

Kinetic studies on the reactions of some tetrakis(arylisocyanide)cobalt(II) complexes with pyridine in 2,2,2-trifluoroethanol

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Abstract

The interaction of pyridine with four tetrakis(arylisocyanide)cobalt(II) complexes, $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ $\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (A), $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (B), $2,6\text{-Et}_2\text{C}_6\text{H}_3$ (C) and $2,6\text{-iPr}_2\text{C}_6\text{H}_3$ (D), have been studied in 2,2,2-trifluoroethanol medium. The kinetics of the reactions were investigated over the 293–318 K temperature range. The reaction profile exhibited two distinct processes, proposed to be an initial fast substitution followed by a slow reduction, for each of the reactions. The pseudo first-order rate constants for both processes increased with increasing concentration of pyridine with the reduction processes exhibiting saturation kinetics at high pyridine concentrations. Steric hindrance plays a significant role in the rates of the reactions, as the rates decrease in the order $k(\text{A}) > k(\text{B}) > k(\text{C}) > k(\text{D})$. The activation enthalpies, ΔH^\ddagger , increase from A to D while the activation entropies, ΔS^\ddagger , are relatively similar for the four reactions, indicating similar transition states and hence similar mechanisms. Complex B was first synthesized and characterized in this study.

Introduction

Early studies, including X-ray crystallographic results, on alkylisocyanide and aryliisocyanide cobalt(II) complexes date back to the nineteen fifties [1–3]. While the initial alkylisocyanide–Co(II) complexes were reported as dimers [4, 5], the aryliisocyanide–Co(II) complexes tended to be pentacoordinate monomeric complexes [6, 7]. In addition to the numerous reported pentakis(aryliisocyanide)cobalt(II) complexes, as perchlorate or tetrafluoroborate salts [1–3, 6–9], several tetrakis(aryliisocyanide)bis(perchlorato)cobalt(II) complexes $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ have also been synthesized. The ease of synthesis for these complexes appears to parallel the steric hindrance of the aryliisocyanide ligands, $2,6\text{-iPr}_2\text{C}_6\text{H}_3\text{NC} > 2,6\text{-Et}_2\text{C}_6\text{H}_3\text{NC} > 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC} > o\text{-MeC}_6\text{H}_4\text{NC}$ [10–13].

Reduction/ligand-substitution reactions of organoisocyanide–Co(II) complexes with tertiary phosphine ligands have also been extensively investigated. Reactions of alkylisocyanide–Co(II) complexes with triarylphosphines and trialkylphosphines tend to yield disubstituted five-coordinate Co(I) complexes, $[\text{Co}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$, $\text{X} = \text{ClO}_4, \text{BF}_4$; usually in good yields [14–20], except when disproportionation to six-coordinate Co(III) and five-coordinate Co(I) complexes, $[\text{Co}(\text{CNR})_4(\text{PR}'_3)_2]\text{X}_3$ and $[\text{Co}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$, respectively, takes place with tri-*n*-alkylphosphines [19, 21, 22]. Reduction/ligand-substitution reactions in pentakis(aryliisocyanide)cobalt(II) perchlorate and

tetrafluoroborate complexes, and in tetrakis(aryliisocyanide)bis(perchlorato)cobalt(II) complexes, exhibit a selection of products having 3:2 and/or 4:1 aryliisocyanide:tertiary phosphine composition, $[\text{Co}(\text{CNR})_3(\text{PR}'_3)_2]\text{X}$ and $[\text{Co}(\text{CNR})_4(\text{PR}'_3)_2]\text{X}$, respectively, depending primarily on the level of steric hindrance in the aryliisocyanide ligand but also somewhat on the tetrakis-complex showing preference for disubstituted Co(I) products while the pentakis-complex often gives monosubstituted product with the same tertiary phosphine ligand [9, 23, 24].

In contrast, reactions of triarylsarsines with alkylisocyanide–Co(II) complexes produce six-coordinate Co(II) complexes containing four alkylisocyanide and two triarylsarsine ligands, *trans*- $[\text{Co}(\text{CNR})_4(\text{AsR}'_3)_2]\text{X}_2$, $\text{X} = \text{ClO}_4, \text{BF}_4$; $\text{AsR}'_3 = \text{AsPh}_3, \text{As}(\text{C}_6\text{H}_4\text{Me-}p)_3, \text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ [25, 26]; except in one instance when both Co(II) and the triarylsarsine are spontaneously oxidized, yielding $[\text{Co}(\text{CNCH}_2\text{Ph})_4\{\text{OAs}(\text{C}_6\text{H}_4\text{Me-}p)_3\}_2](\text{BF}_4)_3$ [27]. Reactions of triphenylstibine produce both $[\text{Co}(\text{CNR})_4(\text{SbPh}_3)_2]\text{X}_2$ and $[\text{Co}(\text{CNR})_4(\text{OSbPh}_3)_2]\text{X}_3$ complexes [28]. Reaction of AsPh_3 with $[\text{Co}(\text{CNPh})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ produced $[\text{Co}(\text{CNPh})_3(\text{AsPh}_3)_2]\text{ClO}_4$ [29], while reactions of AsPh_3 and SbPh_3 with $[\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_5](\text{ClO}_4)_2 \cdot 0.5\text{H}_2\text{O}$ and $[\text{Co}(\text{CNC}_6\text{H}_4\text{Me-}o)_5](\text{ClO}_4)_2$ all yielded the $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes [10, 13]. Reaction of AsPh_3 with $[\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_5](\text{BF}_4)_2 \cdot 0.5\text{H}_2\text{O}$, however, produced $[\text{Co}(\text{CNR})_5]\text{BF}_4$ in poor yield [10].

Despite numerous studies reported on the synthesis and reactions of organoisocyanide–cobalt(II)

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complexes, very little is known about the kinetics of the reduction/ligand-substitution reactions or of the Co(II) \rightarrow Co(I) reduction reactions. Isolation of the transient complexes, $[\text{Co}(\text{CNC}_6\text{H}_{11})_3(\text{PPh}_3)_2](\text{ClO}_4)_2$ [30], $[\text{Co}(\text{CNCHMe}_2)_3\{\text{P}(\text{C}_6\text{H}_4\text{OMe-}p)_3\}_2](\text{ClO}_4)_2$ [31], and $[\text{Co}(\text{CNC}_6\text{H}_{11})_4(\text{PPh}_3)_2](\text{ClO}_4)_2$ [32], in early stages of reduction/ligand-substitution, suggests that $[\text{Co}(\text{CNR})_4\text{L}_2]\text{X}_2$ and $[\text{Co}(\text{CNR})_3\text{L}_2]\text{X}_2$ species may be intermediates in these reactions. Early studies have also shown that pyridine, other aromatic amines, and to a lesser extent dimethyl sulfoxide, cause reduction of both pentakis(arylisocyanide)cobalt(II) complexes and tetrakis(arylisocyanide)bis(perchlorato)cobalt(II) complexes to the corresponding pentakis(arylisocyanide)cobalt(I) complexes, $[\text{Co}(\text{CNR})_5]\text{X}$ [10, 33–35]. With sufficient steric hindrance of the organoisocyanide ligands, however, pyridine-substituted six-coordinate Co(II) complexes can be isolated for both aryliisocyanide and alkylisocyanide complexes, $[\text{Co}(\text{CNC}_6\text{H}_3\text{iPr}_2\text{-}2,6)_4(\text{py})_2](\text{ClO}_4)_2$ [36], $[\text{Co}(\text{CN-CMe}_3)_4(\text{py})_2](\text{ClO}_4)_2$ [37], and $[\text{Co}(\text{CNCHMe}_2)_4(\text{py})_2](\text{ClO}_4)_2$ [38]. Since reduction to the $[\text{Co}(\text{CNR})_5]\text{ClO}_4$ complexes takes place over longer reaction times, these transient Co(II) species may be regarded as intermediates in the Co(II) \rightarrow Co(I) reduction process.

Qualitatively it has also been observed that aryliisocyanide-Co(II) complexes are reduced in the presence of excess (free) aryliisocyanide ligand or coordinating anions [1, 2], and that reaction time increases with steric hindrance of the aryliisocyanide and with exchange of the tetrakis(aryliisocyanide) cobalt(II) complex for the pentakis-complex [35, 36]. For example, a sample of $[\text{Co}(\text{CNC}_6\text{H}_4\text{Me-}o)_5](\text{BF}_4)_2$ reduces completely in a matter of seconds while comparable samples of $[\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_5](\text{BF}_4)_2 \cdot 0.5\text{H}_2\text{O}$ and $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2\text{-}2,6)_5](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ require 2–3 min and 10–15 min, respectively, and $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2)_4](\text{ClO}_4)_2$ needs at least 1 h at room temperature. Our interest in this study is to quantitatively measure the kinetics of the reduction of some tetrakis(aryliisocyanide)bis(perchlorato)cobalt(II) complexes in pyridine and possibly to obtain a clearer picture of the mechanisms for this reduction process.

Experimental

Materials and synthesis of complexes

N-arylformamides, RNHCHO , $\text{R} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$, $2,6\text{-Me}_2\text{C}_6\text{H}_3$, $2,6\text{-iPr}_2\text{C}_6\text{H}_3$ and $2,4,6\text{-Me}_3\text{C}_6\text{H}_2$, were prepared from commercial RNH_2 (Aldrich) and formic acid as described by McKusick and Webster [39], and converted into the aryliisocyanides, RNC , by Becker's modification [40] of a synthesis by Hertler and Corey [41], or through the synthesis by Appel *et al.* [42]. The complexes, $[\text{Co}(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)_4](\text{ClO}_4)_2$ (A), $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2\text{-}2,6)_4](\text{ClO}_4)_2$ (C) and $[\text{Co}(\text{CNC}_6\text{H}_3\text{-iPr}_2\text{-}2,6)_4](\text{ClO}_4)_2$ (D) were prepared as reported in the

literature [10–12]. The compound, $[\text{Co}(\text{CNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_5](\text{ClO}_4)_2$ was also prepared as previously reported [8]. Analar grade pyridine (Rochelle Chemicals) and 2,2,2-trifluoroethanol (Fluka Chemicals) were used without further purification; anhydrous diethyl ether was filtered through an alumina column immediately before use.

Instrumentation

IR spectra were recorded on a Perkin Elmer 2000 FTIR spectrophotometer over the range $4000\text{--}400\text{ cm}^{-1}$. The samples were prepared as Nujol mulls or in solution, solution spectra measured over the range $3000\text{--}1000\text{ cm}^{-1}$. The solutions from the reactions of pyridine with the complexes in $\text{CF}_3\text{CH}_2\text{OH}$ were used in their original state after the reaction was complete, pyridine- $\text{CF}_3\text{CH}_2\text{OH}$ mixture being used as background. Solution electronic spectra were recorded on a Shimadzu UV-2501PC spectrophotometer over the range $1100\text{--}200\text{ nm}$. Carbon, Hydrogen and Nitrogen elemental analyses were performed on a Vario EL CHNOS Elemental Analyser. Percentage cobalt was measured using a Flame Atomic Absorption spectrophotometer, model SpectraAA 220FS (Varian, Australia). Kinetic measurements were obtained from a Shimadzu UV-2501PC spectrophotometer and a Hi-Tech Scientific SF-61 DX2 Single Mixing Stopped-flow spectrophotometer.

Synthesis of tetrakis(2,4,6-trimethylphenylisocyanide) bis(perchlorato)cobalt(II) (B)

$[\text{Co}(\text{CNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_5](\text{ClO}_4)_2$ (500 mg, 50.8 mmol) was dissolved in 25 ml of CH_2Cl_2 and filtered through cotton. To this solution was added 150 ml of peroxide-free diethyl ether in 10 ml aliquots. Initial precipitation was observed after addition of 50 ml of diethyl ether, after the addition of 100 ml the solution changed from green to yellow, and after addition of 150 ml the mixture was chilled in ice for 30 min. The pale orange crystals of $[\text{Co}(\text{CNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_4](\text{ClO}_4)_2$ were removed under suction; yield: 279.6 mg. The crude product was dissolved in a minimum amount of CH_2Cl_2 (5.0 ml) and the resulting green solution was filtered through cotton, using additional 0.5 ml of CH_2Cl_2 as a rinse. Then 10.0 ml of Et_2O was added to the solution dropwise with continuous sweeping of the sides of the flask to induce crystallization. Initial precipitation was observed upon addition of 3.5 ml of Et_2O , but a total of 10.0 ml was added. The reaction mixture was then chilled in an ice bath for 35 min for complete precipitation. The pale golden yellow crystals were filtered under suction and washed with 2.0 ml of Et_2O . Yield: 251 mg (28 mmol, 55%); m.p. $239\text{--}241\text{ }^\circ\text{C}$ (dec).

Anal. Calcd. for $\text{C}_{40}\text{H}_{44}\text{Cl}_2\text{CoN}_4\text{O}_8 \cdot 0.7\text{CH}_2\text{Cl}_2$: C, 54.4; H, 5.2; N, 6.2; Co, 6.6%. Found: C, 54.2; H, 5.3; N, 6.2; Co, 6.4%. Infrared spectra show isocyanide

frequency [$\nu(\text{N}\equiv\text{C})$] at 2201 (~ 2188 sh) cm^{-1} and a split perchlorate band [$\nu(\text{ClO}_4)$] at 1124 (~ 1111 sh) and 1012 (~ 1021 sh) cm^{-1} , indicating mono-coordination. Electronic spectra: λ_{max} (nm; ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 718 (283), 246 (82000) $\{\text{CH}_2\text{Cl}_2\}$; 670 (132), 236 (70000) $\{\text{CH}_3\text{CN}\}$; 875 (651), 261 (65000), 215 (47000) $\{\text{CF}_3\text{CH}_2\text{OH}\}$.

Kinetics

Kinetic measurements were taken on a Shimadzu UV-2501PC UV-Vis spectrophotometer for the slow reactions and on a Hi-Tech SF-61 DX2 Stopped-flow spectrophotometer for the fast reactions. The cell compartments for both instruments were well-thermostatted for constant temperature measurements between the temperatures 293 and 318 K using a Shimadzu thermoelectric temperature controller, TCC-240A, with the UV-2501PC UV-Vis spectrophotometer, while water was circulated from a Neslab RTE 7 thermocirculator to the cell compartment of the stopped-flow equipment. Prior to kinetic measurements, the stabilities of the cobalt(II) complexes and conformance of their solutions to Beer's law were investigated in the solvents CH_2Cl_2 , CH_3CN , and $\text{CF}_3\text{CH}_2\text{OH}$. The complexes were found to conform to Beer's law in $\text{CF}_3\text{CH}_2\text{OH}$ solution (see Figure 1 for a typical plot), but not in the other two solvents.

The kinetics were followed under pseudo-first-order conditions with the pyridine in concentrations 10 times or more than those of the Co(II) complexes. All kinetic studies were followed to more than 90% completion. For the slow processes, the pseudo first-order rate constants (k_s) were obtained from linear regression plots of $\ln(A_t - A_\infty)$ versus time, t , where A_t and A_∞ are the absorbances at time t and $t = \infty$, respectively. The k_s values for the fast processes were obtained from the stopped-flow instrument kinetic software (KinetaSystTM 3) by fitting the decay curves to single exponential analysis. These k_s values for the fast processes

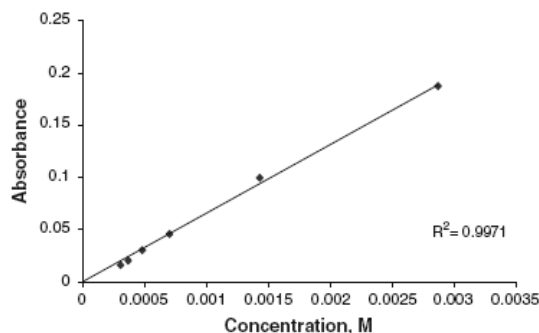
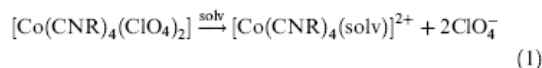


Fig. 1. Beer's plot for $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2-2,6)_4(\text{ClO}_4)_2]$ in trifluoroethanol at 298 K.

are averages of four to five runs for each pyridine concentration.

Results and discussion

It is expected that since the ClO_4^- ions are weakly coordinated, they are displaced by solvent molecules in solution according to Equation 1. The solvated ions can then undergo a rapid substitution on addition of pyridine before final reduction of the cobalt(II) complex to cobalt(I).



All absorbance decay curves show an initial fast increase in absorbance followed by a slow absorbance decrease. Figure 2 shows a typical decay curve for the reaction between $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2-2,6)_4(\text{ClO}_4)_2]$ and pyridine, where we attribute the initial fast increase in absorbance to a substitution process and the slow absorbance decrease to a reduction process. Also, on addition of pyridine, there was an immediate change from green to an almost colourless solution (substitution) followed by slow development of a deep yellow

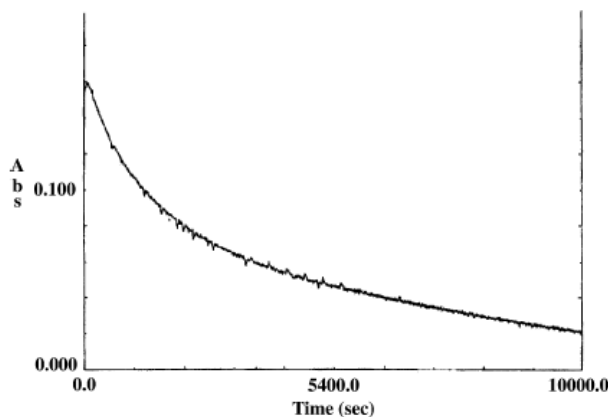


Fig. 2. Typical absorbance decay curve for the reduction of $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2)_4(\text{ClO}_4)_2]$ by pyridine; $[\text{Co(II)}] = 3.19 \times 10^{-4} \text{ M}$, $\lambda_{\text{max}} = 806 \text{ nm}$, $[\text{py}] = 3.30 \times 10^{-3} \text{ M}$, $T = 298 \text{ K}$.

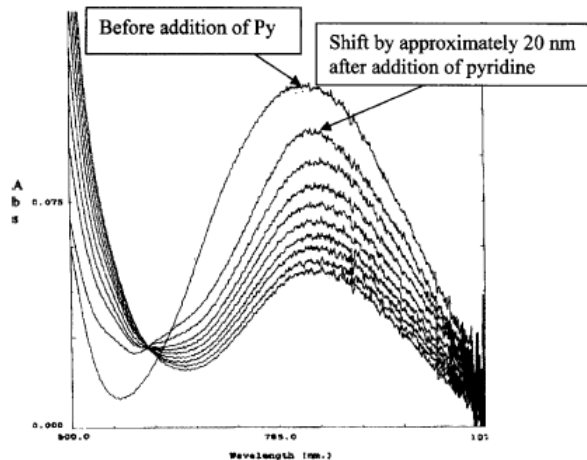


Fig. 3. Spectral changes of a $[\text{Co}(\text{CNC}_6\text{H}_4\text{Et}_2-2,6)_4(\text{ClO}_4)_2]$ solution in trifluoroethanol on addition of pyridine at 298 K.

solution (reduction) which persisted at the end of the reactions. The reduction of the *tetrakis*(arylisocyanide) *bis*(perchlorato)cobalt(II) complexes by pyridine was found to produce *pentakis*(arylisocyanide)cobalt(I) perchlorate salts as the final products. The isolation and characterization of these complexes have been reported in earlier studies [33, 43–45]. Solution infrared spectra of the reaction mixture after completion of the reaction, using $\text{CF}_3\text{CH}_2\text{OH}$ –pyridine mixture for background subtraction, showed two arylisocyanide stretching frequencies, $\nu_{(\text{NC})}$, for these complexes around 2100 and 2150 cm^{-1} , typical for the *pentakis*(arylisocyanide)cobalt(I) complexes.

Addition of pyridine to a freshly prepared solution of $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ in $\text{CF}_3\text{CH}_2\text{OH}$, resulted in a shift of the d–d transition band of the complex about 20 nm towards longer wavelengths (Figure 3). This shift can be attributed to the substitution of the solvent molecules from the Co(II) inner shell by the incoming pyridine ligand (Equation 2).



This complex with the 2,6- $i\text{Pr}_2\text{C}_6\text{H}_3\text{NC}$ ligand has been reported by Becker [36], and similar complexes have been observed by other authors [46–49] in reactions of cobalt(II) protoporphyrin complexes with amine ligands. As explained earlier the fast process was followed using stopped-flow techniques while the slow process was followed using the conventional UV–Vis spectrophotometry.

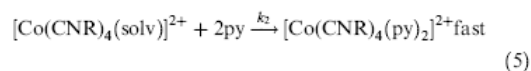
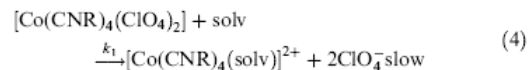
Figure 4 shows a typical linear regression plot for the determination of the pseudo first-order rate constants, k_{2s} . For convenience, we use k_{1s} for the fast substitution reactions and k_{2s} for the slow reduction processes. The reactions were monitored at different concentrations of pyridine. For all the reactions, k_{1s} and k_{2s} increased with increasing concentration of pyridine. Plots of k_{1s} versus concentrations of pyridine

were linear with intercepts. Using the data in Table 1, Figure 5 shows such a plot for the reactions of the four cobalt(II) complexes with pyridine.

The data fit well to the rate law described by Equation 3

$$\text{Rate} = \frac{-d[\text{Co}(\text{CNR})_4^{2+}]}{dt} = k_{1s}[\text{Co}(\text{CNR})_4^{2+}] \quad (3)$$

This is consistent with octahedral substitution involving ligand–ligand replacement *via* a solvated complex according to the following mechanism:



where k_{1s} in Equation 3 above is given by

$$k_{1s} = k_1 + k_2[\text{py}]$$

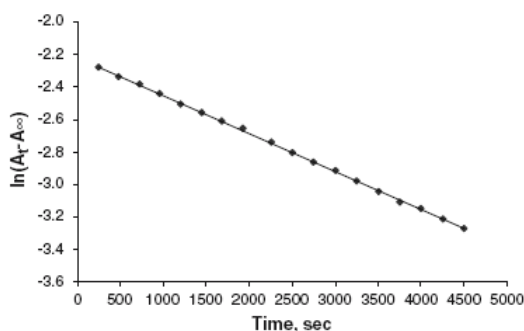


Fig. 4. A linear regression plot of $\ln(A_t - A_\infty)$ versus time for the reaction of $3.19 \times 10^{-4} \text{ M}$ $[\text{Co}(\text{CNC}_6\text{H}_3\text{Et}_2)_4(\text{ClO}_4)_2]$ with $3.30 \times 10^{-3} \text{ M}$ pyridine at 298 K.

Table 1. Pseudo first-order rate constants, k_{1s} , for the substitution reactions between the four $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and pyridine in $\text{CF}_3\text{CH}_2\text{OH}$ at 298 K

$10^3[\text{py}], \text{M}$	k_{1s}, s^{-1}			
	A	B	C	D
3.30	24.7	22.3	19.4	11.9
4.63	26.7	24.4	22.5	12.9
6.61	30.5	27.2	24.7	14.6
7.60	32.6	28.5	26.3	15.6
9.25	35.6	31.7	28.4	18.0
k_1, s^{-1}	19.2	17.1	15.1	8.3
$k_2, \text{M}^{-1} \text{s}^{-1}$	1720	1550	1430	1030

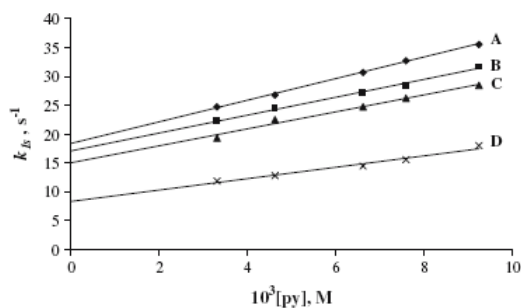


Fig. 5. Plots of observed rate constants (k_{1s}) versus Pyridine concentration for the reaction between the $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and pyridine (fast process) in $\text{CF}_3\text{CH}_2\text{OH}$; $[\text{Co}(\text{CNR})_4]^{2+} = 3.19 \times 10^{-4} \text{ M}$, $T = 298 \text{ K}$.

The fact that k_2 is much greater than k_1 indicates attack by the solvent is a much slower process than attack by the nucleophile.

The slower reduction processes exhibit a somewhat different kinetic behaviour when compared to the substitution processes. Table 2 shows the k_{2s} values for the four arylisocyanide cobalt(II) complexes. Plots of k_{2s} versus concentrations of pyridine gave curves (Figure 6) which are typical of saturation kinetics in which a pre-equilibrium step precedes the rate determining step. Similar non-linear kinetics has been observed by other authors, e.g. in the methylimidazole

Table 2. Pseudo-first order rate constants, k_{2s} , for the reduction of $3.19 \times 10^{-4} \text{ M}$ $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes by pyridine in $\text{CF}_3\text{CH}_2\text{OH}$ at 298 K

$10^3[\text{py}], \text{M}$	$10^4 k_{2s}, \text{s}^{-1}$			
	A	B	C	D
2.64	10.5	5.51	2.12	0.07
3.30	12.4	6.72	2.40	0.08
4.63	14.6	8.60	2.72	0.15
6.61	19.3	9.51	3.01	0.17
7.60	21.0	10.9	3.11	0.18
9.25	22.3	11.4	3.32	0.21
12.14	22.9	12.5	3.41	0.22
15.18	24.4	12.9	3.50	0.24
19.80	24.9	13.3	3.51	0.26
K, M^{-1}	180 ± 8	167 ± 7	142 ± 5	118 ± 3
k_2, s^{-1}	3.90×10^{-3}	1.86×10^{-3}	4.05×10^{-4}	3.86×10^{-5}

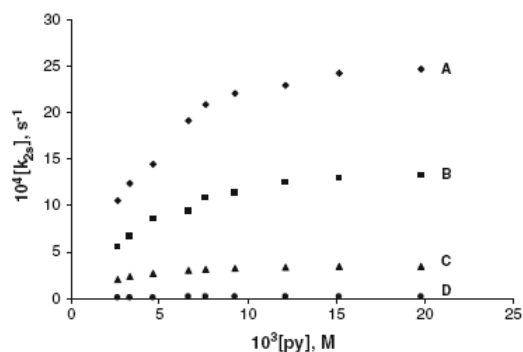


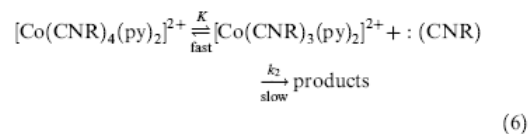
Fig. 6. Plots of observed rate constants for the slow process (k_{2s}) versus pyridine concentration for the reaction between the $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes and pyridine in $\text{CF}_3\text{CH}_2\text{OH}$; $[\text{Co}(\text{CNR})_4]^{2+} = 3.19 \times 10^{-4} \text{ M}$, $T = 298 \text{ K}$.

Table 3. Variation of the electron transfer rate constants (k_2) with temperature for the reactions between the $[\text{Co}(\text{CNR})_4(\text{ClO}_4)_2]$ complexes with pyridine

T, K	$10^4 k_2, \text{s}^{-1}$			
	A	B	C	D
293	35.3	16.1	3.81	—
298	39.0	18.6	4.11	0.51
303	44.0	20.4	5.40	0.92
308	49.2	23.3	6.62	1.31
313	54.1	26.2	7.91	1.60
318	61.2	27.1	8.23	2.12
$\Delta H^\ddagger, \text{kJ mol}^{-1}$	14.5 ± 0.4	16.0 ± 0.4	24.8 ± 0.6	39.5 ± 0.8
$\Delta S^\ddagger, \text{J mol}^{-1} \text{K}^{-1}$	-242 ± 1	-244 ± 1	-226 ± 2	-192 ± 2

catalysed hydrolysis of some *p*-nitrophenyl carboxylate esters [50], the reaction of cobalt(II) protoporphyrin IX dimethyl ester with pyridine and related compounds [46, 49], as well as the aminolysis of sulfamate esters in chloroform [51].

Our observations can be represented by the following mechanism:



for which the rate law can be given as $\text{Rate} = k_{2s}[\text{Co}(\text{CNR})_4]^{2+}$ where

$$k_{2s} = \frac{k_2 K [\text{py}]}{1 + K [\text{py}]} \quad (7)$$

Equation (7) can be re-arranged to give

$$\frac{1}{k_{2s}} = \frac{1}{k_2 K [\text{py}]} + \frac{1}{k_2} \quad (8)$$

From Equation (8), plots of $1/k_{2s}$ versus $1/[\text{py}]$ were linear for all the reactions as shown in Figure 7. Values of k_2 and K obtained from such plots are also given in Table 2.

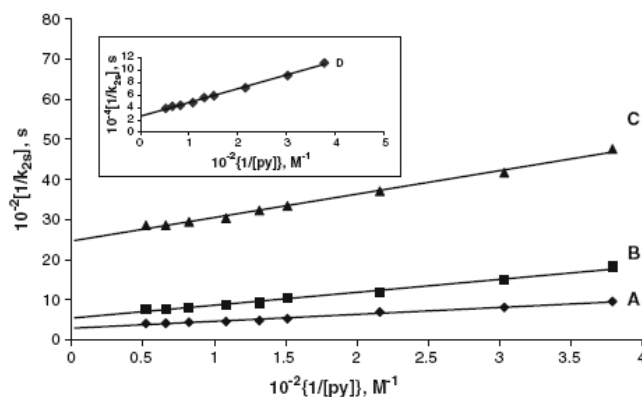


Fig. 7. Plots of $\frac{1}{k_2}$ versus $\frac{1}{[py]}$ for the data given in Table 2. Inset is the same plot for complex D since its scale was not in a similar range as the other three complexes.

The kinetics of the reduction process for each of the cobalt(II) complexes was studied at different temperatures between 293 and 318 K. The rate constants increased with increasing temperature (Table 3) and the data were subjected to Eyring plots (Figure 8). From these plots, activation parameters, ΔH^\ddagger (enthalpy of activation) and ΔS^\ddagger (entropy of activation), were calculated as recorded in Table 3. The activation enthalpy values are positive, and increase from complex A to complex D. This is in agreement with the corresponding decrease in the reactivities of the complexes from A to D. Conversely, the activation entropies are highly negative and comparable for the four complexes investigated (Table 3). This is a reflection of fairly unstable similar transition states involving the participation of the pyridine ligand in the transition states of all the reactions, as earlier proposed in the mechanism shown by Equation 6. This is indicative of similar reaction mechanism for the four reactions. The relatively large pre-equilibrium constants, K , obtained for the reactions are in agreement with such unstable transition states.

Steric hindrance is observed to play a major role in this investigation. The bulkier the arylisocyanide ligand (CNR) becomes, the slower the reaction. This is

true for both the substitution and reduction processes, with complex A (least hindered) being the most reactive and complex D (most hindered) being the least reactive. The order of reactivity is therefore $A > B > C > D$. Since there is no evidence of coordinated pyridine in the final *pentakis*(arylisocyanide)cobalt(I) product of each reaction, the reduction process most likely involves rapid pre-coordination of the dissociated isocyanide ligand to give the *pentakis*(arylisocyanide)cobalt(I) product.

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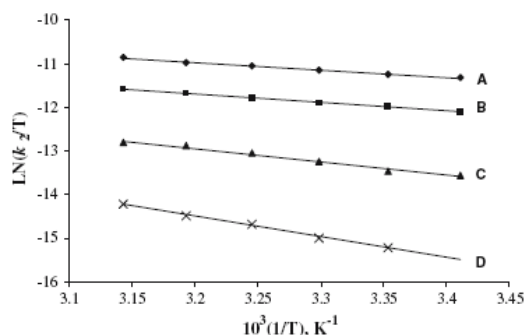


Fig. 8. Eyring plots for the reaction between the $[Co(CNR)_4(CIO_4)_2]$ complexes and pyridine in CF_3CH_2OH .

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