Transition Metal Chemistry (2006) 31:337–339
DOI 10.1007/s11243-005-6398-8

Protonation of chloro-, bromo- and iodo-pentacyanocobaltate(III) complexes

Jonathan F. Ojo, Jide Ige, Grace O. Ogunlusi*, Olanrewaju Owoyomi and Esan S. Olaseni
Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria

Received 19 October 2005; accepted 8 December 2005

Abstract

The reactions between $Fe(Phen)_3^{2+}$[phen = tris-(1,10) phenanthroline] and $Co(CN)_5X^{3-}$ (X = Cl, Br or I) have been studied in aqueous acidic solutions at 25 °C and ionic strength in the range $I = 0.001–0.02$ mol dm^{-3} (NaCl/HCl). Plots of k_2 *versus* $\sqrt{I}$, applying Debye–Huckel Theory, gave the values -1.79 ± 0.18, -1.65 ± 0.18 and 1.81 ± 0.10 as the product of charges (Z_AZ_B) for the reactions of $Fe(Phen)_3^{2+}$ with the chloro-, bromo- and iodo- complexes respectively. Z_AZ_B of ≈ -2 suggests that the charge on these Co^{III} complexes cannot be −3 but is −1. This suggests the possibility of protonation of these Co^{III} complexes. Protonation was investigated over the range $[H^+] = 0.0001$ −0.06 mol dm^{-3} and the protonation constants K_a obtained are 1.22×10^3, 7.31×10^3 and 9.90×10^2 dm^6 mol^{-3} for X = Cl, Br and I, respectively.

Introduction

The reactions of the halo-pentaaminecobalt(III) complexes $[Co(NH_3)X^{2+}]$ (X = Cl, Br or I) with various metal complexes such as ruthenium(II), vanadium(II) and titanium(III) and their mechanistic diagnosis have been reported in the literature[1–5]. In contrast to these pantaamine complexes, the pentacyano analogues $Co(CN)_5X^{3-}$ (X = Cl, Br or I) have yet to be exhaustively studied. After the report of Davies and Espenson on the reduction of these complexes by V^{II} [6], a few workers have studied the reduction of these halo-pentacyano complexes by Ru^{II} (O.T. Ayinde, unpublished work) and Ti^{III} [7] in this laboratory. From all these previous works, the mechanism of the reduction of these complexes by various metal ions has been diagnosed. However, there is no report of the protonation of $Co(CN)_5X^{3-}$ (X = Cl, Br or I) in the acidic solutions. We therefore report our observation of their protonation in acidic medium for the first time.

Experimental

Materials

$K_3[Co(CN)_5N_3]$ which is the starting material for the preparation of $Co(CN)_5X^{3-}$, was synthesised as described in the literature [12, 13]. The purity of the complex was ascertained by its u.v.–visible spectra (λ_{max} 380 nm, $\varepsilon = 600$ dm^3 mol^{-1} cm^{-1}) and IR bands (1290 cm^{-1}, 1596 cm^{-1}, and 2103 cm^{-1}). $Co(CN)_5X^{3-}$ was prepared using the method of Flor and Casabó [13] which involves the treatment of $Co(CN)_5$ N_3^{3-} with KNO_2 in the presence of the coordinating anion X^-. Each complex was purified by dissolving in water and recrystallising from cold EtOH. The complexes were characterized as follows:

$K_3[Co(CN)_5Cl] = \lambda_{max}$ 393 nm, ε= 160 M^{-1} cm^{-1},
IR band – 2111 cm^{-1}
$K_3[Co(CN)_5Br] = \lambda_{max}$ 398 nm, ε= 190 M^{-1} cm^{-1},
IR band – 2114 cm^{-1}
$K_3[Co(CN)_5I] = \lambda_{max}$ 440 nm, ε= 200 M^{-1} cm^{-1},
IR band – 2122 cm^{-1}

$Fe(Phen)_3^{2+}$ was synthesised in the form $Fe(Phen)_3$ $(ClO_4)_2$ and characterized by its visible spectrum ε= 1.09×10^4 m^{-1} cm^{-1}, λ_{max} 510 nm [14]. These values are in agreement with the literature [15]. NaCl (Analar grade) and HCl (May and Baker grade 36%, density 1.18 g cm^{-3}) were used to prepare standardized solutions for maintaining ionic strength.

Kinetics

The reactions between $Co(CN)_5X^{3-}$ (X = Cl, Br or I) and $Fe(Phen)_3^{2+}$ were carried out by the conventional technique using the Unicam Heλios α-u.v./vis. spectrophotometer. First-order rate constants were determined by monitoring decreasing absorbance at the λ_{max} of the $[Fe(Phen)_3^{2+}]$ species ($\lambda_{max} = 510$ nm, ε= 1.09×10^4 m^{-1} cm^{-1}). The oxidant ($Co(CN)_5X^{3-}$) concentration was always in sufficient excess (at least 10-fold) over the reductant concentration to ensure pseudo-first-order condition. The cell compartment of the spectrophotometer was thermostated to the desired temperature within ±0.1 °C. Cell of 1 cm path length was employed in all the studies.

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* Author for correspondence: E-mail: roogunlusi2003@yahoo.co.uk

Results and discussion

Results

Pseudo-first-order plots were obtained for more than three half-lives in all cases. The effect of ionic strength on the rate of reactions over the range I = 0.001 –0.02 mol m^{-3} (NaCl/HCl) (Table 1) gave linear plots of k_2 *versus* $\sqrt{I}$ (Figure 1) with slope of −1.79, −1.65 and −1.81 for X = Cl, Br and I.

Since our Z_AZ_B was ≈ -2 and not −6 as expected, spectral evidence was sought for the protonation of these series of Co^{III} complexes by measuring their peak absorbance at various acid concentrations in the range [H$^+$] = 0.0001–0.06 mol dm^{-3} at fixed ionic strength (0.1 mol dm^{-3}). The observed molar extinction coefficients at various acid concentrations are plotted in Figure 2. If the protonation equilibrium is represented by the equation

$$\mathrm{ML}^{n-} + 2\mathrm{H}^+ \overset{K_a}{\rightleftharpoons} (\mathrm{HL})_2\mathrm{ML}_3^{-(n-2)} \tag{1}$$

where ML^{n-} = Co(CN)$_5$X^{3-} (X = Cl, Br, I).

Protonation constant K_a is given as

$$K_a = \frac{\left[(\mathrm{HL})_2\mathrm{ML}_3^{-(n-2)}\right]}{[\mathrm{ML}^{n-}][\mathrm{H}^+]^2} \tag{2}$$

The proposed rate law for the reaction is thus:

$$\mathrm{Co(CN)_5X^{3-}} + 2\mathrm{H}^+ \overset{K_a}{\rightleftharpoons} [(\mathrm{CNH})_2\mathrm{Co(CN)_3X}]^{-1} \quad \text{(fast)} \tag{3}$$

$$[(\mathrm{CNH})_2\mathrm{Co(CN)_3X}]^{-1} + \mathrm{Fe(phen)}_3^{2+} \overset{K_{ip}}{\rightleftharpoons} 1\mathrm{P} \tag{4}$$

$$1\mathrm{P} \overset{K_i}{\rightleftharpoons} \mathrm{Product} \tag{5}$$

$$\mathrm{Rate} = k_i[\mathrm{IP}]$$

$$k_{obs} = \frac{k_iK[\mathrm{Co(CN)_5X^{3-}}][\mathrm{H}^+]^2}{1 + K[\mathrm{Co(CN)_5X^{3-}}][\mathrm{H}^+]^2} \tag{6}$$

where,

$$K = K_{ip}K_a \tag{7}$$

Table 1. Ionic strength dependence of the second-order rate constants for the reactions between Fe(Phen)$_3^{2+}$ and Co(CN)$_5$X^{3-} at 25 °C; [H$^+$] = 5.0×10^{-4} mol dm^{-3}, Fe(Phen)$_3^{2+}$ = 1.01×10^{-5} mol dm^{-3}, [Co(CN)$_5$Cl^{3-}] = 3.004×10^{-4} mol dm^{-3}, [Co(CN)$_5$Br^{3-}] = 3.022× 10^{-4} mol dm^{-3}, [Co(CN)$_5$I^{3-}] = 3.017×10^{-4} mol dm^{-3}

I (mol dm^{-3})	k$_2$ (dm^{-3} mol^{-1} s^{-1})		
	Co(CN)$_5$Cl^{3-}	Co(CN)$_5$Br^{3-}	Co(CN)$_5$I^{3-}
0.02	0.782	0.755	0.663
0.01	0.971	0.924	0.765
0.008	1.015	0.991	0.785
0.005	1.107	1.034	0.980
0.003	1.165	1.054	0.917
0.002	1.194	1.125	0.994
0.001	1.223	1.163	1.034

k_2 (Second-order rate constants) are averages of two to three runs.

Plot of $\frac{1}{k_{obs}}$ against $\frac{1}{\left[\mathrm{Co(CN)_5X^{3-}}\right]}$ at fixed [H$^+$] should be linear with slope $\frac{1}{k_iK\left[\mathrm{H}^+\right]}$, intercept $\frac{1}{k_i}$ and K_a evaluated from

$$K_a = \frac{a_{pr}}{a_0 \times a^2}$$

and

$$a_{pr} = a_0 - \frac{A}{\varepsilon}$$

(where a, a_0, and a_{pr} are the concentrations of the acid, unprotonated complex and protonated complex respectively, A = final absorbance of the unprotonated complex and ε = molar absorptivity of the unprotonated complex.)

Discussion

According to Debye--Huckel, [8] the influence of ionic strength on the medium of reaction for aqueous medium at 25 °C is given as

$$\log k_{obs} = \log k_0 + 1.02Z_AZ_B\sqrt{I}$$

(where k_0 = rate constant at infinite dilution).

Z_AZ_B which is the product of the charges is the slopes of the linear graph of log k_2 *versus* $\sqrt{I}$ and is expected to be −6 for these systems. The results of the ionic strength dependence show clearly that the reacting species are not Fe(Phen)$_3^{2+}$ and Co(CN)$_5$X^{3-}. The observed slopes of −1.79 ± 0.18, −1.65 ± 0.18 and −1.81 ± 0.10 obtained for the chloro, bromo and iodo complexes respectively, which deviate significantly from −6, suggest that the reacting species are the doubly protonated oxidants in which two of the cyano ligands are protonated to form two HCN ligands in each oxidant. Protonated cyano ligands had been reported by Ojo *et al.* [9] to co-ordinate with ruthenium(II) in aqueous acidic solutions. Protonation of some other transition metal complexes have been reported in the literature for some Ru^{III} complexes by Ige *et al.* [10] and Taube and co-authors [11] had

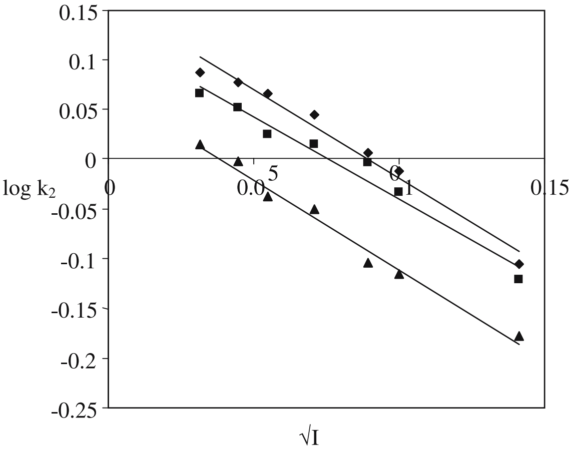

Fig. 1. Ionic strength dependence plots for Fe(Phen)$_3^{2+}$/Co(CN)$_5$X^{3-} at 25 °C, [H$^+$] = 5.0×10^{-4} mol dm^{-3}, I = 0.02–0.001 mol dm^{-3}. Legends ◆ (x = Cl), ■ (x = Br), ▲ (x = I).

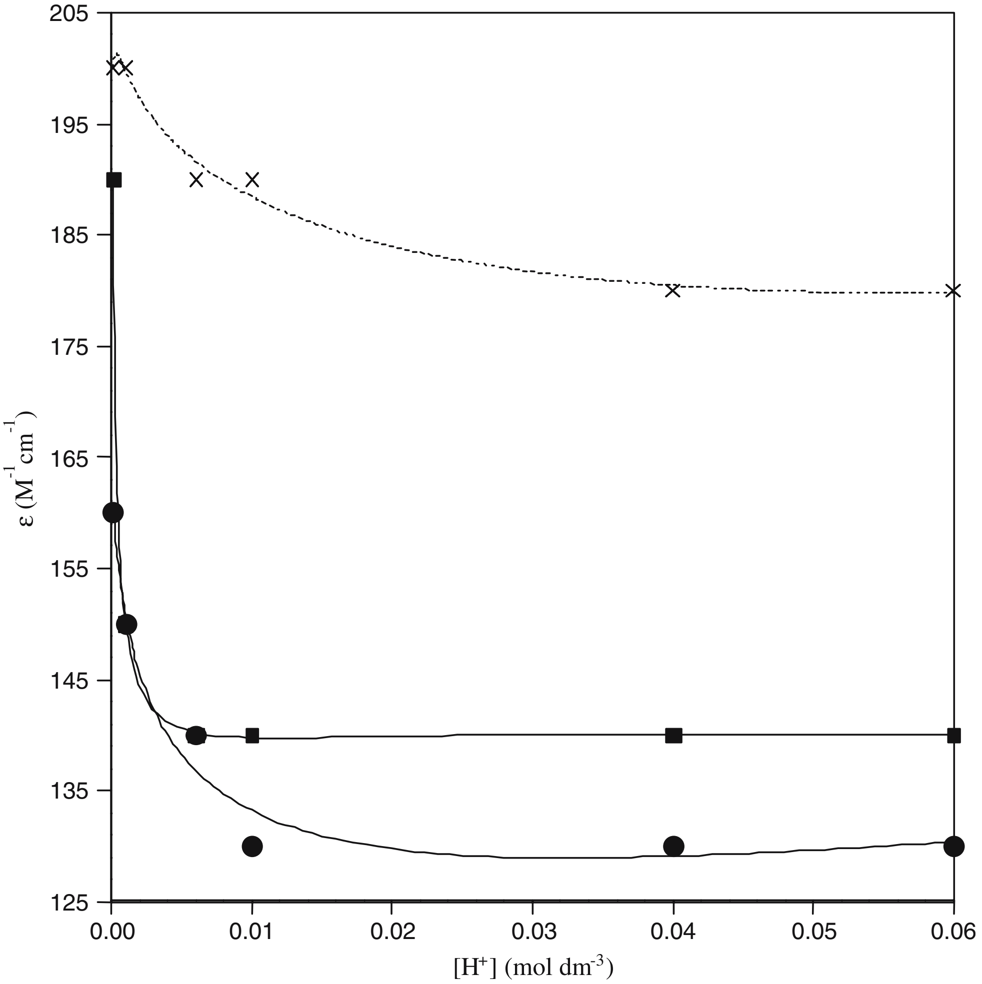

Fig. 2. Plots of ε of $Co(CN)_5Cl^{3-}$ at λ_{max} 393 nm, $Co(CN)_5\ Br^{3-}$ at λ_{max} 398 nm and $Co(CN)_5I^{3-}$ at λ_{max} 440 nm *versus* $[H^+]$; $[Co(CN)_5X^{3-}] = 1.00\times10^{-4}$ mol dm^{-3}, $[H^+] = 0.0001–0.06$ mol dm^{-3}, $I = 0.01$ mol dm^{-3}, $T = 25$ °C. Legends ● (x = Cl), ■ (x = Br), × (x = I).

provided spectral evidence for the protonation of (acetate)pentaaminecobaltate(III) in its reduction by Cr^{2+}, but none has been reported for these Co^{III} complexes by previous workers. Z_AZ_B, which is approximately −2, obtained in this work suggests that the doubly protonated cobalt(III) complexes are more reactive in these cases than the unprotonated species. Evidence was sought for the protonation of these complexes using the method of Ige *et al.* [10] and the protonation constants K_a obtained for the chloro, bromo and iodo complexes are 1.22×10^3, 7.31×10^3 and 9.90×10^2, respectively within the acid range 0.0001–0.06 mol dm^{-3}. Because the protonation constants are large, coloumbic forces of attraction between $2H^+$ and $Co(CN)_5X^{3-}$ are expectedly large in this case and this also shows that the protonation of these complexes is very fast. The protonated species are expectedly more reactive kinetically than the unprotonated species as a result of the distorted octahedral structure of the protonated cyano ligands. This is confirmed by experimental data which shows that the rate more than doubles in the presence of 0.001 mol dm^{-3} $[H^+]$ at all the ionic strengths investigated.

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