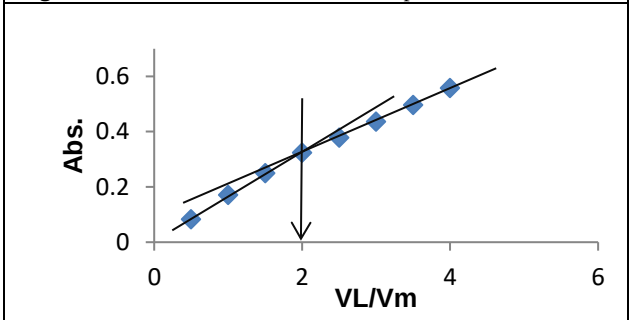


Figure 8. Molar ratio methods of cobalt complex

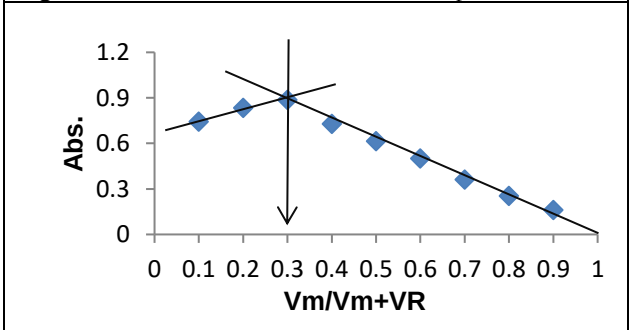


Figure 9. Continuous variation method of cobalt complex

TABLE 2. Some properties of the calibration curve for Cobalt complex

Conc. obey the Beer-Lambert law (µg/mL)	Straight-line equation	slope	ε (L/mol.cm)	S (µg.cm^{-2})	R^2	L.O.D (µg/mL)	L.O.Q (µg/mL)
(0.0589 – 2.946)	y = 0.1004x+ 0.2872	0.1004	4.24×10^4	1.389×10^{-3}	0.9953	0.0209	0.0697

TABLE 3. Shows the absorption values (Am) and (As) of the cobalt complex, as well as the values of (α), (K_{st}) and (K_{inst})

The controlling metal ion	As Value	Am Value	α	K_{st} mol.L^{-1}	K_{inst} L.mol^{-1}	Log K_{st}
Co (II)	0.463	0.835	0.4455	1.5678×10^{8}	6.378×10^{-9}	8.1952

4.2.9. FT-IR spectra of reagent

The FT-IR spectrum of the prepared new ligand shows a broad band belonging to (OH) at 3167 cm-1 due to hydrogen bonding, a band at 3313 cm-1 belonging to (NH), a band at 1658 cm-1 belonging to (C=O), a band at 1604 cm-1 belonging to (C=N), and the (N=N) band at 1454 cm-1, as shown in Figure 10 [27].

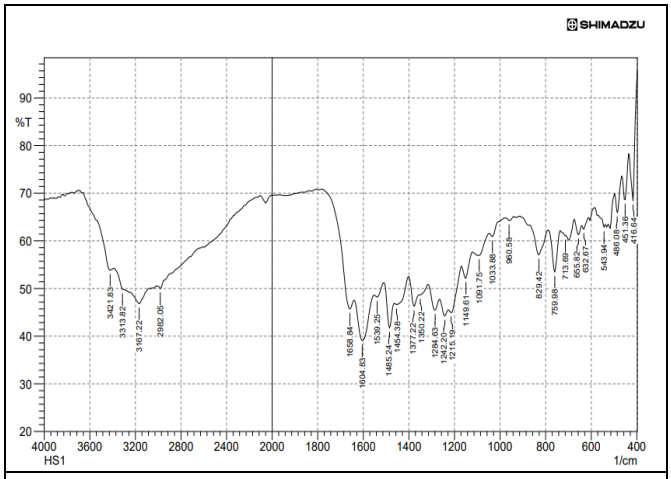


Figure 10. FT-IR spectrum of reagent

4.2.10. Proton NMR spectrum of reagent

From the signals appearing in the ^{1}H-NMR spectrum, the singlet signal at (δ=5.95 ppm, 2H) refers to the proton of the NH2 group, and the multiple signals in the range (δ=6.48-7.79 ppm, 6H) refer to the protons of the aromatic rings. The singlet signal at (δ=8.98 ppm, 1H) refers to the proton of the (CH=N) group, the singlet signal at (10.18 ppm, 1H) refers to the protons of the (OH) group, the singlet signal at (δ=11.07 ppm, 1H) refers to the proton of the NH group, the singlet signal at (δ=11.39 ppm, 1H) refers to the proton of the carboxyl group COOH, the signal at 3.35 ppm indicates the presence of moisture H_2O, and the signal at 2.5 ppm indicates the solvent DMSO [28], as shown in Figure 11.

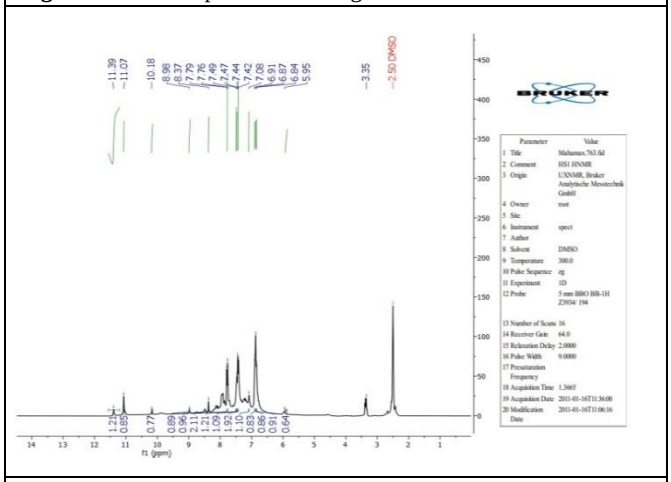


Figure 11. ^{1}H-NMR spectrum for reagent

4.2.11. Carbon NMR spectrum of reagent

From the signals appearing in the 13C-NMR spectrum shown in Figure 12, the signal at (δ= 110-141.06 ppm) belongs to aromatic rings carbons, a signal at (δ= 144.25 ppm) belongs to isomethene carbons (CH=N), and a signal at (δ= 161.76 ppm) belongs to isomethene (C=O) carbon. The last signal appears at (δ= 172.59 ppm) for carbonyl carbon group (C=S), and DMSO-d6 gives a septet signal centered at 39.89 ppm [29]

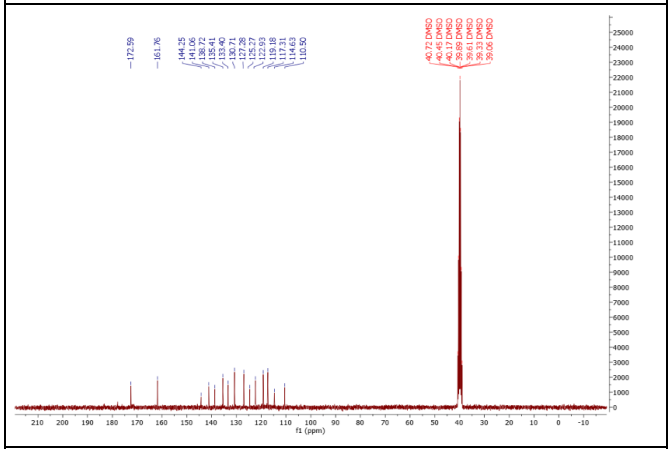


Figure 12. ^{13}C-NMR spectrum for reagent

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Arabic Abstract

باستخدام كاشف عضوي جديد "5-[{3-[(2-carbamothioylhydrazinylidene) methyl]-4-hydroxyphenyl} diazenyl]-2-hydroxybenzoic acid (CMHPHB). تم تقدير عنصرالكوبلت بطريقة طيفية وسريعة وحساسة, تم تشخيص الكاشف والمعقد المحضر بواسطة UV-Vis، في حين تم أخذ أطياف FT-IR و^{1}H-NMR للكاشف الجديد. يمتلك معقد الكوبلت معامل امتصاص مولي قدره 4.24×10^{4} L.mo1^{-1}.cm^{-1}، وحساسية ساندل 1.389×10^{-3}µg.cm^{-2}، وأقصى امتصاص يبلغ 410nm. مع حد كشف قدره (0.0209)µg.mL^{-1} وحد تقدير 0.0697 µg.mL^{-1}، تطاوع تراكيز الفلز لقانون بير-لامبرت ضمن المدى 2.946 – 0.0589 µg.mL^{-1} مع قيمة معامل ارتباط تبلغ 0.9953 التي تشير إلى درجة الخطية للمعايرة القياسية للكوبلت, في المعقد كانت النسبة المولية للكاشف إلى الفلز هي (1:2), وتشير النتائج إلى أن المعقد لديه ثابت استقرارية عالي قدره 1.9693×10^{8} mol.L^{-1}.