

Kinetics and Mechanism of the Substitution Reaction of Amine in (bis(Acetyl Acetonato) Ethylenediimine) (Diamine)Cobalt(III) Perchlorate with N_3^- , Br^- and NCS^-

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ABSTRACT: A series of complexes of the type $trans-[Co(acacen)(amine)_2]ClO_4$, where (acacen) is the (bis(acetylacetonato) ethylenediimine) and the amines are Benzyl amine (bzlan) 1, 2-amino pyrimidine (2ampy) 2, N-methylpirazine (nmpip) 3, 3-methyl pyridine (3mpy) 4, p-toluidine (p-toldn) 5, has been synthesized and characterized by uv-vis. and FT-IR. The kinetics of the substitution reaction of $[Co(acacen)(p-toldn)_2]ClO_4$ with N_3^- , Br^- and NCS^- ions has been investigated in an aqueous solution by using UV-vis. spectroscopy. It has been found that the reaction occurs in two steps, hydrolysis and ligation. The first order rate constants for hydrolysis and ligation reactions in 313K have been determined. The rate of reaction is almost independent of the type and the concentration of anion. So, the interchange dissociative (I_d) mechanism is suggested. The reaction has been carried out in several temperatures and the activation energy for hydrolysis and ligation (for NCS^- anion) reactions have been calculated about 55 and 95 kJ/mol respectively.

KEY WORDS: Kinetics, Mechanism, Cobalt (III) complexes, Amine ligands, Schiff base, activation energy.

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INTRODUCTION

The chemistry of transition-metal complexes with Schiff base ligands continues to be the subject of growing interest [1-4]. Many of these compounds are relevant to the chemistry of vitamins, enzymes, and coenzymes [5-7]. The remarkable chemical similarity between cobalamines and cobaloximes is now well recognized to be consequences of the fortuitous near-identicality of the effective coordinating strengths of these chemically unrelated ligand systems. The conjugated tetradentate ligands are chelating agents that coordinate to the four equatorial positions of square pyramidal or octahedral structures of metal centers. The resulting compounds are known to serve as models for the natural corrin ring complexes, and thus for vitamin B₁₂ and its co-enzyme [7-12]. The properties of model complexes are strongly dependent on the nature of the axial ligands. The mutual interdependence of the properties of the two axial ligands can be assessed by structural, spectroscopic, thermodynamic, and kinetic methods [13-16]. Limited comparisons of properties determined by many of those methods suggest that cobalamines and various models have the same type dependence on the trans-ligands.

In this paper we report the synthesis of trans-[Co(acacen)(amine)₂]ClO₄ complexes where the amines are benzyl amine (bzlan) 1, 2-amino pyrimidine (2ampy) 2, N-methylpiperazine (nmpip) 3, 3-methyl pyridine (3mpyr) 4, and p-toluidine (p-toldn) 5. The kinetics of the substitution reaction of [Co(acacen)(p-toldn)₂]ClO₄ with N₃⁻, Br⁻ and NCS⁻ ions are investigated in an aqueous solution using uv-vis. spectroscopy.

EXPERIMENTAL SECTION

Materials

Bis(acetylacetonate) ethylenediimine (H₂acacen) was prepared based on McCarthy et al method [17]. Co(OH)₂ was freshly prepared prior to each synthesis by adding an aqueous solution of NaOH to a solution of Co(NO₃)₂.6H₂O in water (with a molar ratio of 2:1), filtering the precipitate immediately, and washing it with ethanol. All other compounds were commercial reagent grade and used as received from Merck. All of solvents were purified before using according to standard procedures.

Physical measurements

Absorption spectra were measured by a Shimadzu uv-vis.

Table 1: The yield of synthesizes amine complexes.

Product	Yield of reaction
[Co(acacen)(bzlan) ₂]ClO ₄	51%
[Co(acacen)(2ampy) ₂]ClO ₄	38%
[Co(acacen)(nmpip) ₂]ClO ₄	63%
[Co(acacen)(3mpy) ₂]ClO ₄	43%
[Co(acacen)(p-toldn) ₂]ClO ₄	63%

spectrophotometer. The FT-IR spectra were recorded on a Perkin-Elmer spectrophotometer using KBr pellet technique.

Synthesis of the complexes

A solution of the appropriate amine (0.02mol) in 10mL of ethanol was added to a stirring suspension of freshly prepared complex [Co(acacen)(H₂O)₂] in 100mL acetone through which air was bubbled for 3 hours. To the resulting solution was added 0.02 mol of solid NaClO₄ and the solution was stirred for an hour. The resulting solution was left for 48 hours after which a brown solid product was precipitated. The solid product was filtered off and recrystallized from a dichloroethane-ethanol (2:1v/v) mixture. The brown crystals were isolated by filtration, washed with cold ethanol and then dried in vacuum. The yields of synthesized amine complexes are shown in Table 1.

Kinetic measurements

Rate measurements were performed at various temperatures and ionic strengths using 1.0 M (NaClO₄). Kinetic runs were performed in a thermostat cell coupled to the uv-vis spectrophotometer. The reaction was followed by monitoring the absorbance change at λ_{max} of the amine complex. The data output was analyzed by the linear least-square method to give the first order rate constant (k_{obs}), based on the Eq. (1):

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - kt \quad (1)$$

Where A_t, A₀ and A_∞ are the absorbance at time t, beginning and ending of the reaction, respectively. The slope of the plot of ln(A_t-A_∞) vs. t gives the rate constant (k). Each value reported in this study is the numerical mean of at least three runs and error limits given are 1 standard deviation.

RESULTS AND DISCUSSION

Synthesis

Five Co(III) complexes (1-5) were prepared by air oxidation of $[\text{Co}^{\text{II}}(\text{acacen})(\text{H}_2\text{O})_2]$ in the presence of the appropriate amine (Fig. 1). A slow stream of air was passed through a stirring suspension of $[\text{Co}^{\text{II}}(\text{acacen})(\text{H}_2\text{O})_2]$ in acetone, to which was added excess amine. The air oxidation was continued for a period of 3 hours. Dark brown crystals of these complexes were obtained in good yield (38-63%). All complexes reported here are diamagnetic, as expected for a low-spin d^6 configuration [18].

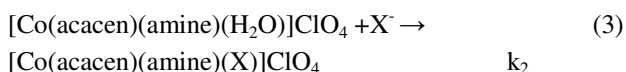
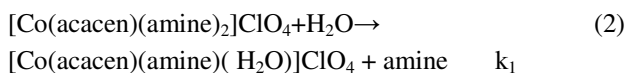
Characterization of the complexes

The results of uv-vis. spectra of the ethanol solution of the $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ complexes are shown in Table 2. These absorption maxima are due to $A_{1g} \rightarrow T_{1g}$ (E_g, A_{2g}).

The IR spectrum of $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ shows a decrease in stretching frequencies of N-H band ($3200\text{--}3400\text{cm}^{-1}$) in comparison to the free amine (3400cm^{-1}), presumably caused by bond formation between N and Co with the subsequent weakening of N-H band (Fig. 2).

Kinetics of the substitution reaction of $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ with N_3^- , Br^- and NCS^-

In this study, we have mainly focused was on the kinetic investigation of substitution reaction; however, to study the effect of incoming ligand, the substitution reaction of Br^- and N_3^- was also tested. The kinetics of the substitution reaction of $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ with N_3^- , Br^- and NCS^- was performed by UV-vis. spectrophotometer. The reaction was determined by monitoring the absorbance change at λ_{max} of the amine complex. It was found that the reaction occurs in two steps, hydrolysis and ligation.



The hydrolysis reaction is faster than ligation reaction ($k_1 \gg k_2$). So, two reactions are independent.

The plot of $\ln(A_t - A_\infty)$ vs. t for hydrolysis reaction in 313K is shown in Fig. 3. The rate constant is 0.1012 min^{-1} ($1.68 \times 10^{-3} \text{ s}^{-1}$). Fig. 4. Shows the changes in absorption

Table 2: UV-vis. absorption maxima of $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ complexes in ethanol.

Complexes	λ_{nm}
$[\text{Co}(\text{acacen})(\text{bzlan})_2]\text{ClO}_4$	430
$[\text{Co}(\text{acacen})(2\text{ampyr})_2]\text{ClO}_4$	388.7
$[\text{Co}(\text{acacen})(\text{mpip})_2]\text{ClO}_4$	440.5
$[\text{Co}(\text{acacen})(3\text{mpyr})_2]\text{ClO}_4$	443.5
$[\text{Co}(\text{acacen})(\text{p-toldn})_2]\text{ClO}_4$	454

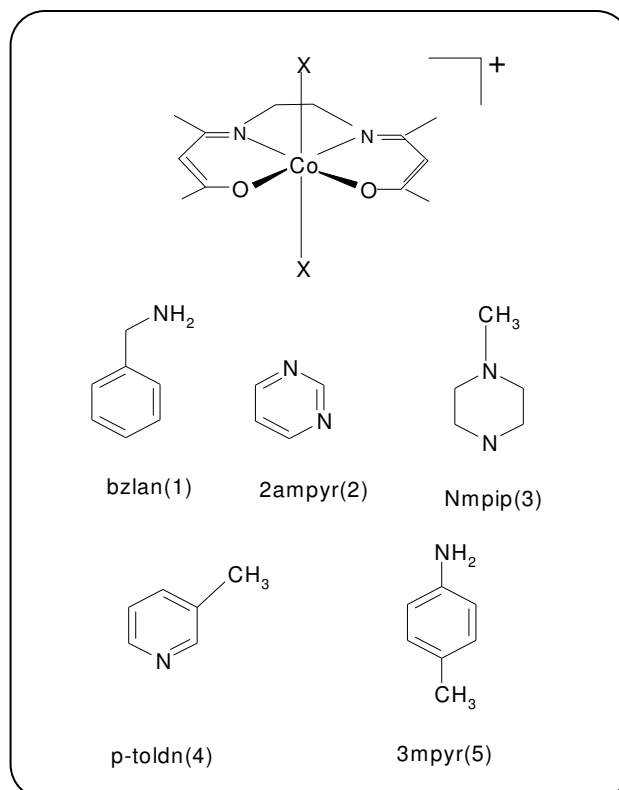


Fig. 1: $[\text{Co}(\text{acacen})(\text{X})_2]\text{ClO}_4$ ($\text{X} = \text{amine}$) complexes.

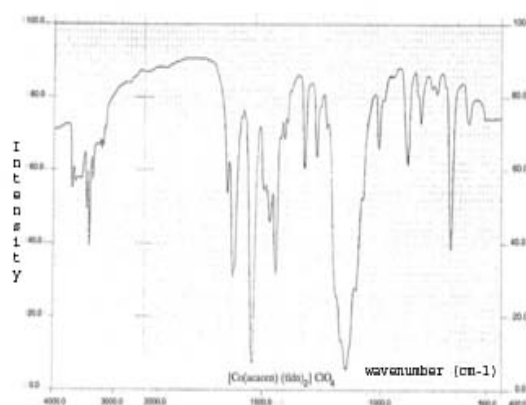


Fig. 2: IR spectrum of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$.

Table 3: The change of the rate constants of the ligation reaction of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ with different types of anions in 313K.

Anion	NCS^-	N_3^-	Br^-
Rate constant(s^{-1})	6.45×10^{-5}	3.79×10^{-5}	2.27×10^{-5}

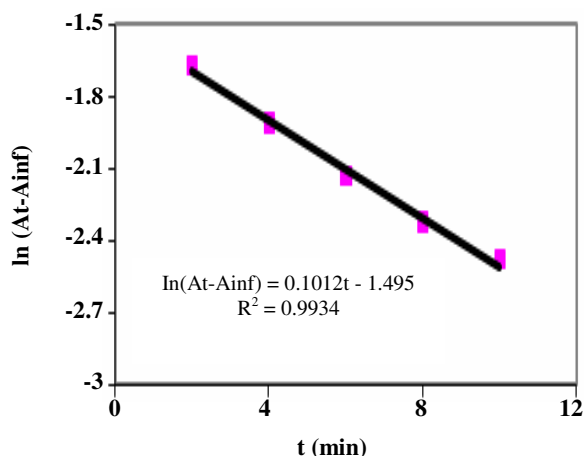


Fig. 3: The plot of $\ln(A_t - A_\infty)$ vs. t for hydrolysis reaction in 313K, $\lambda_{\text{max}} = 340\text{nm}$, $[\text{complex}] = 9.3 \times 10^{-5}$, $[\text{NCS}^-] = 4.65 \times 10^{-4}$.

spectra for the ligation of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ with NCS^- anion. There is an isosbestic point in ligation reaction. Isosbestic points are wavelengths at which the absorbance remains constant as the reactant and product composition changes. One (or preferably more) isobathic points during a reaction strongly suggest that the original reactant is being replaced by one product, or if more than one product, that these are always in a strictly constant ratio. The occurrence of isosbestic points implies the absence of appreciable amounts of reaction intermediates [19]. Thus, it means there is only one product in this reaction.

As indicated in Table 3, the rate of reaction changes only slightly with changes in the incoming ligand (less than a factor of 10). Also, the rate constant of the ligation reaction is approximately independent of the concentration of the anion (Table 4). This independency proves that the mechanism is dissociative interchange (I_d). In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination. This species, which is not described as having an increased coordination number and is not

Table 4: The change of the rate constants of the ligation reaction of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ in different concentrations of NCS^- .

$[\text{NCS}^-]$	1.86×10^{-4}	4.5×10^{-4}	4.65×10^{-3}
Rate constant(s^{-1})	4.37×10^{-5}	4.92×10^{-5}	7.97×10^{-5}

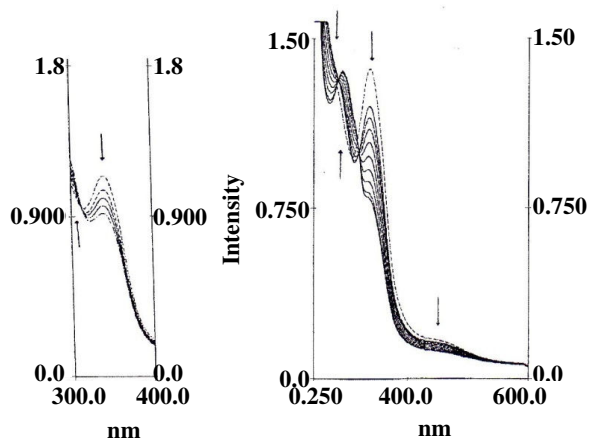


Fig. 4: Changes in absorption spectra for the ligation of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ with NCS^- anion. a) $\Delta t = 1\text{min}$. b) $\Delta t = 40\text{min}$.

directly detectable, then reacts to form the product releasing the initial ligand. Two variations of the interchange mechanism are I_d (dissociative interchange) and I_a (associative interchange). The difference between them is in the degree of bond formation in the first step of the mechanism. If bonding between the incoming ligand and the metal is more important, it is an I_a mechanism. If breaking the bond between the leaving ligand and the metal is more important, it is an I_d mechanism. The distinction between them is subtle, and careful experimental design is required to determine which description fits a given reaction. If the rate of substitution reaction changes only slightly with changes in the anion ligand (within a factor of less than 10), an I_d mechanism will be indicated. However, if the rate of substitution reaction shows a large variation with changes of the anion ligand, an I_a mechanism will be indicated [20].

The rate constant measurement of hydrolysis and ligation reaction (reactions 2 and 3) was carried out in different temperatures and the activation energies calculated were 55.38 and 94.45 kJ/mol respectively (Tables 5 and 6).

Table 5: The plot of $-\ln k$ vs $1/T$ for hydrolysis reaction of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ with the NCS $^-$.

$10^3 T^{-1}$	3.247	3.195	3.145	3.096
$-\ln k$	6.888	5.749	5.762	5.778
$\text{Slope} = \frac{E_a}{R} = 6661.05 \Rightarrow E_a = 55.38$				

Table 6: The plot of $-\ln k$ vs $1/T$ for ligation reaction of $[\text{Co}(\text{acacen})(\text{tldn})_2]\text{ClO}_4$ with the NCS $^-$.

$10^3 T^{-1}$	3.247	3.195	3.145	3.096
$-\ln k$	10.207	9.635	9.200	8.445
$\text{Slope} = \frac{E_a}{R} = 11360.3 \Rightarrow E_a = 94.45$				

CONCLUSIONS

In this study, efforts were made to provide a quantitative measure of anion effect on the ligation reaction of $[\text{Co}(\text{acacen})(\text{amine})_2]\text{ClO}_4$ complexes. It was found that the reaction occurs in two steps, hydrolysis and ligation. The ligation reaction is independent of the type and the concentration of the anion. So, the I_d mechanism is suggested.

In this paper we have studied the kinetics and mechanism of just one amine substitution reaction of five possibilities mentioned previously. The same approach is suggested for investigating other complex reactions. The results of the present study can be taken as useful information for further research.

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