

NON-BRIDGING LIGAND EFFECTS ON THE KINETICS OF REDUCTION OF CHLORO- AND AZIDO-PENTAAMMINECOBALT(III) BY SOME POLYPYRIDYL COMPLEXES OF RUTHENIUM(II)

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ABSTRACT. Pentaamminecobalt(III) complexes, $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ ($\text{X} = \text{Cl}^-, \text{N}_3^-$), are reduced by $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ in aqueous media at a constant ionic strength of 0.5 M (HCl/LiCl). At 308 K, the second order rate constants ($\text{M}^{-1} \text{s}^{-1}$) are as follows: 17.9 for the reduction of the azidocobalt(III) complex by $[\text{Ru}(\text{bipy})_3]^{2+}$, and 1.41 and 2.63 for the $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ reduction of the azido- and chlorocobalt(III) complexes, respectively. Activation enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) were determined from temperature dependence measurements with the following results: $\Delta H^\ddagger = 72.1 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 13.3 \text{ J mol}^{-1} \text{ K}^{-1}$ for the $[\text{Ru}(\text{bipy})_3]^{2+}$ reduction of the azidocobalt(III) complex, while for the reduction of the cobalt(III) complexes by $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$, $\Delta H^\ddagger(\text{N}_3^-) = 20.3 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger(\text{Cl}^-) = 40.6 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger(\text{N}_3^-) = -177 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\Delta S^\ddagger(\text{Cl}^-) = -106 \text{ J mol}^{-1} \text{ K}^{-1}$. The relative rates of electron transfer in the different reactions and the influence of π -acceptor ligands on the ruthenium(II) reduction of the cobalt(III) complexes are discussed.

KEY WORDS: Non-bridging ligands, Pentaamminecobalt(III) complexes, Azidocobalt(III) complex, Chlorocobalt(III) complex, Kinetics of reduction of cobalt(III) complexes, Ruthenium(II) polypyridyl complexes,

INTRODUCTION

A great amount of work has been done on the substitution and redox properties of ruthenium(II and III) complexes [1-3]. This is partly connected with the discovery that some of these complexes, e.g. $\text{cis-}[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $\alpha\text{-}[\text{Ru}(\text{azpy})_2\text{Cl}_2]$, $\text{mer-Ru}(\text{terpy})\text{Cl}_3$ and $[\text{Ru}(\text{phen})_3]^{2+}$ have antitumour activity [4, 5]. This property among others has led to increased interest in the study of their chemical characteristics. Ruthenium(II) cations like $[\text{Ru}(\text{NH}_3)_6]^{2+}$, $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$ and $[\text{Ru}(\text{en})_3]^{2+}$ have been classified as typical outer-sphere reductants [1, 6, 7], basically as a result of their substitution inertness and redox potentials, while $[\text{Ru}(\text{tpmm})(\text{dpp})\text{H}_2\text{O}]^{2+}$, $[\text{Ru}(\text{tpmm})(\text{DPMet})\text{H}_2\text{O}]^{2+}$ and $[\text{Ru}(\text{tpmm})(\text{DPPro})\text{H}_2\text{O}]^{2+}$ are known to be labile as a result of introducing different spectator ligands [8]. Bridging ligands and non-bridging ligands can play significant roles in the reactivities of the complexes. As the reactivity is affected, it is expected that their antitumour activity will also be affected by the nature of the ligands surrounding the metal ion. Most cobalt(III) complexes are low-spin and inert and so most reactions between cobalt(III) and ruthenium(II) complexes proceed rather slowly. However, the identities of ruthenium(II) reductants significantly affect the rates of reduction of cobalt(III) complexes [3]. This work investigates the effect of non-bridging ligands on the redox properties of ruthenium(II) and looks at the reactivity patterns of their pentamminecobalt(III) oxidants.

EXPERIMENTAL

Materials. $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]\text{Cl}$ was prepared according to the method described by Meyer and co-workers [9], which involved initial synthesis of $[\text{Ru}(\text{terpy})\text{Cl}_3]$. This complex was then reduced to $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]\text{Cl}$ by reaction with bipyridine in the presence of triethylamine. Electronic and infrared spectra gave peaks which agreed with literature values [9, 10].

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[Ru(bipy)₃]Cl₂ was obtained from Aldrich Chemicals and used without further purification. [Co(NH₃)₅Cl]Cl₂ and [Co(NH₃)₅N₃]Cl₂ were prepared and characterised following established procedures [1].

Kinetics. All reactions were followed with a Shimadzu UV-2501 PC UV/vis spectrophotometer equipped with a TCC peltier temperature controller for the cell compartment. The ionic strength was kept at 0.5 M with HCl/LiCl. Absorbance changes were monitored at 454 and 477 nm for reactions involving [Ru(bipy)₃]²⁺ and [Ru(terpy)(bipy)Cl]⁺, respectively. Each reaction was studied under pseudo first-order conditions with the concentrations of the Co(III) complexes in large excess. The pseudo first-order rate constants, *k_s*, were obtained from linear regression plots of ln(*A_t* - *A_∞*) against time, *t*.

RESULTS AND DISCUSSION

The reactions between the ruthenium(II) complexes and excess Co(III) concentrations follow first order kinetics in the reductants. The pseudo first-order rate constants, *k_s*, for the reactions were found to increase with increasing concentrations of the oxidants at constant temperature (Tables 1-3). Plots of *k_s* against the concentration of the oxidant were linear for each reaction (Figure 1), indicating that each reaction is also first order with respect to the Co(III) oxidant and second order overall. The second-order rate constants obtained from slopes of such plots for the different reactions at different temperatures are also shown in Tables 1 to 3. This observation is consistent with the rate law:

$$-\frac{d[\text{Ru(II)}]}{dt} = k_s[\text{Ru(II)}] = k_2[\text{Co(III)}][\text{Ru(II)}] \quad (1)$$

$$\text{where } k_s = k_2[\text{Co(III)}] \quad (2)$$

The reactions can generally be represented by the following equations:

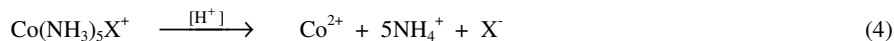
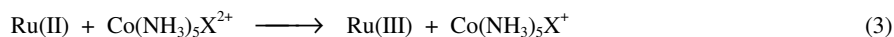


Table 1. Rate constants for the reduction of [Co(NH₃)₅N₃]²⁺ by [Ru(bpy)₃]²⁺ at different temperatures, I = 0.5 M, [Ru(bpy)₃]²⁺ = 2.0 × 10⁻⁵ M.

T, K	10 ⁴ [Co(III), M]	10 ⁴ <i>k_s</i> , s ⁻¹	<i>k₂</i> , M ⁻¹ s ⁻¹	T, K	10 ⁴ [Co(III), M]	10 ⁴ <i>k_s</i> , s ⁻¹	<i>k₂</i> , M ⁻¹ s ⁻¹
303	2.0	2.33	12.22 ± 0.09	318	2.0	9.46	47.54 ± 0.05
	3.2	3.85			3.2	15.2	
	4.0	4.82			4.0	19.1	
	4.8	5.66			4.8	22.8	
	6.0	7.41			6.0	28.5	
308	2.0	3.61	17.88 ± 0.17	323	2.0	14.9	74.51 ± 0.03
	3.2	5.71			3.2	23.8	
	4.0	6.89			4.0	29.8	
	4.8	8.57			4.8	35.8	
	6.0	10.9			6.0	44.7	
313	2.0	6.42	32.05 ± 0.03	328	2.0	22.6	113.3 ± 0.3
	3.2	10.3			3.2	36.1	
	4.0	12.8			4.0	45.3	
	4.8	15.4			4.8	54.9	
	6.0	19.2			6.0	67.7	

Table 2. Rate constants for the reduction of $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ by $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^{2+}$ at different temperatures, $I = 0.5 \text{ M}$.

T, K	$10^4 [\text{Co(III)}, \text{M}]$	$10^4 k_s, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$	T, K	$10^4 [\text{Co(III)}, \text{M}]$	$10^4 k_s, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$
298	2.0	2.03	1.03 ± 0.02	313	2.0	2.98	1.57 ± 0.01
	3.2	3.01			3.2	5.05	
	4.0	4.06			4.0	6.31	
	4.8	5.17			4.8	7.45	
	6.0	6.30			6.0	9.52	
303	2.0	2.21	1.14 ± 0.01	318	2.0	3.31	1.78 ± 0.02
	3.2	3.72			3.2	5.52	
	4.0	4.60			4.0	6.96	
	4.8	5.53			4.8	8.62	
	6.0	6.81			6.0	10.8	
308	2.0	2.61	1.41 ± 0.02	323	2.0	4.08	2.09 ± 0.01
	3.2	4.60			3.2	6.81	
	4.0	5.46			4.0	8.39	
	4.8	6.81			4.8	10.1	
	6.0	8.52			6.0	12.4	

Table 3. Rate constants for the reduction of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^{2+}$ at different temperatures, $I = 0.5 \text{ M}$.

T, K	$10^4 [\text{Co(III)}, \text{M}]$	$10^4 k_s, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$	T, K	$10^4 [\text{Co(III)}, \text{M}]$	$10^4 k_s, \text{s}^{-1}$	$k_2, \text{M}^{-1}\text{s}^{-1}$
298	2.0	2.90	1.40 ± 0.03	313	2.0	7.10	3.24 ± 0.09
	3.2	4.32			3.2	10.9	
	4.0	5.68			4.0	14.0	
	4.8	7.10			4.8	15.3	
	6.0	8.10			6.0	18.5	
303	2.0	3.50	1.74 ± 0.04	318	2.0	8.64	4.07 ± 0.05
	3.2	6.01			3.2	12.1	
	4.0	6.82			4.0	15.9	
	4.8	8.40			4.8	19.5	
	6.0	9.92			6.0	24.9	
308	2.0	5.30	2.63 ± 0.06	323	2.0	10.5	5.33 ± 0.04
	3.2	8.61			3.2	16.5	
	4.0	11.0			4.0	21.4	
	4.8	12.7			4.8	25.6	
	6.0	15.4			6.0	32.2	

$[\text{Ru}(\text{terpy})(\text{bpy})\text{H}_2\text{O}]^{2+}$ undergoes substitution at 298 K with rate constants, k_{sub} , of $(0.75 \text{ to } 15.0) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ [11]. We do not expect any significant difference in k_{sub} for $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+$. In the present study, the chloro- and azido-pentaamminecobalt(III) complexes are reduced by $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+$ under similar conditions with electron transfer rate constants, k_{et} , ($\text{M}^{-1} \text{ s}^{-1}$) of 1.40 and 1.03, respectively. These rate constants are about 4 orders of magnitude higher than the expected substitution rate constant for the same reductant. The fact that k_{et} is much greater than k_{sub} indicates outer sphere electron transfer between the ruthenium(II) reductants and cobalt(III) oxidants.

In the reactivity pattern of the pentaamminecobalt(III) complexes, the order of reactivity for outer sphere reactions is: $k(\text{Cl}^-) < k(\text{N}_3^-) < k(\text{SCN}^-)$ and for inner sphere, $k(\text{Cl}^-) \approx k(\text{N}_3^-) \approx k(\text{SCN}^-)$ [12, 13]. For the $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+$ complex, $k(\text{N}_3^-)$ is slightly less than $k(\text{Cl}^-)$ which

may suggest an inner sphere mechanism, but other mechanistic criteria favour an outer sphere electron transfer mechanism.

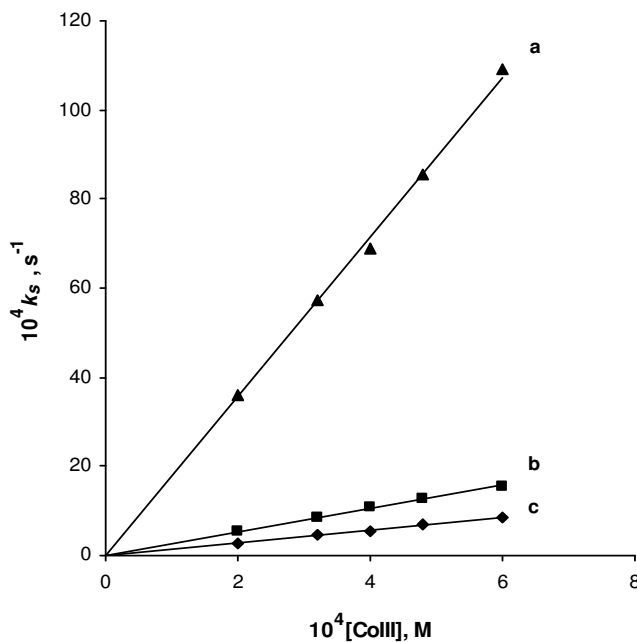


Figure 1. Plot of k_s against Co(III) concentration for the reduction of (a) $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ by $\text{Ru}(\text{bipy})_3^{2+}$, (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by $\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}^+$ and (c) $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ by $\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}^+$, all at 308 K.

In previous studies [1, 6, 14], it has been suggested that the two cobalt(III) complexes are reduced by $[\text{Ru}(\text{NH}_3)_6]^{2+}$, $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$, and $[\text{Ru}(\text{bipy})(\text{bquin})\text{Cl}_2]$ via an outer sphere mechanism. The presence of the H_2O and Cl^- ligands on the ruthenium(II) reductants did not change the mechanism of electron transfer even though these ligands are expected to make the complexes more labile. Our proposed outer sphere reduction by $[\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+$ falls in line with what was observed in these earlier studies. When this complex is compared with other ones, the order of reactivity is $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+} < [\text{Ru}(\text{terpy})(\text{bpy})\text{Cl}]^+ < [\text{Ru}(\text{bipy})(\text{bquin})\text{Cl}_2]$ for reductions of both cobalt(III) complexes. Although Cl^- as a potential bridging ligand increases the reactivity of the ruthenium(II) complexes, the magnitude of the increase seems to be reduced by the steric effects of the non-bridging π -acceptor ligands. Similar effects have been observed in the substitution reactions of ruthenium(II) complexes, where the nature of the non-bridging ligands alters the substitution rate constants by up to five orders of magnitude (Table 4). It becomes obvious that the effect of the non-bridging ligands on the ruthenium(II) complexes is very small on the electron transfer rate constants as compared to the substitution rate constants. If the mechanisms of electron transfer were substitution controlled as observed in many inner sphere reactions [15, 16], then a more significant difference would be expected in the rate constants as the π -acceptor spectator ligands are introduced into the coordination sphere of the ruthenium(II) reductants.

$[\text{Ru}(\text{bipy})_3]^{2+}$ has been shown in earlier studies [17, 18] to be excited to the triplet state ${}^3\text{CT}[\text{Ru}(\text{bipy})_3]^{2+}$ and then quenched to the ground state before oxidation to $[\text{Ru}(\text{bipy})_3]^{3+}$. The process of excitation and quenching was observed to be very rapid. For example, at 293 K ${}^3\text{CT}[\text{Ru}(\text{bipy})_3]^{2+}$ is quenched by Fe^{3+} , Tl^{3+} , Fe^{2+} , and some Co(III) complexes with quenching rate constants that vary from 10^7 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$. In this study, $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ reacts at the same temperature with $[\text{Ru}(\text{bipy})_3]^{2+}$ with a rate constant of $4.31 \text{ M}^{-1} \text{ s}^{-1}$. This obviously cannot be a quenching rate constant.

Table 4. Substitution and electron-transfer rate constants for reactions of some ruthenium(II) complexes at 298 K.

Complex	k_{sub} $\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{et}} (\text{M}^{-1} \text{ s}^{-1})$ for reduction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$		Reference
		X = Cl	X = N_3	
$[\text{Ru}(\text{NH}_3)_6]^{2+}$	-	260	1.82	1, 7
$[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]^{2+}$	0.02 – 0.36	0.18	0.61	6, 19, 20
$[\text{Ru}(\text{terpy})(\text{bipy})\text{H}_2\text{O}]^{2+}$	$(0.75 - 15.0) \times 10^{-4}$	-	-	11
$[\text{Ru}(\text{bipy})(\text{bquin})\text{Cl}_2]$	-	8.89	1.79	14
$[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$	-	1.40	1.03	This work
$[\text{Ru}(\text{bipy})_3]^{2+}$	-	-	7.22	This work

The second order rate constants for all the reactions increased as temperature was increased. From Tables 1-3, Eyring plots were drawn (Figure 2) and activation parameters ΔH^\ddagger and ΔS^\ddagger were respectively obtained from the slopes and intercepts of the plots. These ΔH^\ddagger and ΔS^\ddagger values are compared with values obtained for some typical outer-sphere reactions shown in Table 5. From this table, a plot of ΔH^\ddagger against ΔS^\ddagger values was found to be linear as shown in Figure 3. The three points (j, k and l) representing this study all fall within this linear plot. This further supports outer-sphere mechanism for the reduction of the cobalt(III) complexes by the ruthenium(II) reductants. The positive ΔH^\ddagger and negative ΔS^\ddagger values obtained for reductions by $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ are similar to earlier reports (Table 3) and also in agreement with what is expected for reactions involving ions of similar charges [27]. The positive ΔS^\ddagger obtained in the reduction of the azidocobalt(III) complex by $[\text{Ru}(\text{bipy})_3]^{2+}$ as compared to the other two reactions involving $[\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}]^+$ as a reductant, may be associated with the fact that the overall activation entropy obtained is a composite parameter which reflect both outer-sphere precursor association and electron transfer within the assembly [27] according to equation 5.

$$\Delta S^\ddagger = \Delta S_{\text{os}}^\circ + \Delta S_{\text{et}}^\ddagger \quad (5)$$

Contributions to ΔS^\ddagger by $\Delta S_{\text{os}}^\circ$ and $\Delta S_{\text{et}}^\ddagger$ can vary from one reaction to another thereby affecting ΔS^\ddagger . Similar observations have been reported in some earlier outer-sphere reactions [22, 28].

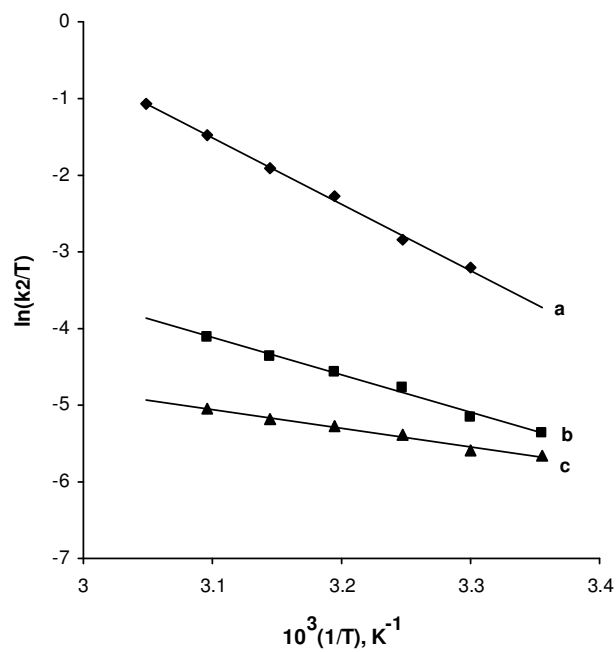


Figure 2. Eyring plots for the reduction of (a) $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ by $\text{Ru}(\text{bipy})_3^{2+}$, (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ by $\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}^+$ and (c) $[\text{Co}(\text{NH}_3)_5\text{N}_3]^{2+}$ by $\text{Ru}(\text{terpy})(\text{bipy})\text{Cl}^+$.

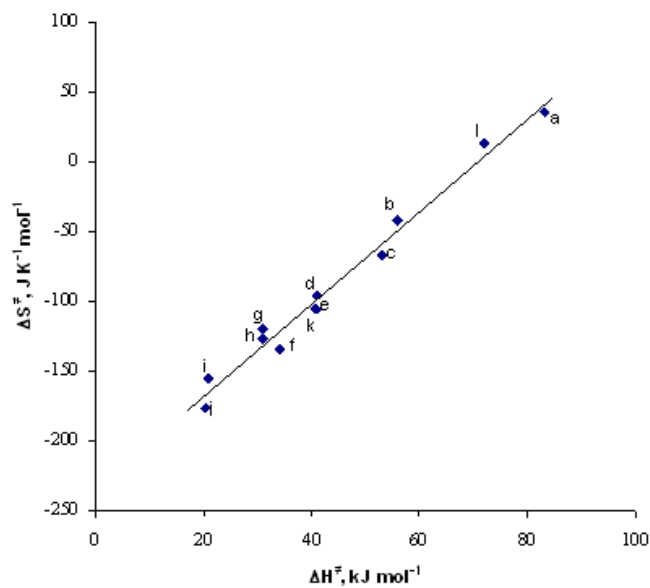


Figure 3. Plot of ΔS^\ddagger against ΔH^\ddagger for some typical outer-sphere reactions. Reactions represented by 'a' to 'l' are indicated in Table 5.

Table 5. Enthalpies and entropies of activation for some outer-sphere redox reactions.

Letter as in Figure 3	Reactants	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	Ref.
a	[W ₂ O ₂ (μ-S) ₂ (μ-edta)] ²⁻ , Fe(phen) ₃ ²⁺	83	36	21
b	[Mo ₂ O ₂ (μ-O) ₂ (μ-edta)] ²⁻ , IrCl ₆ ²⁻	56	-42	22
c	Co ^{III} -Os ^{II} with oligopropyl bridging ligand	53	-67	23
d	[Co(sep)] ^{3+/2+} self-exchange	41	-95	24
e	[Pt(NH ₃) ₅ Cl] ³⁺ , [V(H ₂ O) ₆] ²⁺	41	-105	25
f	[Co(NH ₃) ₅ H ₂ O] ³⁺ , [V(H ₂ O) ₆] ²⁺	34	-134	26
g	[Co(NH ₃) ₅ Cl] ²⁺ , [V(H ₂ O) ₆] ²⁺	31	-121	26
h	[Co(bipy) ₃] ^{3+/2+} self-exchange	31	-127	24
i	[Co(phen) ₃] ^{3+/2+} self-exchange	21	-156	24
j	[Ru(terpy)(bipy)Cl] ²⁺ , [Co(NH ₃) ₅ N ₃] ²⁺	20.3	-177	This work
k	[Ru(terpy)(bipy)Cl] ²⁺ , [Co(NH ₃) ₅ Cl] ²⁺	40.6	-106	This work
l	[Ru(bipy) ₃] ²⁺ , [Co(NH ₃) ₅ N ₃] ²⁺	72.1	13.3	This work

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REFERENCES

- Adegite, A.; Dosunmu, M.; Ojo, J.F. *J. Chem. Soc. Dalton Trans.* **1977**, 630.
- Endicott, J.F.; Taube, H. *Inorg. Chem.* **1965**, 4, 437.
- Tobe, M.L.; Burgess, J. *Inorganic Reaction Mechanisms*, Addison Wesley Longman: New York; **1999**; ch. 4 and 9.
- Hotze, A.C.G.; Broekhuizen, M.E.T.; Velders, A.H.; Kooijman, H.; Spek, A.L.; Haasnoot, J.G., Reedijk, J. *J. Chem. Soc. Dalton Trans.* **2002**, 2809.
- Sigel, H. *Metal Ions in Biological Systems, Metal Complexes as Anticancer Agents*, Dekker: New York; **1980**; pp. 241-2.
- Ige, J.; Nnadi, R.; Ojo, J.F.; Olubuyide, O. *J. Chem. Soc. Dalton Trans.* **1978**, 148.
- Endicott, J.F.; Taube, H. *J. Am. Chem. Soc.* **1964**, 86, 1686.
- Huynh, M.V.V.; Smyth, J.; Weltzler, M.; Mort, B.; Gong, P.K.; Witham, L.M.; Jameson, D.L.; Geiger, D.K.; Lasker, J.M.; Charepoo, M.; Gornikiewicz, M.; Cintron, J.M.; Imahori, G.; Sanchez, R.R.; Marschilok, A.C.; Krajkowski, L.M.; Churchill, D.G.; Churchill, M.R.; Takeuchi, T.K. *Angew. Chem.* **2001**, 113, 4601.
- Takeuchi, K.J.; Thompson, M.S.; Pipes, D.W.; Meyer, T.J. *Inorg. Chem.* **1984**, 23, 1845.
- Bessel, C.A.; Margarucci, J.A.; Acquaye, J.H.; Rubino, R.S.; Crandall, J.; Jircitano, A.J.; Takeuchi, K. *Inorg. Chem.* **1993**, 32, 5779.
- Jaganyi, D.; Hofmann, A.; van Eldik, R. *Angew. Chem. Int. Ed.* **2001**, 40, 1680.
- Przystas, T.J.; Sutin, N. *J. Am. Chem. Soc.* **1973**, 95, 5545.
- Adegite, A.; Iyun, J.F.; Ojo, J.F. *J. Chem. Soc. Dalton Trans.* **1977**, 115.
- Oyetunji, O.; Ngake, B.; Ramontsho, K. *Res. J. Chem. Environ.* **2004**, 8, 32.
- Akinyugba, N.; Ige, J.; Ojo, J.F.; Olubuyide, O.; Simoyi, R. *Inorg. Chem.* **1978**, 17, 218.
- Lappin, A.G. *Redox Mechanisms in Inorganic Chemistry*, Ellis Horwood: England; **1994**; ch. 3.
- Natarajan, P.; Endicott; J.F. *J. Phys. Chem.* **1973**, 77, 1823.

18. Natarajan, P.; Endicott, J.F. *J. Am. Chem. Soc.* **1972**, 94, 3635.
19. Ojo, J.F.; Olubuyide, O.; Oyetunji, O. *J. Chem. Soc. Dalton Trans.* **1987**, 957.
20. Daramola, G.; Ojo, J. F.; Olubuyide, O.; Oriafio, J. *J. Chem. Soc., Dalton Trans.* **1982**, 2137.
21. Oyetunji, O.; Ojo, J.F.; Saïdy, M. *J. Chem. Soc. Nig.* **1991**, 16, 1.
22. Wharton, R.K.; Ojo, J.F.; Sykes, A.G. *J. Chem. Soc. Dalton Trans.* **1975**, 1526.
23. Isied, S.S.; Vassilian, A.; Magnuson, R.H.; Schwarz, H.A. *J. Am. Chem. Soc.* **1985**, 107, 7432.
24. Tobe, M.L.; Burgess, J. *Inorganic Reaction Mechanisms*, Addison Wesley Longman: New York; **1999**; p. 449.
25. Bakac, A.; Hand, T.D.; Sykes, A.G. *Inorg. Chem.* **1975**, 14, 2540.
26. Tobe, M.L.; Burgess, J. *Inorganic Reaction Mechanisms*, Addison Wesley Longman: New York; **1999**; p. 459.
27. Lappin, A.G. *Redox Mechanisms in Inorganic Chemistry*, Ellis Horwood: England; **1994**; p 83.
28. Martin, M.J.; Endicott, J.F.; Ochrymowycz, L.A.; Rorabacher, D.B. *Inorg. Chem.* **1987**, 26, 3012.