

VOLUMES OF ACTIVATION FOR THE REDUCTION OF CHLOROPENTAAMMINE-COBALT (III) BY IRON (II) FROM HIGH PRESSURE SOLUTION KINETICS: THE INFLUENCE OF AN IRON (II)-SULPHATE ION PREEQUILIBRIUM

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Summary

The reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by ferrous ammonium sulphate has been studied at ionic strengths (I) of 1.0, 0.6 and 0.3 mol dm⁻³. The rates of reaction at room pressure are greater than those reported previously in the reduction by iron (II) perchlorate.

The volumes of activation (ΔV^\ddagger) are +35.3, +24.7 and -8.9 cm³ mol⁻¹ at I=1.0, 0.6 and 0.3 mol dm⁻³ respectively. These are interpreted in terms of a rapid pre-equilibrium between iron (II) and sulphate ion to form the iron (II) sulphato complex followed by a rate determining step in forming the bridged intermediate with the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ via either the iron (II) sulphato complex or the hexaaquoiron (II) complex. The ΔV^\ddagger of +35.3 and +24.7 cm³ mol⁻¹ are consistent with the reactions proceeding predominantly via the iron (II) sulphato complex while the reaction whose $\Delta V^\ddagger = -8.9$ cm³ mol⁻¹ tends to proceed via the hexaaquoiron (II) species.

Introduction

The kinetics of the redox reactions of metal ions has been a subject of interest for the past twenty years¹⁻³. Both direct and indirect methods have been established to distinguish between inner sphere and outer sphere types of mechanisms in various systems. Product identification has provided proof of an inner sphere mechanism for the reduction of the halopentaamminecobalt (III) complexes, $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ (X=Cl⁻, Br⁻ etc.) by chromium (II)⁴. The necessary conditions that the reduced forms of the redox systems have to be substitution labile and the oxidized forms substitution inert have been met in the above system. However, if the oxidized form of the reductant is substitution labile, e.g. for the reduction with Fe²⁺ and Eu²⁺, the product identification criterion cannot be applied and hence indirect determination has to be employed. A comparison of stabilities of the transition states⁵ and works in non-aqueous solvent media⁶⁻⁸ for the redox reaction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ have proved to be useful as indirect criteria in distinguishing the mechanisms. Another indirect method involves measurement of the volume of activation (ΔV^\ddagger) from the effect

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of high pressure on the rate of reaction in solution⁹. Elucidation of mechanisms of substitution^{10,11}, isomerization¹², racemization¹³ and electron exchange systems⁹ have been based on analysis of the volumes of activation.

The volumes of activation indicating an inner sphere mechanism for the reduction of some halopentaamminecobalt (III) complexes by iron (II) perchlorate in aqueous solution have been reported¹⁴. We wish to report the volumes of activation for the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by ferrous ammonium sulphate at various ionic strengths. The effect of a preequilibrium involving ferrous and sulphate ions in this particular system can be seen from trends in ΔV^\ddagger .

Materials and Methods

Materials

Chloropentaamminecobalt (III) chloride was prepared by an established method¹⁵ and was then converted to the perchlorate salt by filtering the saturated solution of the chloro-complex into an excess of chilled A.R. perchloric acid (60%). The resulting precipitate of $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$ was filtered, recrystallized from perchloric acid, washed with ethanol followed by ether and then vacuum dried. Analysis was performed by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

Calcd. N: 18.5, H: 3.96, Cl: 28.1%

Found N: 18.84, H: 4.23, Cl: 28.5%

Perchloric acid, sodium perchlorate and ferrous ammonium sulphate were of A.R. grade and were used without further purification. Ferrous ammonium sulphate solutions for kinetic runs were added with appropriate concentrations of perchloric acid, then adjusted to the desired ionic strengths by sodium perchlorate solutions.

Apparatus

The pressure vessel used contains sapphire windows which allow direct measurement of absorbance under pressure and is designed for incorporation in a suitable spectrophotometric cell compartment. This vessel is fitted into a Varian Techtron 635D spectrophotometer. Thermostat temperature in the water bath was maintained to within $\pm 0.05^\circ\text{C}$ using a proportional temperature control unit with a thermister sensor. The water from this bath was circulated through the pressure vessel so that the temperature was kept constant as desired.

Kinetic Measurements

Fresh Co (III) complex solutions were made up each day. Ferrous ammonium sulphate solutions of known ionic strengths were prepared and within two weeks. The two reactants were kept at the desired temperature in the thermostat bath prior to each run for at least 30 minutes. Equal volumes of the reactants (2 ml) were taken by means of pipettes and mixed in a stoppered volumetric flask (5 ml). This reaction

mixture was then transferred to a cylindrical glass cuvette of pathlength 1 cm. A teflon plunger sealed by an o-ring was placed in position. The cuvette was lowered promptly into the thermostated pressure vessel and brought to the desired pressure with an Enerpac handpump. Pressures were measured with a Budenberg gauge. Normally about 5 to 10 minutes were allowed for temperature and pressure equilibrations of the reactants in the pressure vessel. The decrease in absorbance with time was followed spectrometrically on a chart recorder for at least 2-2½ half-lives of the reaction at the maximum of absorption of the Co (III) complex (533 nm) for five different pressures.

Results

The mean values of the rate constants for the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by ferrous ammonium sulphate at various ionic strengths (I) and pressures between 0.001 (room pressure)—1.380 kbars¹⁶ are summarized in Table I, II and III. In all cases first-order kinetic reactions in $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ were observed and the rate constants were evaluated by the Guggenheim method using a computer program. The reactions of ionic strength 1.0 and 0.6 mol dm⁻³ exhibited a marked retardation of the rates upon the application of high pressure while for the reaction of ionic strength 0.3 mol dm⁻³, an acceleration of the rates was found.

The variations of $\ln k$ with pressure were non-linear for I=1.0 and 0.6 mol dm⁻³. These observations implied that ΔV^\ddagger is pressure dependent and the limiting value ΔV_0^\ddagger (as P→0) has to be estimated. This was done by fitting the experimental data to a computer program which calculated the curve of best fit in the form of a polynomial. The polynomial which was found to fit well with the data has the form

$$\ln k_p = \ln k_0 + bP + cP^2$$

where $\Delta V_0^\ddagger = -bRT$ and the compressibility coefficient of activation ($\Delta\beta^\ddagger$) = $-(\partial\Delta V^\ddagger/\partial P)_T = 2cRT$. However, for I=0.3 mol dm⁻³, ΔV^\ddagger is pressure independent since the variation of $\ln k$ with pressure was linear and hence the simpler relation $(\partial\ln k/\partial P)_T = -\Delta V^\ddagger/RT$ was applied to obtain ΔV^\ddagger . The pressure dependence of ΔV^\ddagger is represented in Fig. 1 while Table IV summarizes the values of ΔV^\ddagger together with $\Delta\beta^\ddagger$.

TABLE I: VARIATION OF AVERAGE RATE CONSTANTS WITH APPLIED PRESSURE FOR THE REDUCTION OF $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ BY $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ AT 25°C
 ([Co (III)] = 5×10^{-3} ; [Fe (II)] = 0.1; [H +] = 0.25; I = 1.0 MOL DM⁻³)

Pressure (kbar)	$10^4 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (mol ⁻¹ dm ³ s ⁻¹)
0.001	8.50 (± 0.18)	0.85
0.345	5.06 (± 0.02)	0.51
0.690	4.01 (± 0.13)	0.40
1.035	3.62 (± 0.18)	0.36
1.380	3.19 (± 0.24)	0.32

TABLE II: VARIATION OF AVERAGE RATE CONSTANTS WITH APPLIED PRESSURE FOR THE REDUCTION OF $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ BY $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ AT 25°C
 ($[\text{Co}(\text{III})] = 3 \times 10^{-3}$; $[\text{Fe}(\text{II})] = 0.04$; $[\text{H}^+] = 0.1$; $I = 0.6 \text{ MOL DM}^{-3}$)

Pressure (kbar)	$10^4 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (mol ⁻¹ dm ³ s ⁻¹)
0.001	2.22 (± 0.09)	0.56
0.345	1.53 (± 0.09)	0.38
0.690	1.32 (± 0.06)	0.33
1.035	1.21 (± 0.07)	0.30
1.380	1.08 (± 0.07)	0.27

TABLE III: VARIATION OF AVERAGE RATE CONSTANTS WITH APPLIED PRESSURE FOR THE REDUCTION OF $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ BY $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ AT 25°C
 ($[\text{Co}(\text{III})] = 3 \times 10^{-3}$; $[\text{Fe}(\text{II})] = 0.02$; $[\text{H}^+] = 0.05$; $I = 0.3 \text{ MOL DM}^{-3}$)

Pressure (kbar)	$10^5 k_{\text{obs}}$ (s ⁻¹)	$10^2 k_2$ (mol ⁻¹ dm ³ s ⁻¹)
0.001	8.6 (± 0.9)	0.43
0.690	11.8 (± 0.5)	0.59
1.035	13.2 (± 0.1)	0.66
1.380	14.5 (± 2.7)	0.73

TABLE IV: VOLUMES OF ACTIVATION (ΔV^\ddagger) AND COMPRESSIBILITY COEFFICIENTS OF ACTIVATION ($\Delta \beta^\ddagger$) OF DIFFERENT SOLUTIONS AT 25°C

$\frac{[\text{Fe}(\text{SO}_4)(\text{H}_2\text{O})_5]}{[\text{Fe}^{2+}]}$	ΔV^\ddagger (cm ³ mol ⁻¹)	$\Delta \beta^\ddagger$ (cm ³ mol ⁻¹ kbar ⁻¹)
1.40	+ 35.3 (± 4.9)	- 27 (± 7)
0.67	+ 24.7 (± 5.5)	- 18 (± 8)
0.35	- 8.9 (± 2.5)	≈ 0

TABLE V: IONIC STRENGTH DEPENDENCE FOR THE REDUCTION OF $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ BY Fe (II) AT ROOM PRESSURE.

I (mol dm ⁻³)	$10^2 k_2^a$ (mol ⁻¹ dm ³ s ⁻¹)	$10^2 k_2$ (mol ⁻¹ dm ³ s ⁻¹)
1.7		0.16 ^b
1.0	0.85	0.14 ^c
0.6	0.56	
0.3	0.43	0.07 ^d

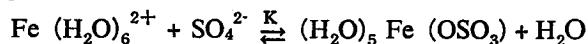
a: temp. = 25°C; in presence of SO_4^{2-} and ClO_4^- ; b (ref. 17), c (ref. 18) and d (ref. 19): temp. = 25.5°C, 25.0°C and 25.8°C respectively in presence of ClO_4^- .

Discussion

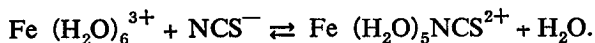
Theoretically, the volume of activation for an electron exchange system⁹ can be considered to arise from coulombic work ($\Delta V_{\text{coul}}^\ddagger$), solvent rearrangement ($\Delta V_{\text{SR}}^\ddagger$), internal rearrangement ($\Delta V_{\text{IR}}^\ddagger$), and ionic strength ($\Delta V_{\text{DH}}^\ddagger$). In the reduction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{F}^-$ or N_3^-) by iron (II), the expected volume of activation arises mainly from $\Delta V_{\text{coul}}^\ddagger$, $\Delta V_{\text{DH}}^\ddagger$ plus the release of water molecules in forming the bridged intermediate. Using the calculated values⁹ of $\Delta V_{\text{coul}}^\ddagger$ and $\Delta V_{\text{DH}}^\ddagger$ for a typical electron exchange system involving metal ions of charge +2 and +3 (-7 and -3.8 cm³ mol⁻¹ respectively at $I = 0.5$ mol dm⁻³), $\Delta V_{\text{coul}}^\ddagger$ and $\Delta V_{\text{DH}}^\ddagger$ contributions for the reduction of the above system are estimated to be -4.7 and -2.4 cm³ mol⁻¹ respectively. The contribution from the release of coordinated and electrostricted water is estimated⁹ as approximately +14 cm³ mol⁻¹, resulting in a predicted net volume change of about +7 cm³ mol⁻¹. This value is comparable with the observed value for the reduction using iron (II) perchlorate¹⁴. At $I = 0.1$ and 1.0 mol dm⁻³ the $\Delta V_{\text{DH}}^\ddagger$ contributions between two ions of +2 charge are -1.4 and -3.1 cm³ mol⁻¹ respectively⁹. Using the above values of $\Delta V_{\text{DH}}^\ddagger$ we may say that in our reduction system at $I = 0.6$ and 1.0 mol dm⁻³, $\Delta V_{\text{DH}}^\ddagger$ values predicted in each case are not significantly different and also small when compared with the experimental volumes of activation observed (+24.7, +35.3 cm³ mol⁻¹).

The large volumes of activation and a much higher rate at room pressure of our system compared to those reported for the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by iron (II) perchlorate, suggest that sulphate ion may be directly involved in the reaction under study.

The equilibrium for the reaction



has a stability constant for the formation of iron (II) sulphato complex of ten²⁰. The ratios of the concentration of the iron (II) sulphato complex to that of the hexaaquoiron (II), $[\text{Fe}(\text{SO}_4)(\text{H}_2\text{O})_5]/[\text{Fe}^{2+}]$ are different in all three cases studied, being 1.4, 0.67 and 0.35 for $I=1.0$, 0.6 and 0.3 mol dm⁻³ respectively. Large changes in volume of activation are possibly associated with the changes in these ratios. A large positive ΔV^0 (+17.4 cm³ mol⁻¹) has been reported⁹ for the similar type of reaction



The expected volume from the formation of the iron (II) sulphato complex could be greater, since the reaction involves a change of charge (ΔZ^2) of -8 units compared to a change of -6 units in the $\text{Fe}^{3+}/\text{NCS}^-$ system. However, the stability constant in the $\text{Fe}^{2+}/\text{SO}_4^{2-}$ system is not as high as in the $\text{Fe}^{3+}/\text{NCS}^-$ system, hence the value of ΔV^0 for the $\text{Fe}^{2+}/\text{SO}_4^{2-}$ system cannot be directly inferred, but could be taken as approximately between +10 and +20 cm³ mol⁻³ depending on the $[\text{Fe}(\text{SO}_4)(\text{H}_2\text{O})_5]/[\text{Fe}^{2+}]$ ratio.

Large positive values of ΔV^\ddagger observed for the redox reaction in the presence of sulphate ion can therefore be interpreted as involving a rapid preequilibrium of the hexaaquoiron (II) and sulphate ion. This is then followed by a slow rate determining step which involves forming a bridged intermediate between the Co (III) complex and the iron (II) sulphato complex via release of coordinated and electrostricted water molecules. However, a bridged intermediate involving the hexaaquoiron (II) species directly is also possible. The contribution of $\Delta V_{\text{coord}}^\ddagger$ between the iron (II) sulphato complex and the Co (III) complex may be regarded as equal to zero since this is a reaction between ions of charge 0 ($\text{Fe}(\text{SO}_4)(\text{H}_2\text{O})_5$) and +2 ($\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$). The volume of activation involving the release of coordinated and electrostricted water molecules (ΔV_1^\ddagger) as mentioned earlier, is +14 cm³ mol⁻¹. Therefore, ΔV^\ddagger (expected) = $\Delta V^0 + \Delta V_1^\ddagger$ should be in the range between 24-34 cm³ mol⁻¹. The observed values at $I=1.0$ and 0.6 mol dm⁻³ (+35.3 and +24.7 cm³ mol⁻¹) are consistent with the expected values. This suggests that the reductions of Co (III) by ferrous ammonium sulphate at $I=1.0$ and 0.6 mol dm⁻³ occur predominantly via the iron (II) sulphato complex pathway. Reduction via the hexaaquoiron (II) would produce a much smaller ΔV^\ddagger . Moreover, marked curvatures in the $\ln(k_p/k_o)$ vs. P plots are observed and $\Delta\beta^\ddagger$ are large in magnitude (-27 and -18 cm³ mol⁻¹ kbar⁻¹) which are consistent with the release of an appreciable number of electrostricted water molecules into the bulk solvent. Further supporting evidence for the iron (II) sulphato complex pathway is that the rates at room pressure are much greater at higher ionic strengths compared to those at lower ionic strengths (see Table V). The increase in the rate of reaction may be due to coordinated sulphate ion labilizing the water molecule trans to it prior to bridge formation.

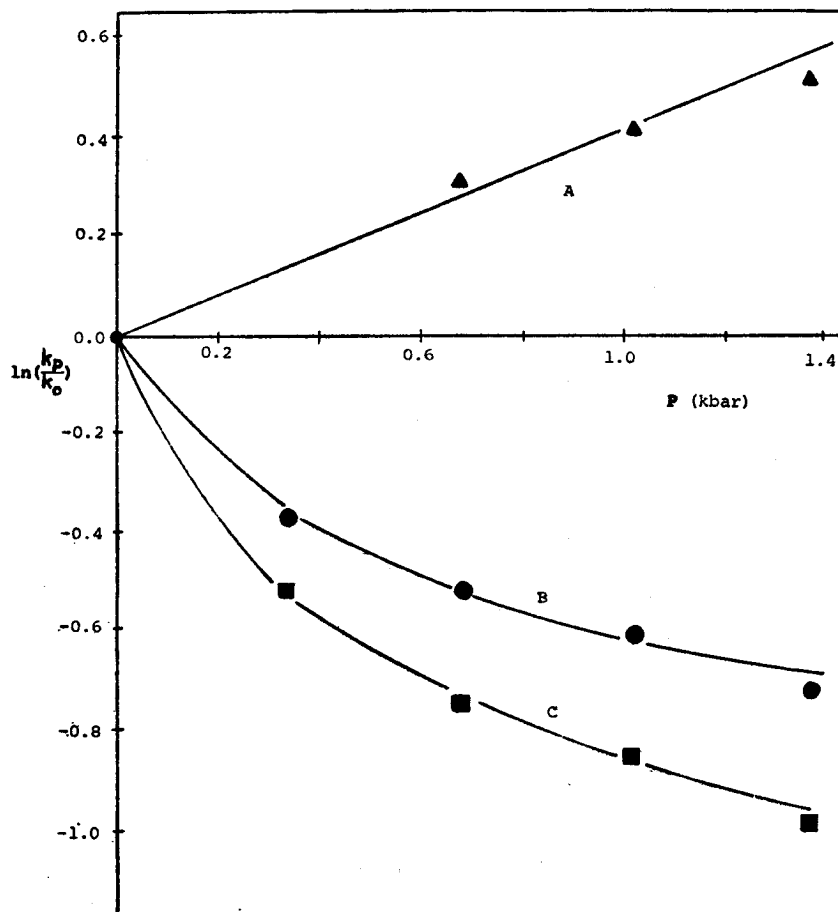


Fig. 1. Pressure dependence of volume of activation for the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ at 25°C

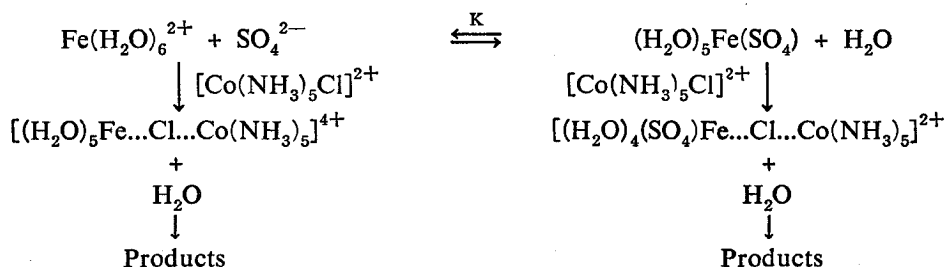
A: $l = 0.3 \text{ mol dm}^{-3}$

B: $l = 0.6 \text{ mol dm}^{-3}$

C: $l = 1.0 \text{ mol dm}^{-3}$

In the case of the reaction studied at an ionic strength of 0.3 mol dm^{-3} , it is apparent from the negative value of ΔV^\ddagger observed ($-8.9 \text{ cm}^3 \text{ mol}^{-1}$) that there is no significant contribution from an iron (II)-sulphate preequilibrium or overall release of water molecules into the bulk solvent. The observed value is close to the expected contributions from the coulombic and ionic strength terms alone (of about $-11 \text{ cm}^3 \text{ mol}^{-3}$) mentioned earlier. It is proposed that the reaction in this case proceeds predominantly via the hexaaquoiron (II) complex pathway, with apparently only a small positive volume contribution from the release of water molecules in forming the bridged intermediate between the Co (III) complex and the hexaaquoiron (II) species. This small volume contribution is similar to that expected for a dissociative interchange, (I_d) mechanism involving coordinated water²¹

In conclusion, we may say that there are two possible pathways in the reactions studied, which can be represented schematically below



Further studies should be made of similar systems in the presence of other anions in order to support the values of ΔV^\ddagger and the proposed mechanisms.

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บทคัดย่อ

จากการศึกษาปฏิกิริยารีดักชันของ $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ โดยเฟอร์รัสแอมโมเนียมซัลเฟตที่ ionic strengths 1.0, 0.6 และ 0.3 mol dm⁻³ พบว่าอัตราเร็วของปฏิกิริยาที่ความดันบรรยากาศมีค่ามากกว่าอัตราเร็วของปฏิกิริยาที่ใช้เฟอร์รัสเปอร์คลอเรตเป็นตัวรีดิวส์

ได้พบว่าปริมาตรกระตุ้น (volume of activation) มีค่าเท่ากับ +35.3, +24.7 และ -8.9 cm³ mol⁻¹ ที่ ionic strengths 1.0, 0.6 และ 0.3 mol dm⁻³ ตามลำดับ จากค่าปริมาตรกระตุ้น อาจสรุปได้ว่ากลไกของปฏิกิริยารีดักชันของ $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ โดยเฟอร์รัสแอมโมเนียมซัลเฟตประกอบด้วย rapid preequilibrium ระหว่าง Fe (II) และ sulphate ion ในการเกิดเป็น iron (II) sulphato complex ติดตามด้วยขั้นกำหนดอัตราปฏิกิริยา (rate determining step) ในการเกิด bridged intermediate ระหว่าง $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ กับ iron (II)-sulphato complex หรือระหว่าง $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ กับ hexaquoiron (II) complex ปริมาตรกระตุ้น +35.3 และ +24.7 cm³ mol⁻¹ สอดคล้องกับปฏิกิริยาส่วนใหญ่ดำเนินผ่านทาง iron (II) sulphato complex ในขณะที่ปริมาตรกระตุ้น -8.9 cm³ mol⁻¹ สอดคล้องกับปฏิกิริยาดำเนินผ่านทาง hexaquoiron (II) complex