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Spectrophotometric determination of Co (II) in analytical sample using anew chromogenic reagent (PTMH)

Mohammed W. Taher

Department of Chemistry/ College of Education for pure science, University of Kerbala, Iraq

Corresponding author email: mohammed.w@s.uokerbala.edu.iq

Sajid. H. Guzar

Department of Chemistry/ College of Education for pure science, University of Kerbala, Iraq

H. D. Hanoon

Department of Chemistry/ College of science/ University of Kerbala, Iraq

Abstract---At the current work, the substrate phenyl hydrazine reacted with selected thiophene-2-carbaldehyde in absolute ethanol and a few drops of glacial acetic acid to give 1-phenyl-2-(thiophen-2-ylmethylene) hydrazine (PTMH) as a selective and sensitive reagent. It was synthesized and studied to determine cobalt spectroscopy in the following detail: at a pH value of 6.0, which greatly increased the selectivity, Co(II) reacted with (PTMH) to form a 1:2 complexes, with absorption peaks at 386 nm for cobalt. Under the optimal conditions, Beers law was obeyed over the ranges of (0.14–5.8) mg/L. The apparent molar absorptivity and Sandell's sensitivities were $7.1360 \times 10^4 \text{ L.mol}^{-1}.\text{cm}^{-1}$, and $8.2585 \times 10^{-4} \text{ }\mu\text{g.cm}^{-2}$. The detection limits were found to be 0.0133 and the limit of quantification is 0.0466.

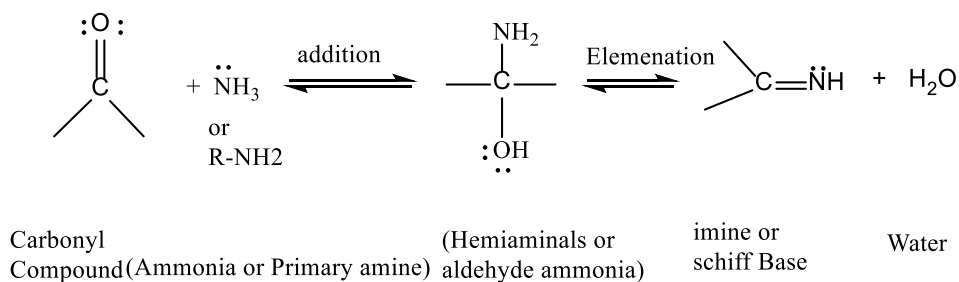
Keywords---optimal conditions, 1-phenyl-2-(thiophen-2-ylmethylene) hydrazine (PTMH), spectrophotometry.

Introduction

Schiff bases were first prepared by the German scientist Hugo Schiff from the condensation of aliphatic or aromatic primary amines and some amino acids with aldehydes and aliphatic or aromatic ketones (carbonyl compounds)^[1]. Schiff bases are characterized by being colored crystals (often yellow) as a weak base that

decomposes with water and strong acids to form carbonyl compounds and amines.^[2] This name has been given to organic compounds containing an imine group or what is known as azomethine group, which consists of a carbon atom bonded to a double bond with a nitrogen atom (C = N)^[3]. The methods used to prepare the bases depend on the different nature of the substances involved in their preparation, the reaction conditions and the type of solvent used, obtaining a product with a high percentage that is distinguished by its high purity^[4]. Schiff bases are prepared from direct condensation by reacting equivalent molar amounts between an aldehyde and a ketone (aliphatic or aromatic) in a suitable solvent (absolute ethanol, dry ether or cyclohexane) and the reaction conditions depend on the nature of the reactants. To form (hemiaminals) or so-called (ammonies aldehyde), which in turn disintegrates into Schiff base as showed in Scheme 1 ^[5]. The properties and stability of Schiff bases mostly depend on the carbonyl compounds as well as on the type of amines, whether aliphatic or aromatic. Both ends of the azomethine group^[6]. Its solubility in water or solvents depends on the nature of its constituent groups^[7]. For example, its solubility in water increases when it is derived from sugars because it contains hydroxyl groups^[8]. While the bases prepared from aliphatic derivatives are distinguished by their liquid state. Compounds derived from ammonia are unstable because they react with each other and form polymers^[9].

Schiff's rules have many applications in the field of analytical chemistry. They have been used in quantitative and qualitative analysis because they are colored keltite complexes with transition metals in most cases^[10]. In industry, they act as accelerators to strengthen rubber^[11]. In the field of polymer science, it is used to catalyze various condensation polymers^[12]. They were used as pesticides in the agricultural field due to the presence of active groups such as chlorine and azo in different types of these compounds. Organophosphorous pesticides are one of the most important groups of pesticides^[13]. Cobalt is one of the elements of the first transition series, has the next outer electron arrangement $3d^74s^2$ and has the ability to form colored complexes in which the five d orbitals are partially filled with electrons^[14].



Scheme 1 Condensation Reaction Method of Schiff base

Experimental

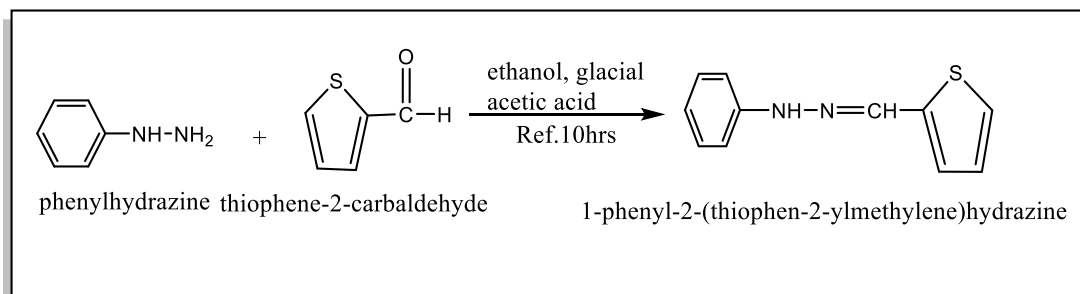
Instrumentation

All chemicals, solvents, and reagents were obtained from commercial sources from the Merck and MACLIN chemical businesses, and were used without

additional purification for this research. Thin layer chromatography (TLC) was used to monitor the reactions. A Stuart SMP 30 electric filament melting equipment was used to record the melting points. On a SHIMADZU FTIR-8400S infrared spectrophotometer, Fourier transform infrared (FTIR) was recorded as potassium bromide discs. INOVA nuclear magnetic resonance spectrometry (500 MHz) was used to measure ^1H NMR spectra using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal standard. . An Agilent Technology (HP) 5973 mass spectrometer was used to collect the data. pH-meter, InoLap, WTW, 135i, Germany.

Synthesis of 1-Phenyl-2-(thiophen-2-ylmethylene)hydrazine ^[1]

In a round-bottom flask with a capacity of 100 mL immersed in a water bath, put (0.01 mole, 1.0841 g) of (phenyl hydrazine) dissolved in 20 mL of absolute ethanol, to which it was gradually added with constant stirring (0.01 mole, 1.1215 g) of thiophene-2-carbaldehyde dissolved in 15 mL ethanol, 3 drops of glacial acetic acid were added as catalyst, mixing reaction with stirring (Reflux) for 10 hours at a temperature at $60\text{ }^\circ\text{C}$, where the reaction was followed up using thin layer chromatography (TLC) using a mixture of solvents (hexane: ethylacetate) at a ratio of (1:3). Following the interaction, the mixture was allowed to dry in the air for 24 hours at ambient temperature, washed with methanol, and recrystallized with 100% ethyl alcohol, and it was discovered that a precipitate (yellow) was generated at a percentage of (69%) with a melting point of ($134\text{-}136$) $^\circ\text{C}$.



Scheme 2 Preparation of the Schiff base

Preparation Of The Buffer Solution

The buffer solution was created by dissolving (0.7708 g, 0.01 mole) ammonium acetate in 1000 ml distilled water and adding concentrated ammonia or concentrated acetic acid solution to create a wide range of acid functions between (pH = 4-12).

Cobalt(II) Determination Procedures

A set of 10 mL volumetric were taken, and 1 mL of metal ion solution was placed in them with 1 mL of the reagent (PTMH) solution both at a concentration of ($1 \times 10^{-3}\text{M}$) and the volume was supplemented by absolute ethanol to be the final concentration ($1 \times 10^{-4}\text{M}$), and then a spectroscopic survey of this solution was

made in the ultraviolet and visible region and within the range (200-800 nm). Against blank solution, using 1 cm thick quartz cells.

Results and Discussion

Study of FT-IR Spectra for Schiff Base

Figure 1 depicts the synthesized ligand's major infrared spectral bands. The spectrum of free ligand showed a peak at (3323 cm^{-1}) assigned for secondary amines^[15], the band at (3099 cm^{-1}) attributed to (C-H) of thiophene ring, and the appearance of absorption bands at (3028 cm^{-1}) assigned for (C-H)^[16] aromatic. And the emergence a peak band at (1598 cm^{-1}) assigned for azomethine group (C=N)^[17], and showed a peak at (1533, 1504 and 1485 cm^{-1}) assigned for (C=C)^[18] benzene .

Magnetic Resonance Spectrometer

¹H-NMR spectra of the Schiff Base (PTMH)

Figure 2 show the ¹H NMR spectra of ligand were recorded in DMSO-d₆ solvent using TMS as standard. The signal at (10.36 ppm) were attributed to one proton of the amine group, the single band at (8.09 ppm) to proton azomethine group (N=CH), the multiple bands at (7.44 to 7.00 ppm) assigned to five protons of aromatic ring, the multiple peaks at (6.98 to 6.72 ppm) attributed to three protons of thiophene ring, the band at (3.38 ppm)^[19] for H₂O, while the peak at (2.50 ppm) associated to the solvent (DMSO-d₆)^[20].

¹³C-NMR Spectra of Ligand (PTMH)

Figure 3 show the ligand spectrum, one carbone of the azomethine group (C=N) is represented by the signal band at (145.0 ppm), the (140.9 ppm) signal band belongs to one carbon in the benzene ring that is linked to nitrogen (C-N), the multiple band at (131.9, 127.5, 126.5, 125.6 ppm) and (129.0, 121.6, 118.7, 114.4, 111.8 ppm) belongs to carbons thiophene and aromatic ring, respectively. The single band at (39.5ppm) related to solvent (DMSO-d₆)^[21].

Mass Spectrum

The mass spectrometry of the prepared ligand was measured and shown in Figure 4 showing a clear absorption of the metal ion (M⁺= 202.0), which corresponds to the proposed formula for the prepared ligand (PTMH).

Absorption Spectra

“UV-Visible Spectrophotometry” : The UV-Vis spectra of the solid Cobalt complex solution in ethanol showed absorption peaks. A considerable difference exists between the maximum values of the ligand (PTMH) and the complex [Co-PTMH] formed by a red shift. as depicted in Table 1 and Figure 5.

Table.1 The “electronic transitions” of (PTMH)ligand and complex[Co-PTMH]

Molecular-formula	λ_{\max} (nm)	Wave number(cm^{-1})	type of Transition
$\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2$	344	29069	$n \rightarrow \pi^*$
	243	41152	$\pi \rightarrow \pi^*$
	224	44642	$\pi \rightarrow \pi^*$
$[\text{Co}(\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2)\text{Cl}_2$	386	25906	CT
	300	33333	$n \rightarrow \pi^*$
	252	39682	$\pi \rightarrow \pi^*$

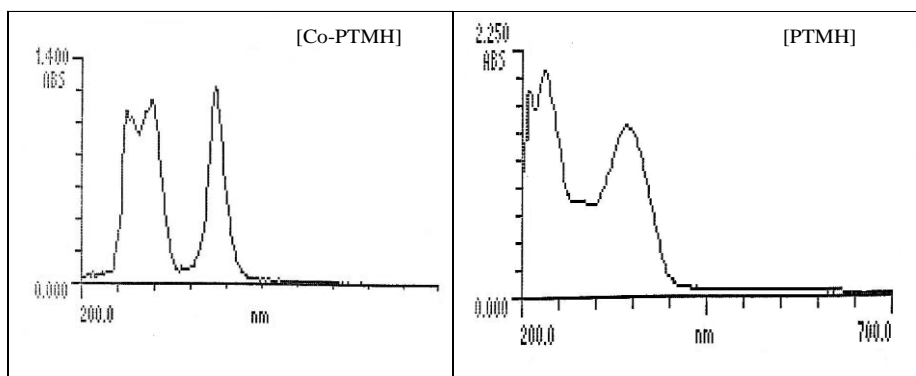


Fig. 5 The “UV-Vis spectrum” of ligand(PTMH) and complex[Co-PTMH].

Optimization of reaction conditions

pH effect

In a 10 mL flask set, 1 mL of cobalt ion solution of concentration (1×10^{-3} M) was poured with 1 mL of the ligand concentration (1×10^{-3} M) and the volume was filled with buffer-solution by adjusting the pH value from pH range = 4-11. After mixing 1 mL of cobalt ion with 1 mL of the ligand and adjusting the acidic function with the extent of the absorption log at the largest cobalt wavelength, we notice an increase in the absorption values at pH = 6 and then return to the decrease due to the appearance of unstable groups of cobalt ion, as shown in the figure.6

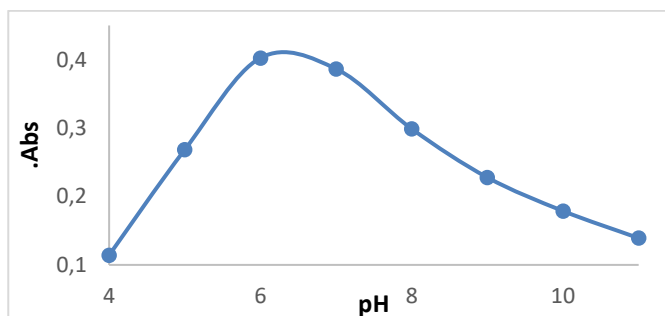


Fig6. Effect pH value

Studying Effect of the Reagent

Concentration

A group of volumetric bottles with a capacity of 10 mL was taken, in which was placed 1mL of metal ion solution at a concentration ($1 \times 10^{-3} \text{M}$), then different volumes of ligand solution were added at a concentration ($1 \times 10^{-3} \text{M}$) ranging between (4-0.4 mL) and completed the volume by the function The optimal acidity of each complex as show in figure.7 which shown that the concentration of the ligand (PTMH) has an influence. The behavior of the detector in this study is similar to what researchers found in other spectroscopic studies^[22].

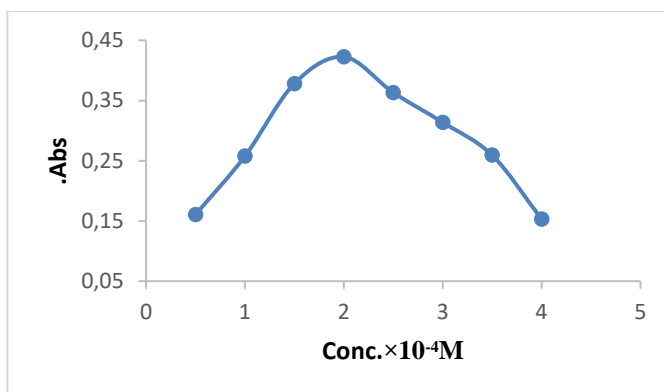


Fig.7 Effect of ligand concentration

The Effect of Time

figure. 8 shows the adsorption of ionic compound of cobalt which were formed under optimal conditions, with the result that the complexes were approximately stable for 90 min. The findings of this investigation revealed that the produced ligand, like other reagents used in spectroscopy of other ions, may be utilized to detect the amount of these ions^[16].

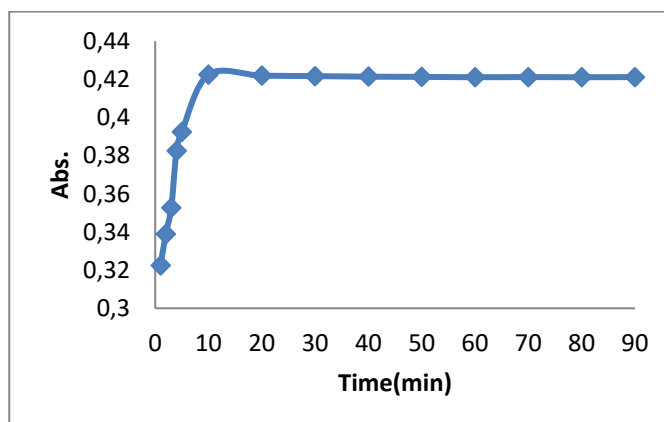


Fig.8 time has an effect on stability, of the Co^{+2} complex

Effect of the Temperature

The stability of the chemical may be affected by temperature, so the effect of temperature (10-80) $^{\circ}$ C was studied in the optimal conditions as in figure.9

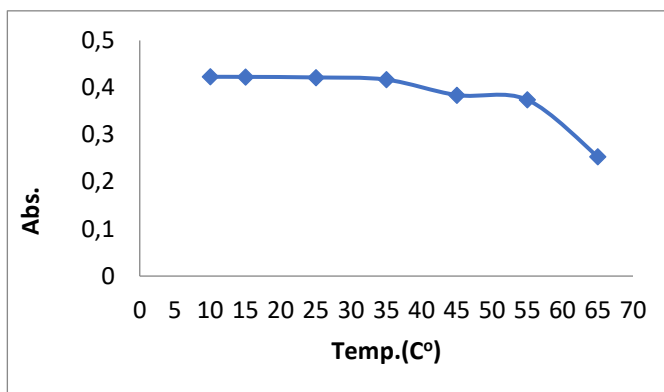


Fig. 9 The effect of temperature on the complex's stability.

The absorption values of the complexes reach their peak and offer the optimum absorption value at a temperature between (10-25) $^{\circ}$ C, and subsequently drop with increasing temperature, as shown by the practical findings. The cause for this is owing to the complexes' limited stability or their disintegration at high temperatures [23].

Studying the Calibration Curve

A group of 10 mL volumetric bottles was taken and 1 mL of metal ion solution with different concentrations was placed in them (1×10^{-3} – 1×10^{-5} M) for the cobalt ion, which is equivalent to (0.14–5.8) mg/L for Co^{2+} , then the best concentration of each ligand was added to it and the volume was completed with the best pH function for each complex, then the absorbance was measured for all solutions. The calibration curve follows Lambert-equation Beer's for a range of concentrations of (0.14–5.8 $\mu\text{g}/\text{mL}$) for Co^{2+} . As shown in tables 2 the approach is quite sensitive and may be used to detect metals at low concentrations and figure. 10 for cobalt complexes.

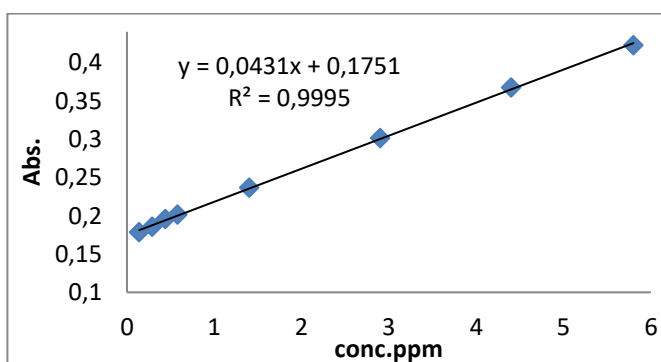


Fig.10 Calibration curve of (Co-PTMH) complex.

Table.2. construction of calibration curve of (Co-PTMH complex.)

[Co-PTMH] Conc. ppm	Regression Equation	Slope	ϵ (L.mol. ⁻¹ .cm ⁻¹)	R ²	S ($\mu\text{g.cm}^{-2}$)	L.O.D ppm	L.O.Q ppm
0.14–5.8	0.0431x+ 0.1751	0.0431	7.136×10^4	0.999 5	8.2585×10^{-4}	0.0133	0.0466

Studying Stoichiometry of the Composition Complexes

The stoichiometric of the cadmium complex was found using two methods :

Job method Use various metal ion (0.5-4 mL) and ligand (0.5-4 mL) sizes to obtain the metal ion to ligand ratio (1:2) (M:L) as indicates Figure 11.

Mole rate method A constant and known concentration of Cobalt ion was utilized with varying concentrations of ligand (0.5×10^{-4} - 4×10^{-4} M) to determine the metal ion to ligand ratio, and the study results revealed that the ratio is (1: 2) (M : L) as shown figure.12

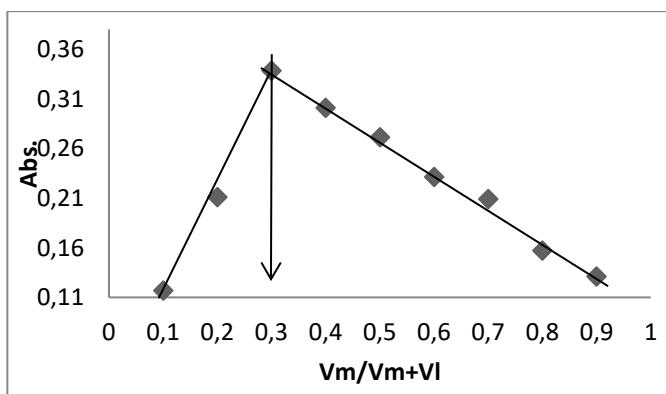


Fig.11 Job method of complex Co(II)

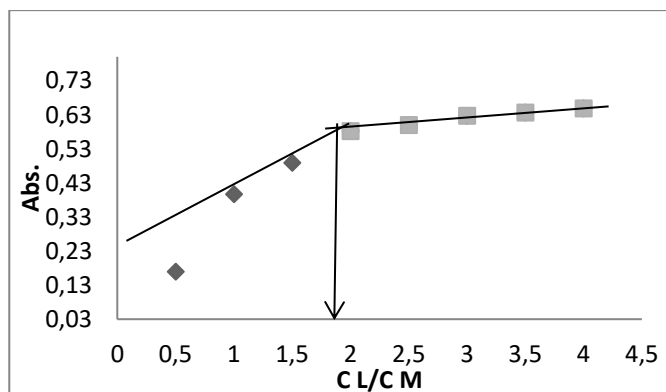


Fig.12 molar ratios of complex: Co(II)

Study the stability calculation of the (Co-PTMH) complex

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

The determination metal ion	As Value	Am Value	α	K_{st} mol.L ⁻¹	K_{inst} L.mol ⁻¹	Log K_{st}
Co (II)	0.3952	0.6398	0.3822	724803124	1.37969×10^{-9}	8.86022

The results of molar ratios show how stable the cobalt complex is by figuring out how much dissociation and how long it stays together.

Study the determination of "thermodynamic function" to complexes formation

The "thermodynamic functions ΔH , ΔG , and ΔS " were calculated, and the results are shown in table 4 and figure 13.

$$\text{Slope} = \frac{-\Delta H}{2.303 R} \text{-----(1-1)}$$

$$\Delta G = -RT \ln k_{st} \text{-----(2-1)}$$

$$\Delta G = \Delta H - T \Delta S \text{-----(3-1)}$$

Table.4. The influence of temperature on the (Co-PTMH) complex's thermodynamic function

T (K)	1/T K ⁻¹	Log K_{st}	($-\Delta H^\circ$) (K. J/mole)	($-\Delta G^\circ$) (K.J /mole)	($-\Delta S^\circ$) (K.J /mole . K)
288	0.003472	8.86022	0.004099	48.84979	0.169603
298	0.003356	8.84337		50.44984	0.169281
308	0.003247	8.817419		51.98977	0.168785
318	0.003145	8.788492		53.50165	0.168231
328	0.003049	8.776161		55.10666	0.167996
338	0.002959	8.752413		56.63308	0.167541

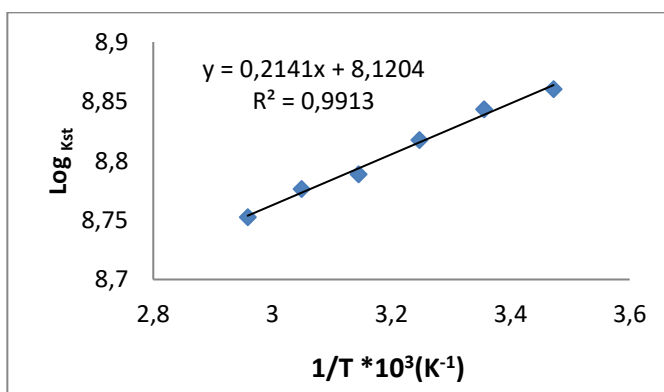


Fig.13 Relation ship of Log K_{st} and 1/T of (Co-PTMH) complex.

Precision

The standard deviation and relative standard deviation of the complexes formed were calculated, and the table5 shows the values obtained based on five readings for each complex with three different concentrations.

Accuracy

Calculating the relative error (percent Erel) and the recovery ratio (percent Re) of the complexes produced, as shown in the time table6, was used to tune the analytical spectroscopic approach.

Table 5. Standard deviation values and percentage standard deviation

Comp. of ion	Conc. Of ion ($\mu\text{g}/\text{mL}$)	S.D	R.S.D%
Co (II)	0.29	0.00103	0.5594
	0.58	0.00145	0.7244
	4.4	0.00179	0.4880

TABLE 6. The pre-processing ratio of ligand complexe and the relative percentage erro

Complex ion	Analytical value ($\mu\text{g}/\text{mL}$)	d	%E _{real}	%Re
[Co-PTMH]	0.29	-0.051	-0.175	99.82
	0.58	0.032	0.056	100.056
	4.4	0.057	0.012	100.012

Conclusion

Briefly, the base compound Schiff 1-phenyl-2 (thiophene-2-ylmethylene)hydrazine was prepared, because it is an economical and easy to prepare compound in the laboratory. It was used as a ligand that reacts with a cobalt ion to form a colored complex. The proposed method is very simple and sensitive for cobalt determination, because of the stability of the formed compound over two hours, which consists of the reaction of the metal ion with the reagent, low consumption of the reagent, removal of analytical error, reduced interference and statistical analysis, all these things make this method sensitive for cobalt determination.

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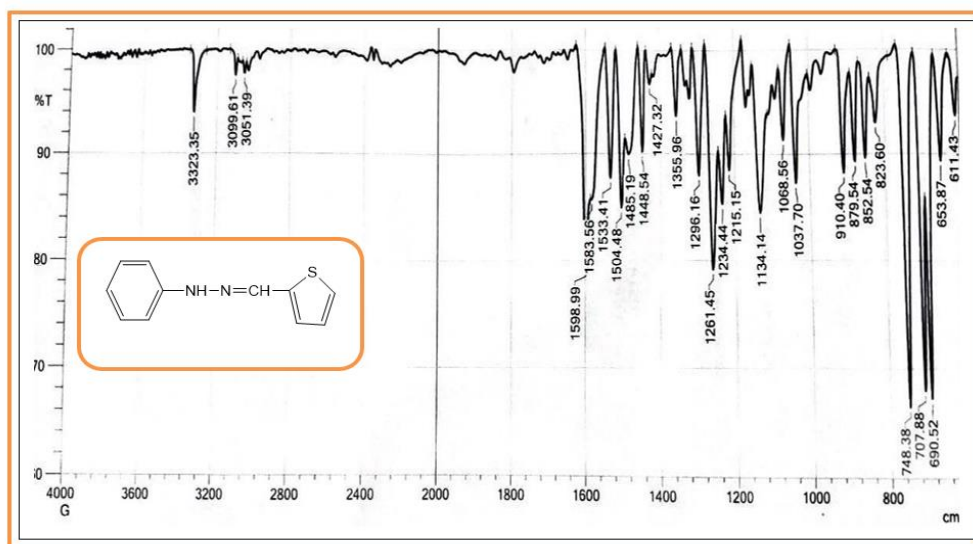
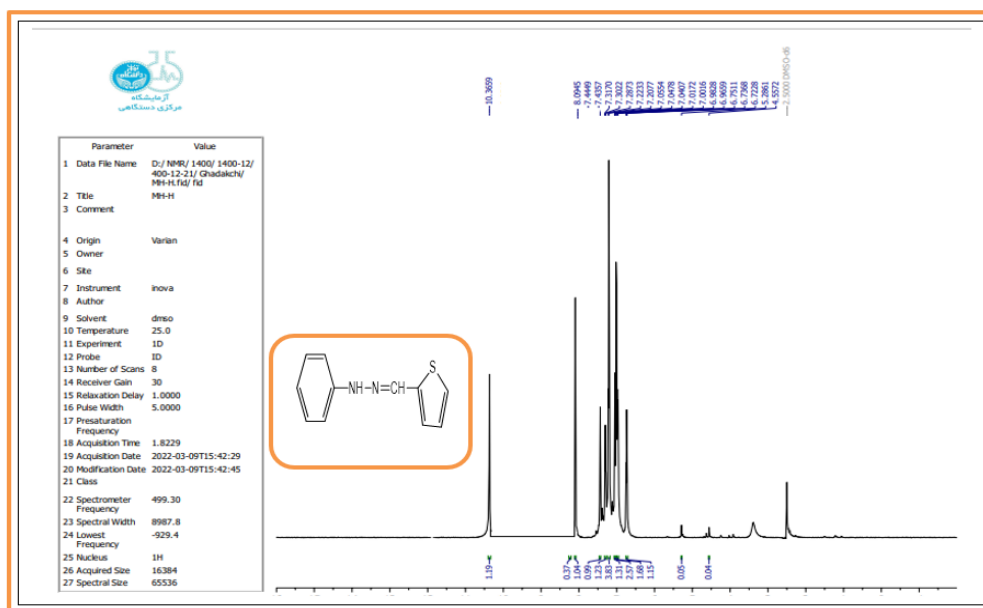


Fig. 1: Show FT-IR spectra for ligand

Fig. 2: Show ¹H NMR spectra for ligand

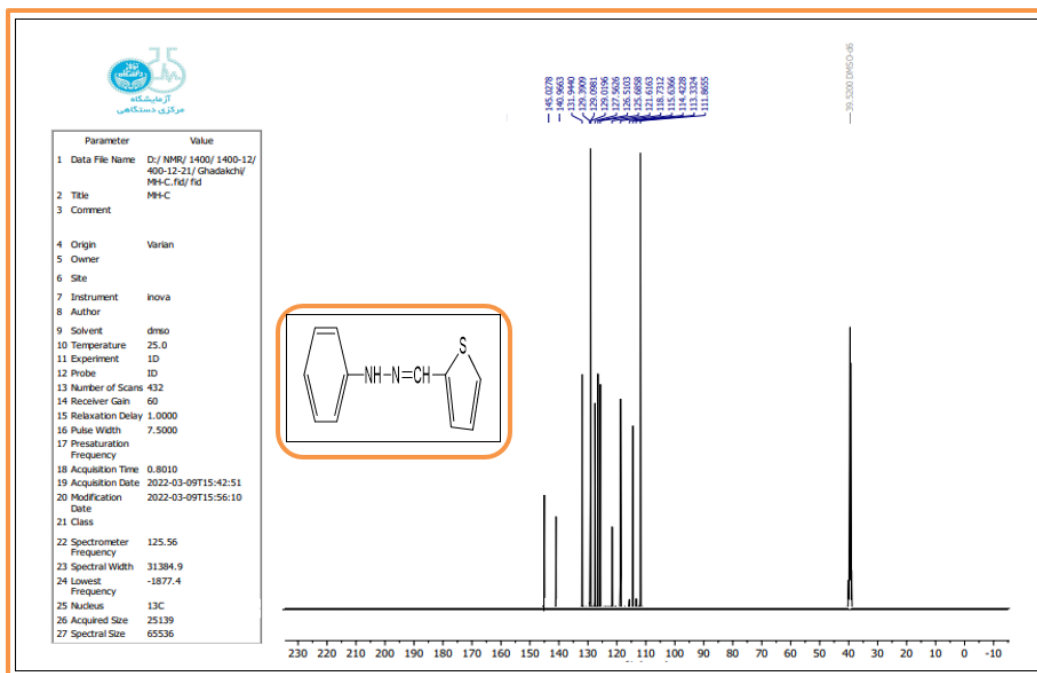
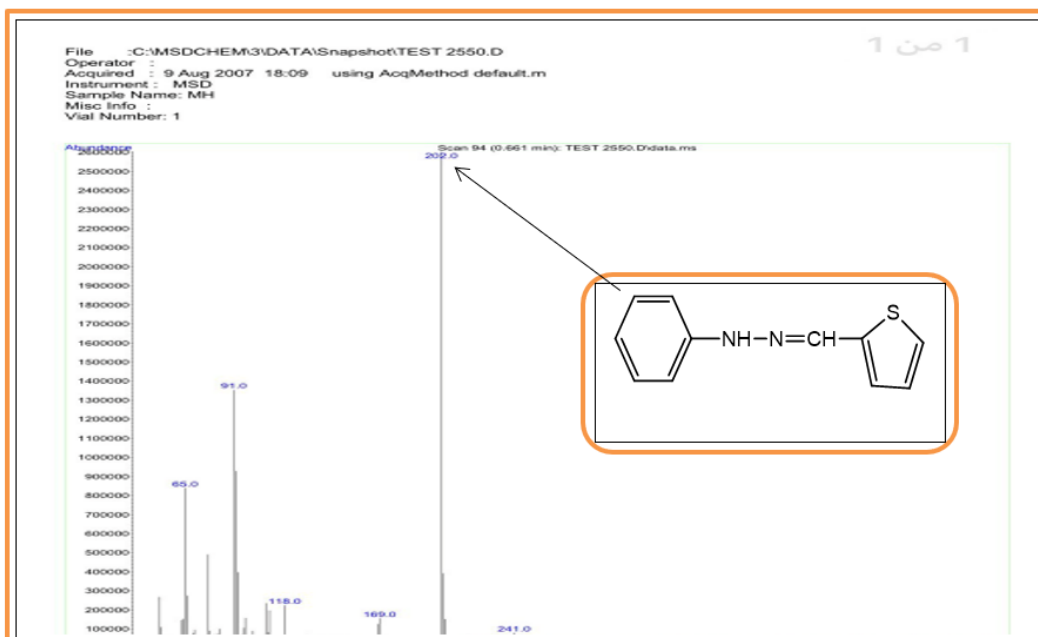
Fig. 3: ^{13}C NMR Spectra of ligand

Fig. 4: Mass spectra of ligand

References

1. Hanoon, H. D., Abd Al Hussain, H. A. & Abass, S. K. Synthesis and characterization of azetid-2-one and 1, 3-oxazepine derivatives using Schiff bases derived from 1, 1'-biphenyl-4, 4'-diamine. in *Journal of Physics: Conference Series* vol. 2063 12010 (IOP Publishing, 2021).
2. Croitor, L. *et al.* Evolution from discrete mononuclear complexes to trinuclear linear cluster and 2D coordination polymers of Mn (II) with dihydrazone Schiff bases: Preparation, structure and thermal behavior. *Polyhedron* 206, 115329 (2021).
3. Kargar, H., Ardakani, A. A., Tahir, M. N., Ashfaq, M. & Munawar, K. S. Synthesis, spectral characterization, crystal structure determination and antimicrobial activity of Ni (II), Cu (II) and Zn (II) complexes with the Schiff base ligand derived from 3, 5-dibromosalicylaldehyde. *J. Mol. Struct.* 1229, 129842 (2021).
4. Kostova, I. & Saso, L. Advances in research of Schiff-base metal complexes as potent antioxidants. *Curr. Med. Chem.* 20, 4609–4632 (2013).
5. Şener, İ., Şener, N. & Gür, M. Synthesis, structural analysis, and absorption properties of disperse benzothiazol-derivative mono-azo dyes. *J. Mol. Struct.* 1174, 12–17 (2018).
6. Dalia, S. A. *et al.* A short review on chemistry of schiff base metal complexes and their catalytic application. *Int. J. Chem. Stud.* 6, 2859–2866 (2018).
7. Ardean, C. *et al.* Factors influencing the antibacterial activity of chitosan and chitosan modified by functionalization. *Int. J. Mol. Sci.* 22, 7449 (2021).
8. Altowyan, A. S., Ahmed, H. A., Gomha, S. M. & Mostafa, A. M. Optical and thermal investigations of new schiff base/ester systems in pure and mixed states. *Polymers (Basel)*. 13, 1687 (2021).
9. Sun, J., Yang, Y., Wang, J. & Lu, B. Ammonia assisted regulation of nitrogen-type in carbonaceous support applied for oxygen reduction reaction. *Appl. Surf. Sci.* 558, 149958 (2021).
10. Kimura, I. *et al.* Maternal gut microbiota in pregnancy influences offspring metabolic phenotype in mice. *Science (80-.)*. 367, eaaw8429 (2020).
11. Swallow, A. J. *Radiation Chemistry of Organic Compounds: International Series of Monographs on Radiation Effects in Materials*. vol. 2 (Elsevier, 2016).
12. Zhang, W. *et al.* Hydrazone-Linked Heptazine Polymeric Carbon Nitrides for Synergistic Visible-Light-Driven Catalysis. *Chem. Eur. J.* 26, 7358–7364 (2020).
13. Li, X., Zhang, D., Liu, Z., Xu, Y. & Wang, D. Synthesis, characterization of a ternary Cu (II) Schiff base complex with degradation activity of organophosphorus pesticides. *Inorganica Chim. Acta* 471, 280–289 (2018).
14. Coplen, T. B. & Shrestha, Y. Isotope-abundance variations and atomic weights of selected elements: 2016 (IUPAC Technical Report). *Pure Appl. Chem.* 88, 1203–1224 (2016).
15. M. A. C. M.Haniffa, Y. C.Ching, C. H.Chuah, K. Y.Ching, and N. S. L. Synergistic effect of (3-Aminopropyl) Trimethoxysilane treated ZnO and corundum nanoparticles under UV-irradiation on UV-cutoff and IR-absorption spectra of acrylic polyurethane based nanocomposite coating. *Polym. Degrad. Stab.* 159, 205–216 (2019).
16. Abu-Dief, A. M. *et al.* Synthesis and characterization of Fe (III), Pd (II) and Cu (II)-thiazole complexes; DFT, pharmacophore modeling, in-vitro assay and

- DNA binding studies. *J. Mol. Liq.* 326, 115277 (2021).
17. Srivastava, A. K., Yadav, P., Srivastava, K. & Prasad, J. Synthesis, characterization, biological and electrochemical investigation of copper (II) complexes containing 4-chloro-2-[2, 6-diisopropylphenylimino) methyl] phenol Schiff base ligand and aromatic diinines. *Chem. Data Collect.* 32, 100659 (2021).
 18. A. G. Al-shahwany, and A. O. O. Synthesis and Study some new Schiff Bases Derived from Pyrazolo-Coumarin. *Rafidain J. Sci.* 30, 78–90 (2021).
 19. Thota, A., Boga, K., Arukula, R., Narayan, R. & Rao, C. R. K. Dianiline conjugated Schiff base molecule: Electrical and electrochemical properties. *Synth. Met.* 247, 240–247 (2019).
 20. Anand, T., Kumar, A. S. K. & Sahoo, S. K. A novel Schiff base derivative of pyridoxal for the optical sensing of Zn²⁺ and cysteine. *Photochem. Photobiol. Sci.* 17, 414–422 (2018).
 21. Raafid, E., Al-Da'amy, M. A. & Kadhim, S. H. Determination and Identification of Nickel (II) Spectroscopy in Alloy Samples Using Chromogenic Reagent (HPEDN). in *IOP Conference Series: Materials Science and Engineering* vol. 871 12025 (IOP Publishing, 2020).
 22. Haniffa, M. A. C. M., Ching, Y. C., Chuah, C. H., Ching, K. Y. & Liou, N.-S. Synergistic effect of (3-Aminopropyl) Trimethoxysilane treated ZnO and corundum nanoparticles under UV-irradiation on UV-cutoff and IR-absorption spectra of acrylic polyurethane based nanocomposite coating. *Polym. Degrad. Stab.* 159, 205–216 (2019).
 23. M. H. Atiyah, and A. F. H. Spectrophotometric Determination of Micro Amount of Copper (II) Using a New of (Azo) Derivative, Study of Thermodynamic Functions and Their Analytical Application. *Syst. Rev. Pharm.* 11, 171–181 (2020).
 24. Widana, I.K., Sumetri, N.W., Sutapa, I.K., Suryasa, W. (2021). Anthropometric measures for better cardiovascular and musculoskeletal health. *Computer Applications in Engineering Education*, 29(3), 550–561. <https://doi.org/10.1002/cae.22202>
 25. Gandamay, I. B. M., Antari, N. W. S., & Strisanti, I. A. S. (2022). The level of community compliance in implementing health protocols to prevent the spread of COVID-19. *International Journal of Health & Medical Sciences*, 5(2), 177-182. <https://doi.org/10.21744/ijhms.v5n2.1897>