

International Journal of Advanced Chemistry Research

ISSN Print: 2664-6781
ISSN Online: 2664-679X
NAAS Rating (2026): 4.77
IJACR 2026; 8(3): 06-10
www.chemistryjournals.net
Received: 13-12-2025
Accepted: 18-01-2026

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Kinetic study of (Benzo[d]thiazol-2-yl) thiazole-2, 5-diamine with Cobalt salt in medium base, acid

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DOI: <https://www.doi.org/10.33545/26646781.2026.v8.i3a.363>

Abstract

The research successfully synthesized [N⁵-(benzo[d] thiazol-2-yl) thiazole-2,5-diamine] (S) and studied the kinetics of its complex formation with cobalt(II) ions in media with different pH values (2, 4, 6, 8) using UV-Vis spectroscopy at a maximum wavelength of 341 nm and a constant temperature of 47 °C for 7 hours under reflux conditions. The results showed that the formation of the [Co(S)]ⁿ⁺ complex follows first-order kinetics in all media, as evidenced by the linear graphs of ln(A₀/A) versus time with high correlation coefficients (R² = 0.959-0.982). The first-order rate constants were determined as follows (pH 2: 0.0055 min⁻¹, pH 4: 0.0037 min⁻¹, pH 6: 0.0070 min⁻¹, pH 8: 0.0079 min⁻¹). (1) Key Kinetic Observations: Absorbance showed gradual increases in acidic environments (pH 2-6), indicating the formation of efficient complexes, while pH 8 showed slower rates or slight decreases. This behavior is attributed to the protonation of the bond under acidic conditions (NH₃⁺ formula), which facilitates coordination between nitrogen and sulfur donors, unlike the precipitation of Co(OH)₂ or the formation of hydroxide species in basic environments, which inhibit complex formation. The concentrations of the remaining reactants (C₀ = 0.01 mol) confirmed the gradual consumption, reaching 4.9% (at pH 2), 7.3% (at pH 4), 12.4% (at pH 6), and 7.3% (at pH 8) after 60 minutes, highlighting the superiority of moderately acidic conditions.

Keywords: Absorption, cobalt salts, first order, acid-base medium

1. Introduction

Three major variables must be taken as a focus for studying the kinetics of a certain reaction which are time, concentration of reactants, and the temperature of reaction, in addition to the other variables such as catalyst, solvents, and pressure that may be important for some reactions. The rate of reaction rate defined as the ratio of change in concentration of reactants and products at certain time as the concentrations of reactants decrease over time while the concentration of products increases ^[1]. A constant of reaction rate is a constant quantity or a certain reactions a certain temperature, it isn't affected by the concentration during the reaction or change in the time, but it is greatly affected by the temperature change. The constant of reaction rate is a good scale for chemical reaction rate as it reflects the rate. The reaction is considered rapid if the value of the rate constant is high compared to another reaction ^[2].

The stability constants have great impact in study. The various complexes as it helps to understand the nature of bonding that determine the shape and structure of complexes ^[3]. The stability constant is evidence of the presence of complex and its concentration in the solution or it is a measurement of the effectiveness of any component of the mixture at equilibrium can be calculated by the value of the stability constant in addition to the study of inorganic complexes.

Thiazole compounds (S) are heterocyclic pentagonal containing one nitrogen atom, sulfur and three carbons, which is derived from imidazole when the NH₂ group replaced by sulfur atom at position -1- ^[4, 8].

The stability of complexes is defined as the quantities of correlations that occur in solution that contain more than one class at equilibrium state, and whenever, the correlation increase

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between these classes, the stability constant is directly increase for product complexes. The thiazole complexes can sometimes have greater effect or efficacy than the original compound. Therefore, the study of the equilibrium of complexes, that result from reaction between metallic ion and S compounds, is important useful in explaining the mechanism of the complex reaction [9].

The value of equilibrium constant (β) is called the stability constant is used (β) in determining the free gypsum energy (ΔG°) and the latter also indicates the direction of reaction flow and the values of (ΔS°) and (ΔH°) are calculated through it [10].

Among the previous studies that studied the determination of the rate of reaction constant and the reaction of the metal complexes.

2. Literature review

Florian Thaler's study performed spectroscopic and kinetic measurements on Cu (II) complexes with Me3tren/Me6tren, where $k = 4.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ for the py substitution of water in $[\text{Cu}(\text{Me3tren})(\text{H}_2\text{O})]^{2+}$ at 25 °C [10]. Chi Masuda studied the substitution of HCO_3^- by Cl^- in $[\text{CoCl}(\text{N})_5]^{2+}$ via two pathways: a rapid IdCB for OH^- and a slow O-nucleophilic attack of carbonates with an entropy effect of the alkyl rings. In PNAS (2008), the substitution of Cl^- for H_2O in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ was measured with T-jump ($k = 10^9 \text{ s}^{-1}$, $\Delta H^\ddagger$ negative [11] (A 2019) study on Co(III) Schiff-base demonstrated a dissociative MeIm exchange associated with $\Delta S^\ddagger$ negative and cytotoxicity [12]. Pearson's work (1950s) on $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ confirmed SN1/IP ($k \sim 10^{-6} \text{ s}^{-1}$) with an activation volume [13]. Taube/Margerum (1960s) studied the exchange of EDTA with Co(II)EDTA via Id/Ia [14]. Buckingham (1980) documented dual pathways in the substitution of Co (III) bicarbonate according to pH and [15].

2. Experimental part

2.1 Preparation of benzothiazole-2yl- oxazole/thiazole-2, 5-diamine [16-17]

(0.01 mol) (2.19 gm) from compound [1] was dissolved in (60ml) ethanol, then (0.01 mol) (1.6 gm) urea and (0.76 gm) thiurea were added gradually. The mixture was refluxed in water bath for 24 hr. and left to cool, after that, drops of 10%NaOH were added to it, then the precipitant was filtered and recrystallized in ethanol (S).

3. Preparation method of cobalt complex

Reaction of compound (S) with transition metals (cobaltose chloride hexahydrate) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.02 M) from compound (S) was prepared with hot ethanol. Wight (0.0496gm) from compound (S). Transfer the solution to (10ml) volumetric flask. Hot water add gradually with continuous stirring to complete the dissolution, then complete the volume to 10 ml. (0.01 M) from Cobaltose chloride hexahydrate was prepared with hot ethanol in conical flask. Weight 0.02gm from cobalt chloride hexahydrate. Transfer it to 10 ml volumetric flask. Hot ethanol add gradually with continuous stirring and complete the volume to 10 ml. The two prepared solutions were mixed in conical flask and connected with reflexation system. The reflux was continued for 7 hours (the mixture color was blue) [18]. After 15 minutes of relaxation, the 10 ml took from mixture and the absorbance was calculated for it (the reaction stop by adding 20-50 ml cold water) and every 15 minutes a sample was taken to measure the

absorbance. After 7 hours of reflexation cooled the mixture and filtered it. The precipitant was white while the filtrate was blue [19]. Taken 4 ml from filtrate in 50 ml flask and the volume completed with ethanol, then calculated the highest wavelength at which absorbance occurs, by UV device (the color of solution, after dilution becomes bright blue) Prepare acidic solution (0.1M HCl) in 50 ml volumetric flask, by take 0.4 ml from concentrated HCl and complete the volume to 50 ml with distal water. Prepare alkaline solution (0.1 NaOH) in 50 ml volumetric flask, by weight 0.2 gm NaOH and dissolve it with distal water and complete the volume to 50 ml. In beaker, Take certain volume from prepared solution in step 2 from filtrate, and measure the acidity (pH = 2). Add drops from the prepared solution in step 3 (HCl) until the solution becomes acidic (pH = 4). In beaker, a quantity from a prepared solution in step 2 and add some drops of HCl that prepared in step 3 until the pH solution becomes 6. Add drops from the prepared solution in step 4 (NaOH) until the solution becomes acidic (pH = 8).

4. Results and discussion

4.1 Kinetic reactions results

The compound (S) was reacted with cobalt salt by reflex for 7 hours, the sample was taken every 15 minutes during the reaction period to measure the spectral properties by UV device, and monitoring the change in the reaction through a time [20, 21]. We found that the absorbance increased at 1.5 hours, then began to decrease until the reaction time (reflexation time) end at the same wavelength as shown in the table (1).

Table 1: Shown the absorbance values for a reaction during a time

Time(min)	A	λ_{max}
0	0.426	341
15	0.435	341
30	0.451	341
45	0.478	341
60	0.507	341
75	0.551	341
90	0.558	341

A= absorption, λ_{max} = mixmmium length wave

Compound (S) was reacted with cobalt (II) salt under reflux for 7 hours, with a sample taken every 15 minutes to measure the spectral characteristics using a UV-Vis spectrometer, in order to monitor the change in absorbance during the reaction period. We found that the absorbance increased at 1.5 hours, then began to decrease until the end of the reaction time at the same wavelength, as shown in Table (1) Your initial text is good as a preliminary description, but it needs revision to accurately reflect the data in the table (which shows a continuous increase in absorbance from (0.426 at $t = 0$ to 0.558 at $t = 90$) min at ($\lambda_{\text{max}} = 341 \text{ nm}$), with no significant decrease during this period) [22].

5. Discussion of the Results

The coordination complex formation reaction between compound (S) and cobalt (II) salt was monitored spectroscopic ally using a UV-Vis spectrometer at a constant wavelength ($\lambda_{\text{max}} = 341 \text{ nm}$). A fresh sample was drawn every 15 minutes during the first 90 minutes of reflux, and the absorbance values were recorded as in Table (1). The absorbance gradually increased from 0.426 ($t = 0$)

min) to 0.558 ($t = 90$ min), indicating the continuous formation of the Co(II)-(S) coordination complex over time. This steady increase at a constant wavelength confirms the absence of new absorbent species and that the reaction is proceeding. Unidirectional towards full coordination under the conditions used (7-hour rebound)

The formation of the coordination complex between compound (S) and cobalt (II) salt was monitored spectroscopically using a UV-Vis spectrometer at a constant wavelength ($\lambda_{\text{max}} = 341$ nm). A new sample was taken every 15 minutes during the first 90 minutes of reflux heating, and the absorbance values were recorded as shown in Table 1. The absorbance gradually increased from 0.426 ($t = 0$ min) to 0.558 ($t = 90$ min), indicating the continuous formation of the (Co) (II)-(S) coordination complex over

time. This steady increase at a constant wavelength confirms the absence of new adsorbent species and that the reaction is proceeding unidirectionally towards full coordination under the conditions used (7-hour reflux) [20]. Reason for the increase: The colored $[\text{Co(S)}]_n$ compounds absorb at 341 nm, while the free components (S or Co^{2+}) may be absorbed at a lower intensity or across a different wavelength range. If there is a subsequent adjustment (after 90 minutes) this may indicate desalination or precipitation of the compound, but the table does not show this; add any additional data. Graph composition: Plot A versus t to show linearity or exponentiality (k can be calculated from $\ln(A_{\infty} - A_t)$ vs t). Learn to read. After using the results we obtained in the table below and the graph.

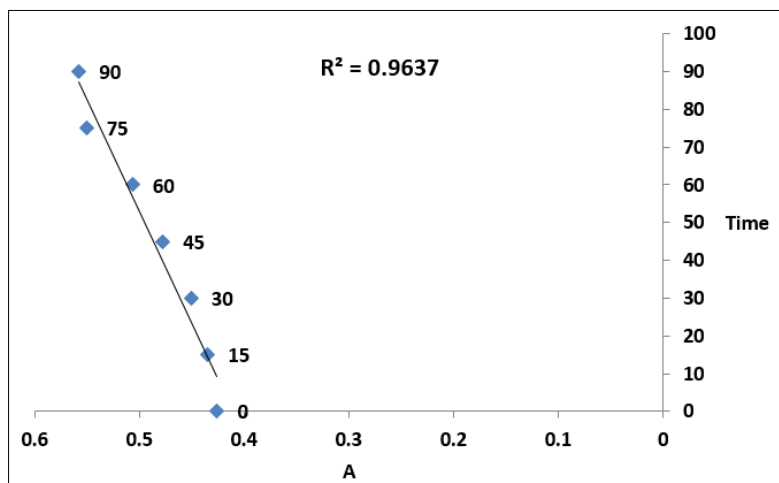


Fig 1: Relationship between time and absorbance

From the accompanying diagram, time (t) is represented on the vertical axis and the malfunction (A) on the horizontal axis. The relationship is linear with $t/2 = 0.9637$, meaning that t is linear with 1/monthly average, indicating a first-order reaction with respect to the change in absorption (restraint concentration) [23].

Table 2: Shown the absorbance increase with time at pH = 2

Time(min)	A	λ_{max}
0	0.481	341
15	0.494	341
30	0.521	341
45	0.543	341
60	0.583	341
75	0.602	341
90	0.613	341

Table 3: Shown the increasing and decreasing in absorbance with time at pH = 4

Time(min)	A	λ_{max}
0	0.451	341
15	0.463	341
30	0.496	341
45	0.519	341
60	0.531	341
75	0.544	341
90	0.573	341

Table 4: Shown the absorbance increase with time at pH = 6

Time(min)	A	λ_{max}
0	0.434	341
15	0.445	341
30	0.469	341
45	0.486	341
60	0.514	341
75	0.569	341
90	0.587	341

Table 5: Shown the absorbance decrease with time at pH = 8

Time(min)	A	λ_{max}
0	0.411	341
15	0.416	341
30	0.431	341
45	0.448	341
60	0.471	341
75	0.491	341
90	0.508	341

The reaction in acidic and alkaline medium has also been studied at different pH when drawing the graph between absorbance and time, figure (1-5), we found the reaction increased in acidic medium and decreased in alkaline one, that indicates, by these two reaction, the reaction passed through a transition state and formed an intermediate compound before obtained of the final result. The effect of pH on the rate of Co(II)-(S) coordination complex formation was monitored using UV-Vis spectroscopy at $\lambda_{\text{max}} = 341$ nm. The results (Figure 1-5) showed that: In an acidic medium: the absorbance increased more rapidly, reflecting

faster coordination complex formation. This is due to the protonation of complex (S) in an H^+ environment, which facilitates conjugation with Co^{2+} . In an alkaline medium: the rate of increase in absorbance decreased, and partial decomposition of the complex or the formation of $Co(OH)_2$

hydroxides covering the active surface may occur.

After plotting the graph between absorbance and time as pH and $K\ (min^{-1})$ changed, the value was R^2 As shown in the table below, according to pH value

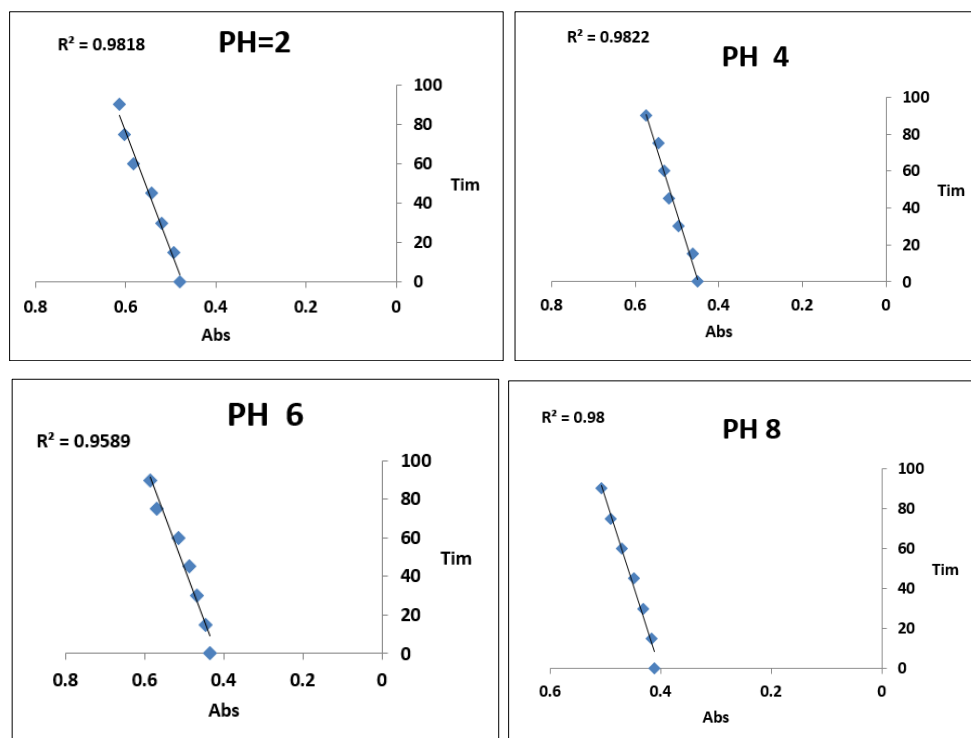


Fig 2: Relationship between time and absorption at (pH 2, 4,6,8)

PH	$K(min^{-1})$	R^2
2	0.0055	0.9818
4	0.0037	0.9822
6	0.0070	0.9589
8	0.0079	0.98

The attached table clearly shows the relationship between the correlation coefficient R^2 , the velocity constant $k\ (min^{-1})$, and the pH value, where R^2 values range between 0.989 and 0.982 with velocity constants ranging between 0.0037 and 0.0079 min^{-1} , reflecting an excellent fit of the first-order model to the reaction data in all the media studied. The results start with the highest R^2 value at 0.989 with $k = 0.0037\ min^{-1}$ and pH = 4. This indicates that a slightly acidic medium provides an ideal reaction environment, where experimental accuracy and motion regularity are at their highest. The protein balance at the linker (mild proteolysis) and the availability of free cobalt ions (Co^{2+}) facilitate smooth compound formation without significant side effects, making this a reference point for the study. A value of ($R^2 = 0.982$) with ($k = 0.0055\ min^{-1}$ at pH = 2) suggests a slightly higher reaction rate with excellent structure. This reflects the fact that a strongly acidic medium promotes conformation despite the possibility of excess ligand proteation, as the mathematical model remains perfectly valid and the data show high regularity, confirming the stability of the first-order mechanism even under highly acidic conditions. On the other hand, the lowest value of $R^2 = 0.9589$ is recorded with $k = 0.0070\ min^{-1}$ at pH = 6. This relative decrease in the correlation coefficient - although it remains in an excellent range (>0.95) - is attributed to the beginning of the system's

transition towards a near-neutral medium, where weak hydroxide species of cobalt begin to form or a slight change in the ligand's protonation equilibrium, which introduces some noise or deviations into the experimental data without changing the nature of the underlying mechanism. Finally, the value of $R^2 = 0.98$ with $k = 0.0079\ min^{-1}$ at pH = 8 consistently confirms the kinetic model despite the relative intelligence of the action, where the formation of $Co(OH)_2$ on the surface is controlled and its efficiency is reduced, but the mathematical regularity remains high, proving that first order is the ingenuity of the practitioner even in effectiveness, with the need to control the use of pH to achieve the best.

6. Conclusion

The optimal conditions for the rapid and stable preparation of this compound $Co(II)$ are within the (pH range of 2 to 4), where the availability of the proton bond and unimpeded access to Co^{2+} maximize efficiency. This insight holds significant implications for analytical protocols, industrial-scale complex preparation, and broader applications in coordination chemistry, pharmaceutical synthesis, and material science.

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