

Investigation and characterization of hydrazine and phenylhydrazine complexes of ruthenium(III)1,2-diaminopropanetetraacetate: facile electrochemical and chemical reduction of hydrazines in relevance to nitrogenases

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Abstract

Interaction of hydrazines $N_2H_4X^+$ ($X = H/Ph$) with $[Ru(HL)(OH_2)]$ (**1**) ($L = 1,2$ -diaminopropanetetraacetate, PDTA) has been investigated by potentiometry, spectrophotometry and electrochemistry in aqueous solution at $25^\circ C$. The deprotonation and hydrolysis constants of **1** and its hydrazinium adducts formed in $0.1 M Na_2SO_4$ solution were determined by potentiometry, while the second order rate constant k_1 and k_2 for the formation of $[Ru(HL)(N_2H_4X)]^+$ and $[Ru(L)(N_2H_4X)]$ were determined kinetically by spectrophotometry. At pH 2.8, the complex **1** exhibited a quasi-reversible one-electron reduction step at ($E_{1/2}$) $-0.251 V$ vs. SCE and the hydrazinium adducts obtained in situ in the presence of excess (100 equiv) $N_2H_4X^+$ showed an additional multi-electron (two-electron per metal at a time) reduction step at ($E_{1/2}$) $-0.046/-0.158 V$ (vs. SCE) in the case of $X = H/Ph$, respectively in sampled-dc. The hydrazines, $N_2H_4X^+$ were reduced electrolytically by holding the potential at -0.150 and $-0.250 V$ (Hg-pool) vs. SCE, respectively, and chemically by using H_2 at atmospheric pressure, ascorbic acid, catechol, Zn-dust and $NaBH_4$ in the presence of these hydrazinium adducts. The turnover numbers, moles of ammonia formed per mole of metal per hour, have been calculated, discussed and compared with those of EDTA (ethylenediaminetetraacetate) analogue. The plausible reaction mechanism for the chemical and the electrochemical reduction of $N_2H_4X^+$ to ammonia and/or aniline and the implication of these results on the possible function of nitrogenases have also been proposed. The complex $[Ru(HL)(N_2H_5)]HSO_4$ and $[Ru(HL)(N_2H_4Ph)]Cl$ were synthesized and characterized. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium; 1,2-Diaminopropanetetraacetate; Hydrazine; Phenylhydrazine; Electrochemical; Chemical; Reduction; Ammonia; Aniline

1. Introduction

During the past century, chemists have sought economical methods for fixing atmospheric dinitrogen to use as it a raw material in fertil-

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izer, explosive and other chemical industries [1–12]. Despite the simplicity of the reactants, the development of energy-efficient and large-scale process for the fixation of molecular nitrogen still has been one of the challenging tasks. On the other hand, biological systems fix the dinitrogen exclusively to ammonia under ambient conditions [13–15]. Although many isolated systems have been found to be thermodynamically favorable for fixing dinitrogen [13], but none of them was found to be useful to produce ammonia with significant yields. As a consequence of high activation energy, the reduction reaction of dinitrogen requires a suitable catalyst to produce ammonia at a useful rate. In this direction, intensive research efforts are being carried out for the past four decades using cofactors, model compounds and various transition metal complexes to mimic this ideal reaction under ambient conditions as well as to make the system economically more viable [1–12,16–20]. Recently, a major breakthrough has been made in the field of crystallographic structures of both the protein components of nitrogenase and their metal centers which focus the investigations toward the mechanistic pathways and assembly of multicentered metalloenzyme [21]. Even then, the synthesis of exact analogs for the FeMo cofactor has not been accomplished. Nevertheless, the biological reaction has been hypothesized to proceed via metal bound diazene and hydrazine intermediates [14], the reactions of bound diazenes, hydrazines and its derivatives are of immense interest and also these studies are forefront for finding the detailed mechanistic features of the enzymatic system. Hence, many transition metals, cofactors and model compounds containing hydrazines were synthesized and characterized [22–27]. Meanwhile, attempts have also been made with the help of these isolated hydrazine complexes as catalysts to reduce hydrazine and its derivatives to ammonia and amine in aqueous and non-aqueous media or mixture of both [22–24]. Although, fairly good turnovers of ammonia have reportedly been obtained in non-aqueous

solvents, these reactions did not meet with much yield in aqueous solution due to concomitant evolution of hydrogen gas.

Recently, it has been reported that the EDTA (ethylenediaminetetraacetate) complexes of ruthenium(III) are the first example to activate and reduce the N–N bonds in hydrazines and azide to ammonia/amine catalytically in aqueous solutions without the evolution of H₂ gas [28–30]. The high turnover rates and coulombic efficiencies prompted us to study further into the reduction of these substrates with other aminiopolycarboxylic acid complexes, and to contribute towards the development of a simple water soluble homogeneous transition metal catalyst in the intriguing N–N bond reductions. Herein we report the results of the study on the interactions of N₂H₅⁺ and N₂H₄Ph⁺ with [Ru(HL)(OH₂)] (L = 1,2-diaminopropanetetraacetate, PDTA) (**1**) by potentiometry, spectrophotometry and voltammetry. The resultant complexes have been used as catalysts for the chemical and electrochemical reduction of N₂H₄X⁺ in acidic solution. The turnover number, moles of ammonia per mole of catalyst per hour has been calculated. Apart from this, the isolation of [Ru(HL)(N₂H₅)]HSO₄ and [Ru(HL)(N₂H₄Ph)]Cl complexes has been reported. The implications of these observations on the possible function of nitrogenases are discussed.

2. Experimental

2.1. Materials and methods

Hydrated ruthenium(III) chloride from Arora Matthey; 1,2-Diamminopropane-*N,N,N',N'*-tetraacetic acid (H₄L, H₄PDTA), sodium borohydride from Aldrich Chemicals; phenylhydrazinehydrochloride (N₂H₄XCl, X = Ph) from Allied Chemicals; hydrazine sulphate (N₂H₄XHSO₄, X = H), L-ascorbic acid (H₂Asc), catechol (H₂Cat), zinc dust from BDH chemicals were obtained. Zero grade argon and hydrogen gases obtained from IOLAR were used after purifica-

tion with vanadous sulphate and alkaline pyrogallate solutions. All the other reagents used were of AR grade. The complex $\text{K}[\text{Ru}(\text{HL})\text{Cl}] \cdot 2\text{H}_2\text{O}$ was prepared starting with $\text{K}_2[\text{RuCl}_5(\text{OH}_2)]$ and it was characterized subsequently by physicochemical techniques as described elsewhere [31,32]. The electrolyte solution having desired pH ($1-5 \pm 0.01$) was prepared by mixing 0.2 M CH_3COONa with 1:1 H_2SO_4 solution. The complex, $\text{K}[\text{Ru}(\text{HL})\text{Cl}] \cdot 2\text{H}_2\text{O}$ as studied by spectrophotometry readily undergo aquation in aqueous solution to give $[\text{Ru}(\text{HL})(\text{OH}_2)]$. Thus, $[\text{Ru}(\text{HL})(\text{OH}_2)]$ (**1**) was considered as the precursor in the present investigation.

2.2. Physical measurements

All potentiometric titrations were performed by Metrohm Swiss model 665 Dosimat coupled to E-649 magnetic stirrer, a combination of glass and reference electrode and 682 auto Titroprocessor. The electrode system was calibrated as usual below 3.5 and above 10.5 pH by using standard HCl and NaOH solutions [33]. In a typical experiment, a 50-ml solution of **1** (1 mM) in 0.1 M Na_2SO_4 titrated against NaOH under Ar at 25°C. Similar titrations were also carried out on **1** in the presence of 1 equiv of $\text{N}_2\text{H}_4\text{X}^+$ salt.

The electronic absorption spectra were recorded by Shimadzu UV-vis NIR scanning spectrophotometer UV 3101 PC. The kinetic measurements were conducted on Hi-Tech Stopped flow spectrophotometer coupled to an Apple data processor. The rate data were obtained by monitoring the characteristic absorption band at 365 nm for N_2H_5^+ and 540 nm for $\text{N}_2\text{H}_4\text{Ph}^+$ complexes. The experiments were performed under pseudo-first order conditions and the resultant data were analyzed with the help of data acquisition program for not less than two half life periods. The ionic strength was kept constant at 0.2 M with KCl and the reaction was thermostated to $25 \pm 0.1^\circ\text{C}$.

Electrochemical studies were performed by EG&G PAR 174A Polarographic Analyzer and PAR 175 Universal Programmer coupled with a high precision Houston X-Y recorder. A PAR 303 SMDE assembly consisting of a dropping mercury (DME, 3.85 mg s^{-1}) or a hanging mercury drop (HMDE 0.021 cm^2) as working, Pt-wire as auxiliary and a SCE as reference electrodes in a single compartment cell were used. PAR model 273A Potentiostat/Galvanostat equipped with 270/250 Electrochemical software and a 4DX2-66 Gateway 2000 PC outfitted to a three electrode cell assembly with glassy carbon (0.0314 cm^2) working, Ag/AgCl (0.222 V vs. NHE) in 3 M NaCl reference and Pt-wire separated from the analytical solution by vycor tip counter electrodes were used. All potential-current plots were recorded in the range +0.2 and -0.8 V . The effects of pH, [**1**] and $[\text{N}_2\text{H}_4\text{X}^+]$ on the faradaic current were studied by adapting the procedures reported earlier [28]. The criteria of diffusion controlled process and electrochemical reversibility at DME were followed according to the Meites techniques [34].

The controlled potential coulometry was conducted by using EG&G PAR models 173 Potentiostat/Galvanostat and 179 digital coulometer provided with a three-electrode cell assembly. The cell consisted of Hg-pool (4 cm convex diameter) in the main compartment along with a Pt-mesh counter separated by a glass frit, SCE reference electrodes and a glass disc agitator. The electrolysis were performed in a 25-ml buffer solution containing $5 \mu\text{mol}$ of **1** and 0.5 mmol of $\text{N}_2\text{H}_4\text{X}^+$ ($\text{X} = \text{H}$ and pH) at desired pH (1.9 or 2.8) by holding the potential at a predetermined value for at least 10 h under Ar at 25°C. The hydrazines (0.5 mmol) were also reduced chemically in 25 ml of deaerated buffer solution (pH, 1.9 and 2.8) containing $5 \mu\text{mol}$ of complex and by bubbling H_2 gas at 1 atmosphere ($5-10 \text{ ml min}^{-1}$) or by adding 0.5 mmol of H_2Asc , H_2Cat , Zn-dust or NaBH_4 as reducing agents. The product ammonia produced during the reaction was estimated at 1-h interval by

employing Orion EA-940 ion analyzer equipped with ammonia gas sensing membrane electrode [28]. Formation of aniline as the side product was spotted with vanadium solution [35].

2.3. Synthesis

2.3.1. $[Ru(HL)(N_2H_5)]HSO_4$

A solution of 0.514 g (1 mmol) of $K[Ru(HL)Cl] \cdot 2H_2O$ was dissolved in a minimum volume of deoxygenated distilled water. To this solution, 0.133 g (1.02 mmol) $N_2H_5HSO_4$ was added and the resulting mixture stirred under Ar for about 60 min at 35°C. The yellow solution was concentrated in a freeze-dryer and extracted with excess cold ethanol. The fine yellow powder was filtered, washed with 9:1 acetone–water mixture and dried under vacuum. Anal. Found: C, 24.65; H, 3.84; N, 10.41%. Calc. C, 24.72; H, 3.96; N, 10.48%. IR (KBr) ν : 3315 (m, N–H), 1732 (m, COOH) 1638 (sh, COO) 1485, 1447 (m, N–H defor) 1258 cm^{-1} (w, CO). UV λ_{max} (ϵ): No band at 360 nm. CV (V vs. SCE): E_{pc} , -0.256 V; E_{pa} , -0.198 V.

2.3.2. $[Ru(HL)(N_2H_4Ph)]Cl$

An aqueous solution of 0.514 g (1 mmol) of $K[Ru(HL)Cl] \cdot 2H_2O$ was treated with 0.149 g

(1.02 mmol) N_2H_4PhCl under Ar with constant stirring at 30°C until the initial pale yellow color changed to reddish yellow. The reddish yellow solution was made into gel, followed by precipitation with cold absolute ethanol. The precipitate was filtered, washed with 9:1 acetone–water mixture and dried under vacuum. Anal. Found: C, 37.24; H, 4.34; N, 10.16%. Calc. C, 37.19; H, 4.41; N, 10.20%. IR (KBr) ν : 3381 (m, N–H), 1743 (m, COOH) 1642 (sh, COO) 1475, 1447 (m, N–H defor) 1278 cm^{-1} (m, CO). UV λ_{max} (ϵ): 400 (1375 $M^{-1} cm^{-1}$) and 530 nm (1340 $M^{-1} cm^{-1}$). CV (V vs. SCE): E_{pc} , -0.180, -0.268 and -0.378 V; E_{pa} , -0.148, -0.202 V.

3. Results and discussion

3.1. Interaction of hydrazines with $[Ru(HL)(H_2O)]$

3.1.1. Potentiometry

The titration of **1** showed three buffer regions between $a = 0-1$, $1-2$, and $2-3$ (Fig. 1a) corre-

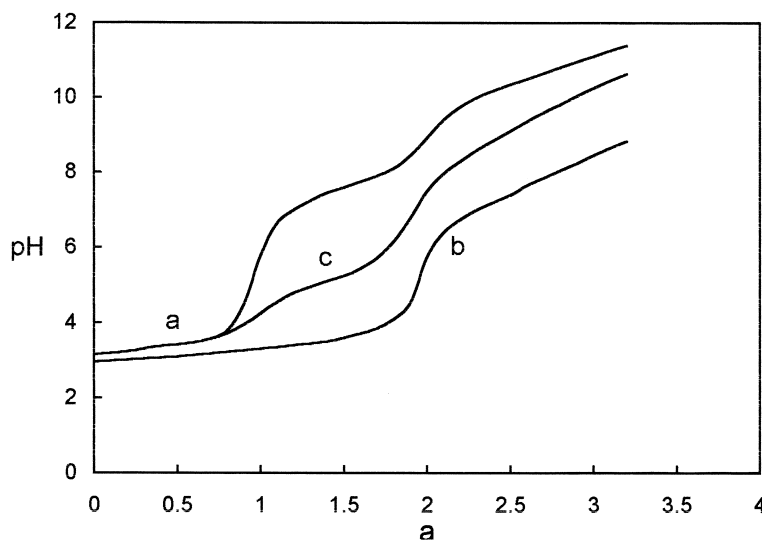


Fig. 1. Potentiometric titration curves of (a) the complex **1**, 1 mM; (b) the mixture of complex **1**, 1 mM and $N_2H_5HSO_4$, 1 mM; (c) the mixture of complex **1**, 1 mM and N_2H_4PhCl , 1 mM, each in 0.1 M Na_2SO_4 at 25°C. a = Moles of base added per mole of complex **1**.

sponding to the stepwise neutralization of one proton from carboxylic acid and two by metal hydrolysis, respectively. The acid dissociation constant, pK_a for the formation of $[\text{Ru}(\text{L})(\text{OH}_2)]^-$ and the two hydrolysis constants (pK_{OH}) for the formation of $[\text{RuL}(\text{OH})]^{2-}$ and $[\text{RuL}(\text{OH})_2]^{3-}$ species calculated from the pH data are 2.38, 7.60 and 10.92, respectively, which are in good agreement with reported values by spectrophotometry [36]. The titration of **1** in the presence of $\text{N}_2\text{H}_5\text{HSO}_4$ showed the neutralization of two protons in the buffer region $0 < a < 2$ and one proton in the higher buffer region as seen in Fig. 1b. The dissociation constant of the carboxylic proton calculated in the buffer region $a = 1.3\text{--}1.8$ is 2.42, assuming that the acidic proton of $\text{N}_2\text{H}_5\text{HSO}_4$ neutralizes before $a = 1.2$ [37]. The dissociation constant (6.82) calculated between $2 < a < 3$ is attributed to the liberation of proton of the coordinated N_2H_5^+ , replacing the water molecule from the coordination sphere which is hydrolyzable at higher pH. Concomitantly, oxidative decomposition/disproportionation of coordinated N_2H_5^+ ligand to nitrogen and ammonia was

observed. As a result, the pale yellow color rapidly changed to reddish yellow through pink [37].

The complex **1** in the presence of $\text{N}_2\text{H}_4\text{Ph}^+$ exhibited three buffer regions $0 < a < 1$, $1 < a < 2$ and $2 < a < 3$ separated by two inflections at $a = 1$ and 2 (Fig. 1c). The acid dissociation constants calculated from the first and second buffer regions are 2.41 and 5.22, which correspond to the deprotonation of carboxylic acid and $\text{N}_2\text{H}_4\text{Ph}^+$ protons, respectively. Like in the case of N_2H_5^+ , the oxidative decomposition of $\text{N}_2\text{H}_4\text{Ph}^+$ occurred at higher pH. The feeble increase in the pK_a value of $\text{N}_2\text{H}_4\text{Ph}^+$ was considered as an evidence for its coordination to the metal through the phenyl substituted nitrogen [29].

3.1.2. Spectrophotometry

Complex **1** in 0.2 M $\text{CH}_3\text{COONa}\text{--}\text{H}_2\text{SO}_4$ mixture (pH 2.8) exhibited two absorption maxima at 285 ($2420 \text{ M}^{-1} \text{ cm}^{-1}$) and 365 ($650 \text{ M}^{-1} \text{ cm}^{-1}$) nm (Fig. 2a). Upon the addition of N_2H_5^+ , the color of the complex did not change, neither did a new band appear in the absorption

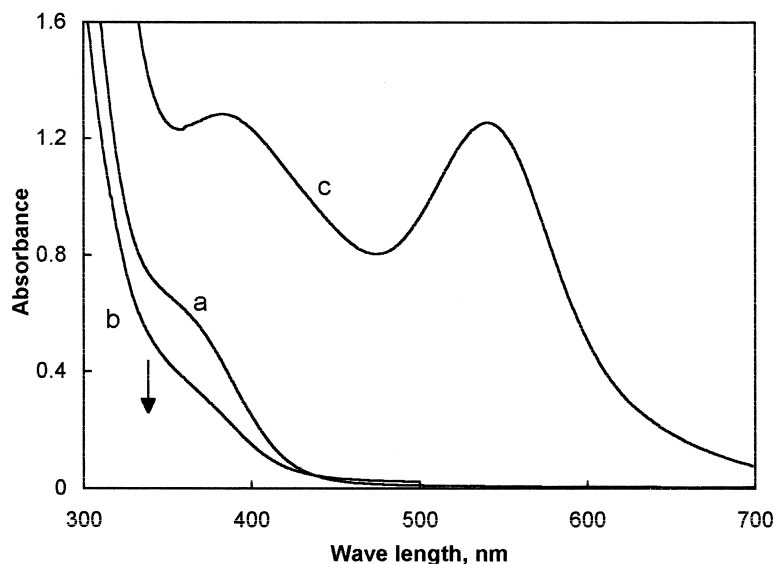
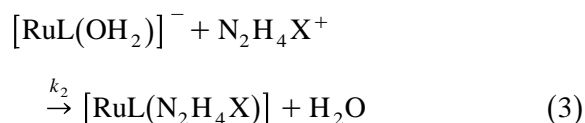
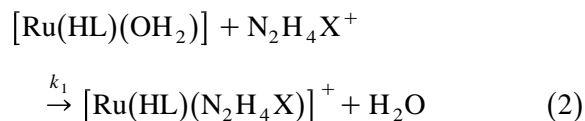
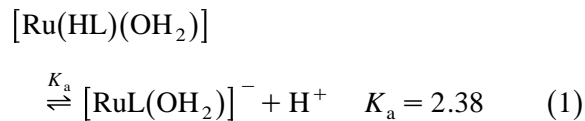


Fig. 2. Absorption spectra of (a) the complex **1**, 1 mM; (b) the mixture of complex **1**, 1 mM and $\text{N}_2\text{H}_5\text{HSO}_4$, 1 mM; (c) the mixture of complex **1**, 1 mM and $\text{N}_2\text{H}_4\text{PhCl}$, 1 mM, at pH 2.8.

spectra. However, the intensity of the shoulder at 365 nm, a characteristic for the Ru–OH₂ bond significantly reduced as seen in Fig. 2b. On the other hand, the addition of N₂H₄Ph⁺ to **1** produced a rapid color change from pale yellow to reddish brown accompanying with two new absorption bands (Fig. 2c) at 400 (1350 M⁻¹ cm⁻¹) and 540 (1320 M⁻¹ cm⁻¹) nm. The plot of change in absorbance (ΔA) at 365 or 540 nm vs. [N₂H₄X⁺] indicated the formation of 1:1 hydrazinium complexes [Ru(HL)(N₂H₄X)]⁺ as proposed in the potentiometry.

The kinetics of the reaction of **1** with N₂H₄X⁺ were studied under pseudo first order conditions at pH 2.8 at 25 ± 0.1°C. The reactions were conducted by monitoring the absorbance change at 365/540 nm for N₂H₅⁺/N₂H₄Ph⁺, respectively. The observed rate (k_{obs}) was dependent on the substrate concentration as well as the pH of the solution. It increased linearly with increase in concentration of N₂H₄X⁺ as shown in Fig. 3, which revealed the completion of reaction in N₂H₅⁺ and existence of a reverse reaction in N₂H₄Ph⁺ solutions. In both cases, the observed rate, k_{obs} data at different pH, further showed its dependence

between the pH 2.0 and 4.0 and independence on either side of it which may be explained by the following equations.



where, X = H or Ph. Then, k_{obs} can be defined as

$$k_{\text{obs}} = \frac{\{k_1[\text{H}^+] + k_2 K_a\}[\text{N}_2\text{H}_4\text{X}]}{\{[\text{H}^+] + K_a\}}$$

From the plots $k_{\text{obs}}\{[\text{H}^+] + K_a\}/[\text{N}_2\text{H}_4\text{X}]$ vs. [H⁺], the second order rate constants k_1 and k_2 were evaluated as 0.016, 0.755 M⁻¹ s⁻¹ for N₂H₅⁺ and 1.32, 53.76 M⁻¹ s⁻¹ for N₂H₄Ph⁺ complexes, respectively. The rate constant k_2

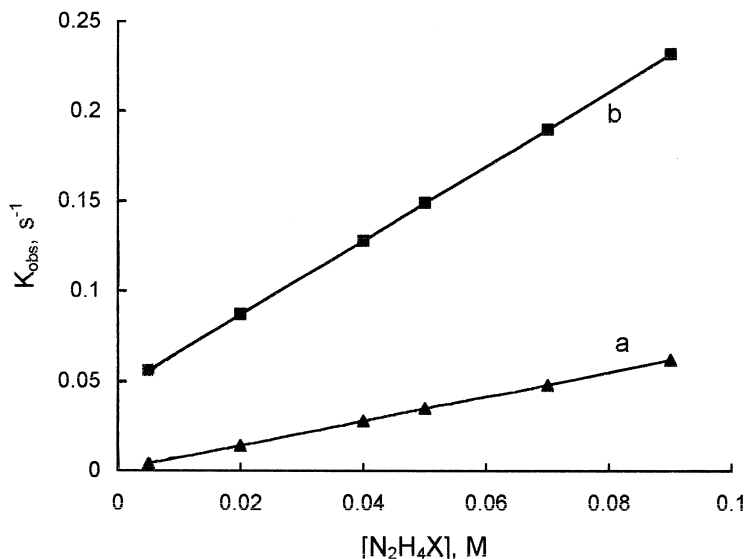


Fig. 3. Plot of k_{obs} vs. [N₂H₄X⁺] for (a) X = H; (b) X = Ph. In each case, pH = 2.8, [1] = 0.5 mM and $T = 25^\circ\text{C}$.

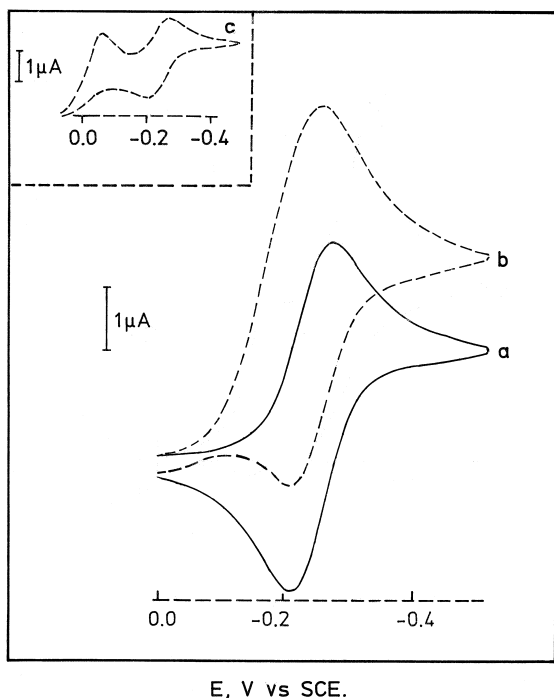


Fig. 4. CV responses of (a) the complex **1**, 1 mM; (b) the mixture of complex **1**, 1 mM and $\text{N}_2\text{H}_5\text{HSO}_4$, 1 mM; (c) the mixture of complex **1**, 1 mM and $\text{N}_2\text{H}_5\text{HSO}_4$, 100 mM. pH in all cases was set to 2.8. Scan speed = 0.1 V s^{-1} .

was significantly greater than k_1 in either case, showing the greater reactivity of $[\text{Ru}(\text{L})(\text{OH}_2)]^-$ than $[\text{Ru}(\text{HL})(\text{OH}_2)]$ with $\text{N}_2\text{H}_4\text{X}^+$. Moreover, the k_1 and k_2 values are hundred times larger for $\text{X} = \text{Ph}$ than that for $\text{X} = \text{H}$, indicating the larger affinity of ruthenium towards the former ligand.

Comparison of the rate constants k_1 and k_2 with those of EDTA analogue [27,28,38] showed that the complex **1** reacts relatively faster with $\text{N}_2\text{H}_4\text{X}^+$ than the EDTA analogue. This extra reactivity of **1** may be attributed to the inductive nature of methyl group substituted on the ethylene collar, which labilises the $\text{Ru}-\text{OH}_2$ bond more. As a result the substitution reaction becomes easy.

3.1.3. Voltammetry

Sampled-dc and CV responses of **1** alone and in the presence of various equivs of $\text{N}_2\text{H}_4\text{X}^+$ salts were studied between +0.2 and -0.8 V in

the range of pH 1 to 5. Some of its important CV responses are presented in Figs. 4 and 5, and the voltammetric data relevant to these studies are described in Table 1. At pH 2.8, the complex **1** exhibited its $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ wave at $E_{1/2} = -0.251 \text{ V}$ in sampled-dc. The analysis ($E_{1/4}-E_{3/4}$; i_d vs. $[\mathbf{1}]$; E_{de} vs. $\log(i/i_d - i)$) data suggested that the electrode reaction is quasi-reversible and diffusion controlled like the EDTA analogue. This reduction wave apparently shifted to anodic side along with an enhancement in $E_{1/4}-E_{3/4}$ and I values when a solution of 1 to 10 equiv of N_2H_5^+ salt was injected into the experimental solution. However, it split into two when some more quantity (10–100 equiv) of N_2H_5^+ salt was added. The data measured in the presence of 100 equiv of N_2H_5^+ revealed that the first wave at -0.046 V and the second at -0.251 V involved two and one electron, respectively. Furthermore, an anodic shift in the first wave while no change in the second wave with the increase in concentration (10–60 equiv) of N_2H_5^+ was observed. Similarly, the complex **1** in the presence of $\text{N}_2\text{H}_4\text{Ph}^+$ salt (< 10 equiv) exhibited three closely separated waves at -0.158 , -0.234 and -0.340 V with overall diffusion current

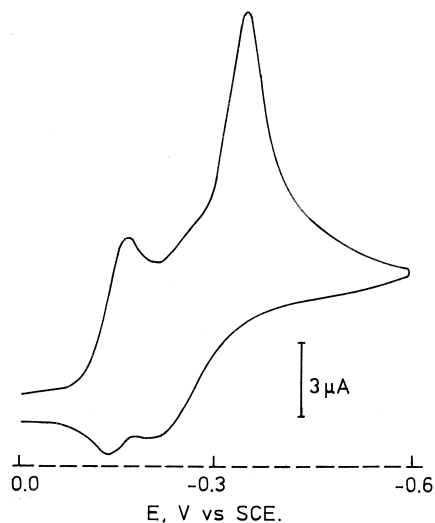


Fig. 5. CV responses of the mixture of complex **1**, 1 mM and $\text{N}_2\text{H}_4\text{PhCl}$, 1 mM at 0.1 V s^{-1} . pH was set to 2.8.

Table 1

Sample-dc and cyclic voltammetric data of **1** and its hydrazinium adducts in the presence of 100 equiv of $N_2H_4X^+$ at pH 2.8 and 25°C

Compound	Sampled-dc			Cyclic voltammetry ^a				
	$E_{1/2}$ V	$E_{1/4}-E_{3/4}$ mV	I	E_{pc} V	E_{pa} V	ΔE_p mV	$E_{p/2}-E_p$ mV	i_{pa}/i_{pc}
[Ru(HL)(OH ₂)]	-0.251	55.0	1.32	-0.275	-0.212	63.0	62.0	0.95
[Ru(HL)(N ₂ H ₅) ⁺	-0.046	32.0	1.98	-0.078	-	-	33.0	-
	-0.251	55.0	1.03	-0.268	-0.204	64.0	57.0	0.66
[Ru(HL)(N ₂ H ₄ Ph) ⁺	-0.158	30.0	1.28	-0.165	-0.134	31.0	31.0	-
	-0.234	59.0	1.24	-0.252	-0.190	62.0	60.0	-
	-0.340	49.0	1.70	-0.354	-	-	54.0	-

^aScan speed: 0.1 V s⁻¹.

triple to that of Ru(III)/Ru(II) wave. The wave heights and $E_{1/2}$'s of these responses showed negligible dependence on concentration (10–100 equiv) of $N_2H_4Ph^+$. On the other hand, the wave analysis data indicated that the electrode reactions at -0.158, -0.234 and -0.340 V involve two, one and one electron, respectively. Moreover, the enhanced diffusion current (Δi_d at -0.50 V in the presence of 1 or 100 equiv of both $N_2H_4X^+$ salts varied with the change in solution pH. They were maximum in the pH range 2.5 to 3.5 and gradually decreased on either side. Amperometric titration of **1** with $N_2H_4X^+$ at -0.5 V had further confirmed the formation of [Ru(HL)(N₂H₄X)]⁺ adducts in solution.

In CV, the complex **1** at pH 2.8, exhibited a pair of peaks at -0.275 V in reductive scan and -0.212 V in oxidative scan corresponding to the Ru(III)/Ru(II) couple ($E_{1/2}$, -0.251 V). Peak intensities of these responses were proportional to the square root of scan speed and the concentration of **1**, while the $i_{pa}/i_{pc} \sim 1$. The cathodic response, in the presence of < 10 equiv of $N_2H_5^+$, increased in height while its foot spread towards more positive potential due to the development of new reduction peak which was well-separated in higher concentrations of $N_2H_5^+$ salt. Of the two, the first peak shifted anodically with the increase in concentration (< 60 equiv) of $N_2H_5^+$ and cathodically with increase in scan speed. The intensity of the composite peak at -0.275 V in Fig. 4(b) in the presence of 1 equiv and those of the resolved

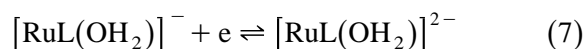
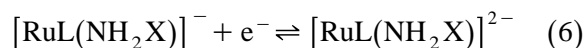
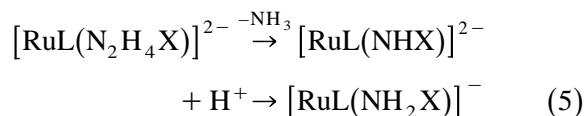
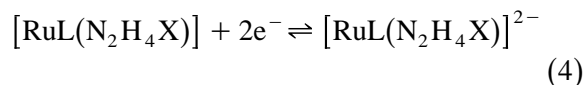
peaks at -0.046 V and -0.251 V seen in Fig. 4(c) increased linearly with the square root of scan speed. Besides, the anodic response of **1** at -0.212 V appeared as a low intense peak at high (> 0.1 V s⁻¹) and tended to disappear at low scan speeds. Anodic response corresponding to the first peak at -0.046 V did not appear (Fig. 4c) at scan speed < 1.0 V s⁻¹ or after limiting the cathodic scans to the foot of the second peak. However, this appeared as low intense peak at about +0.004 V when the CV was performed at high (< 30 V s⁻¹) scan speeds with a glassy carbon electrode. This infers that the first two-electron wave is microscopically reversible and the reduced products are kinetically labile decomposing to another reducible form.

When 1 equiv of $N_2H_4Ph^+$ salt was added, the complex **1** showed three cathodic responses at -0.181, -0.268 and -0.384 V in the forward scan and two responses at -0.149 and -202 V in the reverse scan as the counterparts of the first two cathodic peaks (Fig. 5). The potentials of these peaks shifted non-stoichiometrically to anodic side with the increase in the concentration of $N_2H_4Ph^+$ salt. Subsequently, the intensities of all the peaks enhanced meaningfully except in the case of the second peak where it was reduced due to the high lability of the electroactive species. The intensities of all three cathodic responses varied linearly as a function of square root of the scan speed. The data in Table 1 further confirmed the first peak as a two-electron process and the other two as

one-electron process each. Moreover, the anodic response (-0.356 V vs. Ag/AgCl) of the third cathodic peak (-0.526 V vs. Ag/AgCl) was also observed at high scan speeds ≥ 30 V s $^{-1}$ suggesting a chemical change coupled to the electron transfer process at these potentials.

3.1.4. Mechanism of electroreduction of $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]^+$ and $[\text{Ru}(\text{L})(\text{N}_2\text{H}_4\text{X})]$ complexes

Unlike the aquo complex **1**, the hydrazinium complexes, $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]^+$ and $[\text{Ru}(\text{L})(\text{N}_2\text{H}_4\text{X})]$ which are rapidly produced in solution in the presence of (10–100 equiv) of $\text{N}_2\text{H}_4\text{X}^+$ salt are electroactive and undergo two-electron reduction ($E_{1/2}$, -0.046 / -0.158 V, respectively) to give the corresponding Ru^I complexes. These complexes are unstable and rapidly decompose to 1 mol of ammonia and 1 mol of imido complex, $[\text{Ru}(\text{HL})(\text{NHX})]^-$ or $[\text{RuL}(\text{NHX})]^{2-}$ on account of the migration of two electrons from Ru(I) to the N of coordinated $\text{N}_2\text{H}_4\text{X}^+$ ligand which leads to the heterogeneous cleavage of N–N bond. The resulting imido complexes are less stable in acidic solutions and protonate to give the respective amino species which may reduce by one electron at -0.250 (N_2H_5^+)/ -0.340 V ($\text{N}_2\text{H}_4\text{Ph}^+$) or undergo aquo substitution liberating another mole of ammonia. One-electron reduction of the aquo species occurs at -0.235 V in the case of $\text{N}_2\text{H}_4\text{Ph}^+$. The reactions of $[\text{RuL}(\text{N}_2\text{H}_4\text{X})]$ at the electrode are given in Eqs. (4)–(7). Similar reactions may be applicable for the species $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]$.



3.2. Catalytic reduction of hydrazines

3.2.1. Constant potential coulometry

The $\text{N}_2\text{H}_4\text{X}^+$ salts were electrolytically reduced under argon at -0.150 and -0.250 V, respectively, in the presence of $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]^+$ at pH 1.9 and 2.8 to check the catalytic ability of the metal in **1**. In all cases, the reduction of $\text{N}_2\text{H}_4\text{X}^+$ was only observed. Moreover, ammonia in the case of N_2H_5^+ and equal amounts of ammonia and aniline in the case of $\text{N}_2\text{H}_4\text{Ph}^+$ were produced larger than the stoichiometric amounts, thus justifying the first reduction step (Figs. 4c,5) as a multi-electron step. The plots, moles of ammonia formed per mole of complex vs. the electrolysis time were linear in the case of both substrates. The turnover number, moles of ammonia formed per mole of catalyst per hour as calculated from the slope of these plots are presented in Table 2 along with the data reported for EDTA analogue. It is noted that with a given substrate, the turnover number at pH 2.8 is nearly double to that of the value at pH 1.9, implying that the N–N bond in $[\text{Ru}(\text{L})(\text{N}_2\text{H}_4\text{X})]$ is in more activated form than that in $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]^+$. It is further noted that at a given pH, the turnover number in the case of $\text{N}_2\text{H}_4\text{Ph}^+$ is lower than that of one-half of N_2H_5^+ . This is obvious because an equivalent of aniline is subsequently produced along with ammonia in the case of $\text{N}_2\text{H}_4\text{Ph}^+$. From this data, it may be concluded that the activity of the central metal atom in $[\text{Ru}(\text{L})(\text{N}_2\text{H}_5)]$ and $[\text{Ru}(\text{HL})(\text{N}_2\text{H}_5)]^+$ complexes is relatively reduced when Ph is substituted on the bound N of N_2H_5^+ ligand. It is also noted from this data that the substitution of methyl group in PDTA also reduces the ruthenium activity from moderate to a considerable (3–20%) extent with a given substrate at a given pH. In all cases, the coulombic efficiency was found to be nearly 100%. The solutions at the end of electrolysis showed the same voltammetric behaviour as described above and yielded ammonia at the same rate as before when electrolysed again

Table 2

Turnover number of moles of ammonia produced per mole of **1** per hour during the reduction of $\text{N}_2\text{H}_4\text{X}^+$ salt in the presence of various electron sources at 25°C. a: Present data; b: reported data for EDTA. Value given in parenthesis is efficiency of the reducing agent with respect to ammonia produced

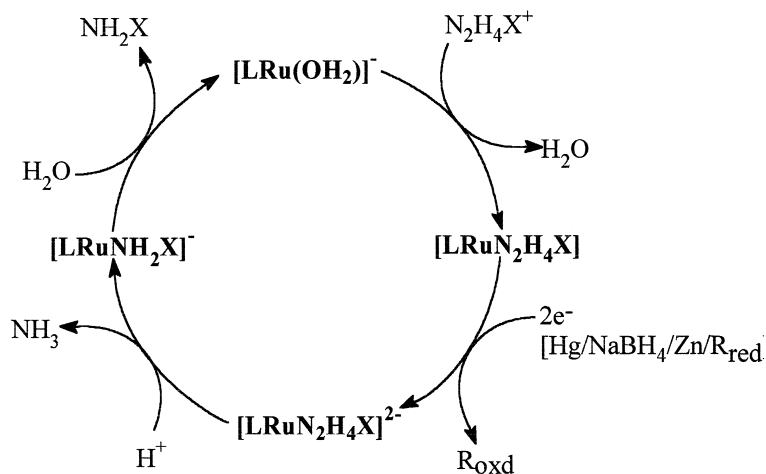
Substrate	pH		Turnover number					
			Hg-pool	Zn-dust	NaBH_4	H_2 -gas	H_2 Asc	H_2 Cat
N_2H_3^+	2.8	a	14.8	41.0 (68)	16.4 (25)	5.3	15.6	3.8
		b	18.4	52.8 (74)	17.3 (30)	5.4	10.8	2.8
	1.9	a	8.0	35.5 (62)	12.2 (19)	2.6	11.0	2.1
		b	9.5	42.0 (64)	13.5 (23)	2.3	8.8	1.6
$\text{N}_2\text{H}_4\text{Ph}^+$	2.8	a	5.3	24.0 (65)	4.9 (10)	1.7	5.8	1.3
		b	6.0	29.4 (68)	5.7 (16)	1.9	2.5	0.9
	1.9	a	2.7	17.6 (60)	3.7 (09)	0.9	2.6	0.9
		b	2.8	21.7 (65)	3.9 (13)	1.1	1.6	0.5

after adding some more amount of substrate and adjusting the pH to its initial value. Thus, the catalytic activity of the metal was proved to be intact during the reduction cycle.

3.2.2. Chemical reduction

The $\text{N}_2\text{H}_4\text{X}^+$ salts were also reduced under similar conditions using Zn-dust, NaBH_4 , H_2 , H_2 Asc and H_2 Cat. In these studies, the reaction was assumed to be initiated by bubbling the cylindrical H_2 at 1 atm. or by adding 0.5 mmol of other reducing agents to 5 μmol of

$[\text{Ru}(\text{HL})(\text{N}_2\text{H}_4\text{X})]^+$ in 0.5 mmol of $\text{N}_2\text{H}_4\text{X}^+$ salt under constant stirring for 10 h. The moles of ammonia produced per mole of catalyst were increased linearly with the reaction time. The turnover numbers calculated with respect to ammonia are described in Table 2 along with those obtained for EDTA analogue under identical conditions. The data obtained with **1** revealed that at a given pH, the turnover number is maximum with Zn and increases in the order $\text{H}_2\text{Cat} < \text{H}_2 < \text{H}_2\text{Asc} < \text{NaBH}_4 < \text{Zn}$. The large turnover numbers with Zn and NaBH_4



$\text{R}_{\text{red}} = \text{H}_2, \text{H}_2\text{Asc}$ and H_2Cat ; $\text{R}_{\text{Oxd}} = 2\text{H}^+, \text{Asc}$ and Quinone

Scheme 1. $\text{R}_{\text{red}} = \text{H}_2, \text{H}_2\text{Asc}$ and H_2Cat ; $\text{R}_{\text{Oxd}} = 2\text{H}^+, \text{Asc}$ and Quinone.

might be possible if the reaction proceeds through charge transfer, free radical and/or both the mechanism. The low turnover number for H_2Cat and H_2 is expected due to low reactivity of undissociated catechol (pK_a , 9.32, 13.0) and low solubility of H_2 gas in the medium at room temperature and atmospheric pressure. However, the catalytic efficiency (moles of ammonia formed per mole of reductant) was nearly 100% with H_2Asc and H_2Cat and less in other cases as seen in Table 2. The efficiency of Zn and $NaBH_4$ with a given substrate at a given pH are explained by their instabilities in acidic environment. The data in Table 2 also suggested that the turnover number for a given substrate with a reducing agent at a given pH is lower for PDTA complexes than those for EDTA. This could be due to the positive inductive effect of the extra methyl group present in the former complexes.

3.2.3. Mechanism of the reduction of hydrazines

On the basis of the above data (Table 2), a cyclic mechanism involving **1** (only with the deprotonated form) for the catalytic reduction of $N_2H_4X^+$ to ammonia and/or aniline is presented in Scheme 1. In this mechanism, complex **1** reacts with the substrate producing the respective monomeric hydrazinium adducts. These are highly reactive and readily take electrons, two per metal, externally from the source (Hg-cathode, Zn-dust or $NaBH_4$) or the reducing agent, R_{red} (H_2 , H_2Asc or H_2Cat) giving the respective Ru^I complexes. Preliminary kinetic data with H_2 , H_2Asc and H_2Cat [39] revealed that the electron transfer from these compounds to the metal center occurs through a complex formation step producing intermediate species of the type $[Ru(L)(N_2H_4X)(R_{red})]$ [39] which subsequently decomposes to give $[Ru^I(L)(N_2H_4X)]^{2-}$. These reduced species are less stable and decompose to give ammonia and/or aniline sequentially through the formation of Ru^{III} -imido $[Ru(L)(NHX)]$ and amine $[Ru(L)(NH_2X)]$ complexes. The latter complexes are very labile and undergo substitution

by another mole of substrate ($N_2H_4X^+$) or water to give **1** to repeat the above process.

4. Concluding remarks

The present study revealed that the complex **1** reacts with the hydrazines, $N_2H_4X^+$ spontaneously to corresponding monomeric complexes $[Ru(HL)(N_2H_4X)]^+$ and $[Ru(L)(N_2H_4X)]$. These complexes undergo two-electron reduction at low potentials to give unstable Ru^I species, which in turn shuffle its electrons to the adjacent N–N bond thereby initiating the heterogeneous cleavage of N–N bonds followed by the liberation of ammonia and/or aniline. The second order rate constants for the formation of these adducts are significantly greater than the corresponding EDTA analogue, ultimately showing the high potentiality of **1** towards nucleophilic substitutions. This remarkable increase is probably attributed to the presence of electron donor methyl group, making the substitution of the incoming group easy. These hydrazinium adducts mediate the reduction of $N_2H_4X^+$ salts to give ammonia and/or amine at the Hg-electrode or in the presence of chemical reductants, viz Zn-dust, $NaBH_4$, H_2 , H_2Asc and H_2Cat . In most cases, the turnover number of ammonia formed per mole of catalyst per hour was slightly lower with **1** than that of the corresponding EDTA analogue, which may be again attributed to the electron donating property of extra methyl group present in PDTA. The charge transfer from the chemical reductants to the metal atom externally in the case of Zn-dust and $NaBH_4$ and through coordination in the case of H_2 , H_2Asc and H_2Cat is the probable mechanism. The labile nature of $Ru-OH_2$ bond and electron conducting ability of ruthenium to coordinated –N atom of $N_2H_4X^+$ are probably responsible for the efficient catalytic activity of **1** and the dual function of activating simultaneously both the substrate and the reductant molecules at ruthenium center like in the proposed mechanism of biological nitro-

gen fixation by the Mo–Fe and Fe-proteins of the nitrogenase enzyme.

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