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Synthesis, spectra and electrochemistry of dinitro-*bis*-{2-(phenylazo)pyrimidine} ruthenium(II). Nitro–nitroso derivatives and reactivity of the electrophilic nitrosyl centre

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Abstract. Silver-assisted aquation of blue *cis-trans-cis*-$RuCl_2(Raapm)_2$ (**1a–1e**) leads to the synthesis of solvento species, blue-violet *cis-trans-cis*-$[Ru(OH_2)_2(Raapm)_2](ClO_4)_2$ [Raapm = *p*-R-C_6H_4-N=N-C_4H_3-NN, (**2a–2e**), abbreviated as N,N′-chelator, where N(pyrimidine) and N(azo) represent N and N′ respectively; R = H (**a**), *p*-Me (**b**), *p*-Cl (**c**), *m*-Me (**d**), *m*-Cl (**e**) that react with NO_2 in warm EtOH to give violet dinitro complexes of the type, $Ru(NO_2)_2(Raapm)_2$ (**3a–3e**). The nitrite complexes are useful synthons of electrophilic nitrosyls, and on triturating the dinitro compounds with conc. $HClO_4$, nitro-nitrosyl derivatives are isolated. The solution structure and stereoretentive transformation in each step have been established from ^{1}H NMR results. The compounds are redox active and display one metal-centred oxidation and successive ligand-based reductions. The ν (NO) >1900 cm^{-1} strongly suggests the presence of linear Ru–N–O bonding. The electrophilic behaviour of metal-bound nitrosyl has been proved in one case by reacting with a bicyclic ketone, camphor, containing an active methylene group and an arylhydrazone with an active methine group. Diazotization of primary aromatic amines with strongly electrophilic mononitrosyl complexes in acetonotrile and dichloromethane solutions has been thoroughly studied.

Keywords. 2-(Arylazo)pyrimidine; arylhydrazone; amines; electrophilic nitrosyl centre.

1. Introduction

The nature of the chemical reactions of organic substrates can be significantly affected by their coordination to metal ions. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species. Amidinates, as ligands, have attracted considerable attention in recent years not only because of their versatile coordination abilities but also since some of their transition metal complexes are very useful. The ruthenium chemistry of diimine ligands (**1**) is an area of significant current interest, particularly with regard to the photophysical and photo-chemical properties exhibited by such complexes. Diimine ligands are strong *p*-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d^6, $S = 0$). In consequence, an interesting aspect of the ruthenium diimine chemistry has been to study the remarkable *p*-interaction between the filled t_2 orbitals of ruthenium(II) and the low-lying vacant *p**-orbital of the diimine chromophore. The extent of *p*-interaction in these complexes depends primarily on the nature of the diimine ligands, which again depends on the nature of the groups linked to the two carbons and the two imine-nitrogens. The presence of other *p*-acceptor ligands within the coordination sphere may also have significant influence on the *p*-interaction between the diimine ligands and ruthenium(II). For the past few years, nitric oxide (NO) has been the focus of discussion because of the discovery of its role in immune defence mechanisms, neuronal signalling processes, cardiovascular systems and in environmental chemistry.[1,2–7] Recently, we have developed the arylazopyrimidine chemistry of ruthenium and have synthesised dichloro componds $RuCl_2(Raapm)_2$ and diaquo species $[Ru(OH_2)_2(Raapm)_2]$ [Raapm = *m*- and *p*-R-CH-N=N-CH-N-N (**2a–2e**), R = H, *p*-Me, *p*-Cl, *m*-Me, *m*-Cl and abbreviated as N,N′-chelator, where N(pyrimidine) and N(azo) represent N and N′ respectively]. In this paper, I examine the reactivity of NO_2^- towards $[Ru(OH_2)_2(Raapm)_2]^{2+}$ and the reactions of the complexes derived there-

from. The nitrites $Ru(NO_2)_2(Raapm)_2$ (**3a–3e**) are useful synthons of nitrosyls, and mononitrosyl compounds are produced in perchloric acid media[8–18]. The electrophilicity of bound NO has been established by reacting with nucleophiles like camphor (cmp) which is a bicyclic ketone with active methylene and an arylhydrazone (ahz) with an active methine group. Diazotozation of primary amines with nitroso complexes has been examined.

2. Experimental

2.1 *Materials*

Literature methods were used to prepare Raapm, *ctc*-$RuCl_2(Raapm)_2$[7], *ctc*-$[Ru(OH_2)_2(Raapm)_2](ClO_4)_2$, alkylidenearylhydrazone, ArCH = NNHPh (Ar = Ph, *p*-MeC_6H_4), arylazooxime ArN=NC(=NOH)Ph and camphorquinone monoxime. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, India). The purification of MeCN and preparation of $[n\text{-}Bu_4N][ClO_4]$ respectively used as solvent and supporting electrolyte in electrochemical experiments carried out as per the literature.

2.2 *Physical measurements*

Microanalytical data (C, H, N) were collected using a Perkin–Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a Jasco UV-Vis-NIR V-570 spectrophotometer. IR spectra were obtained using a Jasco 420 spectrophotometer (using KBr disks, 4000–200 cm^{-1}). The ^1H NMR spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} M in acetonitrile. Electrochemical work was carried out using an EG&G PARC Versastat computer-controlled 250 electrochemical system. All experiments were performed under an N_2 atmosphere at 298 K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

2.3 *Preparation of the complexes*

CAUTION! Perchlorates of heavy metal ions with organic ligands are potentially explosive. Due care must be exercised to avoid explosion hazards, although we have not encountered any problem using a small quantity at a time.

2.3a *Preparation of cis,trans,cis-dinitro-bis-{-2-(p-tolylazopyrimidine}ruthenium(II), ctc-$Ru(NO_2)_2(Meaapm)_2$ Two independent methods were employed for synthesis. Method (a)* – To an EtOH blue-violet solution (15 cm^3) of *ctc*-$[Ru(OH_2)_2(Meaapm)_2](ClO_4)_2$ (0·1 g, 0·14 mmol) was added 0·019 g (0·27 mmol) of solid $NaNO_2$, and the mixture was stirred at 343–353 K for 12 h. The violet solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with H_2O and dried *in vacuo* over $CaCl_2$. Analytically pure (**7b**) was obtained after chromatography over an alumina (neutral) column on eluting the violet band with toluene–acetonitrile (4 : 1, *v*/*v*) and evaporating slowly in air. The yield was 0·088 g (80%).

Method (b) – To a CH_2Cl_2–Me_2CO (1 : 1, *v*/*v*, 30 cm^3) solution of *ctc*-$RuCl_2(Meaapm)_2$ (**4b**) (0·1 g, 0·18 mmol) was added an H_2O–Me_2CO solution of $NaNO_2$ (0·024 g, 0·35 mmol). The mixture was stirred at 343–353 K for 30 h. The resulting violet solution was processed as in method (a) to give analytically pure dinitro complexes; yield, 0·021 g (20%). The high yield in method (a) prompted us to follow this route for the syntheses of the other complexes (**3b–3e**). The yields varied in the range 65–85%.

2.3b *Preparation of ctc-$[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$(**4b**): ctc*-$Ru(NO_2)_2(Meaapm)_2$ (**3b**) (0·1 g, 0·17 mmol) and conc. $HClO_4$ (3 cm^3) were placed in a small beaker, and the mixture was triturated with a glass rod for 1 h. The mixture quickly changed from violet to orange-red colour. The pasty mass was extracted with CH_2Cl_2 (4×5 cm^3) and concentrated under reduced pressure. The dark red crystalline product was separated by filtration, washed with chilled H_2O containing a few drops of dil. $HClO_4$ and dried *in vacuo* over P_4O_{10} to yield analytically pure (**4b**) [yield 0·092 g (70%)]; (**4c**) [yield, 0·078 g (60%)] and (**4d**) [yield 0·081 g (65%)] were prepared similarly starting with (**3c**) (0·1 g, 0·16 mmol) and (**3d**) (0·1 g, 0·13 mmol), respectively.

2.3c *Interconversion: $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (**4b**) $Ru(NO_2)_2(Meaapm)_2$ (**3b**):* To an aqueous solution of (**4b**) (0·1 g, 0·13 mmol) was added

an equivalent amount of KOH in the same solvent. The orange-red solution immediately turned violet, and was extracted with CH_2Cl_2. The solvent was removed by evaporation under reduced pressure and the pasty mass was dissolved in a minimum vol. of CH_2Cl_2, and chromatographed on an alumina (neutral) column. A deep violet band was eluted with toluene–acetonitrile (4 : 1, *v*/*v*). The identity of the product as (**3b**) was checked by comparing properties with an authentic sample. The yield was almost quantitative.

2.3d *Preparation of [Ru(cmpo)(Meaapm)$_2$]ClO$_4$ (**5a**): Method (a)* – (Coupling with the nitroso derivative) To a solution of $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (0·2 g, 0·26 mmol) in 20 cm^3 MeOH were added 0·032 g (0·26 mmol) camphor (cmp) and NaOMe (0·015 g, 0·26 mmol). The mixture was boiled under reflux for 2 h. During this period the initial orange-red solution gradually turned blue-violet. The solution was cooled and filtered. To the filtrate, a saturated aqueous solution of $NaClO_4$ was added and allowed to evaporate slowly in air. The precipitate was collected by filtration, washed with chilled H_2O followed by Et_2O and dried *in vacuo* over P_4O_{10}. The dry mass was dissolved in a minimum vol. of CH_2Cl_2 and was chromatographed on a silica gel column in toluene. A deep blue-violet band was eluted with toluene-acetonitrile (3 : 1, *v*/*v*) and evaporated on a steam-bath. Analytically pure (**5a**) was obtained after drying *in vacuo* over P_4O_{10}. The yield was 0·14 g (70%).

Method (b) – (Direct reaction with the diaquo complex (**2a**)) Camphorquinone monoxime (cmpoH) (0·049 g, 0·27 mmol) and NaOMe (0·015 g, 0·27 mmol) were added to a solution of $[Ru(OH_2)_2(OMeaaiMe)_2](ClO_4)_2$ (0·2 g, 0·27 mmol) in MeOH (20 cm^3), and the mixture was refluxed for 4 h. The solution was then cooled and processed as in method (a). The yield was 0·16 g (75%). The product from methods (a) and (b) gave the same analytical results.

2.3e *Preparation of [Ru(taao)(Meaapm)$_2$]ClO$_4$ (**5c**): Method (a)* – (Coupling with nitroso derivative) To a MeOH solution (20 cm^3) of $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (0·2 g, 0·26 mmol) equivalent amounts of *p*-Me-C_6H_4–CH=NNHPh (0·054 g, 0·26 mmol) and NaOMe (0·015 g, 0·26 mmol) were added. The mixture was boiled under reflux for 2 h. The orange-red solution changed to red-violet. The volume of the solution was reduced to one-third of the original and cooled. A saturated aqueous solution of $NaClO_4$ was added to it. The precipitate that resulted was filtered and dried. Analytically pure (**5c**) was obtained by column chromatography as described in (**5a**). The yield was 0·15 g (70%). [Ru(phaao)(Meaapm)$_2$]ClO$_4$ (**5b**) was prepared (yield, 75%) similarly using PhCH=NNHPh instead of *p*-Me-C_6H_4–CH=NNHPh.

Method (b) – (Direct reaction with diaquo complex) 0·065 g (0·27 mmol) *p*-Me-C_6H_4–C(=NOH)N=NPh (taaoH) and 0·015 g (0·27 mmol) NaOMe were added to a MeOH solution (20 cm^3) of $[Ru(OH_2)_2(MeaaiMe)_2](ClO_4)_2$ (0·2 g, 0·27 mmol) and the whole heated to reflux for 4 h. The reaction solution was processed as above to give (**5c**) [yield, 0·17 g (75%)]. (**5b**) was prepared [yield, 70%] similarly using PhC(=NOH)N=NPh (phaaoH) instead of *p*-Me-C_6H_4–C(=NOH)N=NPh (taaoH). Analysis results from both methods are identical.

2.3f *Reaction of primary amines with [Ru(NO)(NO$_2$)(Meaapm)$_2$]ClO$_4$ (**5b**): Method (a)* – To a acetonitrile solution (20 cm^3) of $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (0·2 g, 0·26 mmol) equivalent amounts of aniline (0·054 g, 0·26 mmol) was added. The mixture was stirred for 30 min at room temperature and then evaporated to dryness using a vacuum pump. The crude product was then extracted with 30 ml of ice-cold water and the aquous solution collected by filtration. To the aquous solution an aquous solution of alkaline ***b***-naphthol was added with continuous stirring over a period of 15 min. Red crystals of 1-phenylazo-2-naphthol were separated and recrystalised from methanol. The residue was dried and dissolved in dichloromethane where upon brown crystals of $[Ru(S)(NO_2)(Meaapm)_2]ClO_4.H_2O$ (S = CH_3CN) (**6a**–**6e**) were obtained.

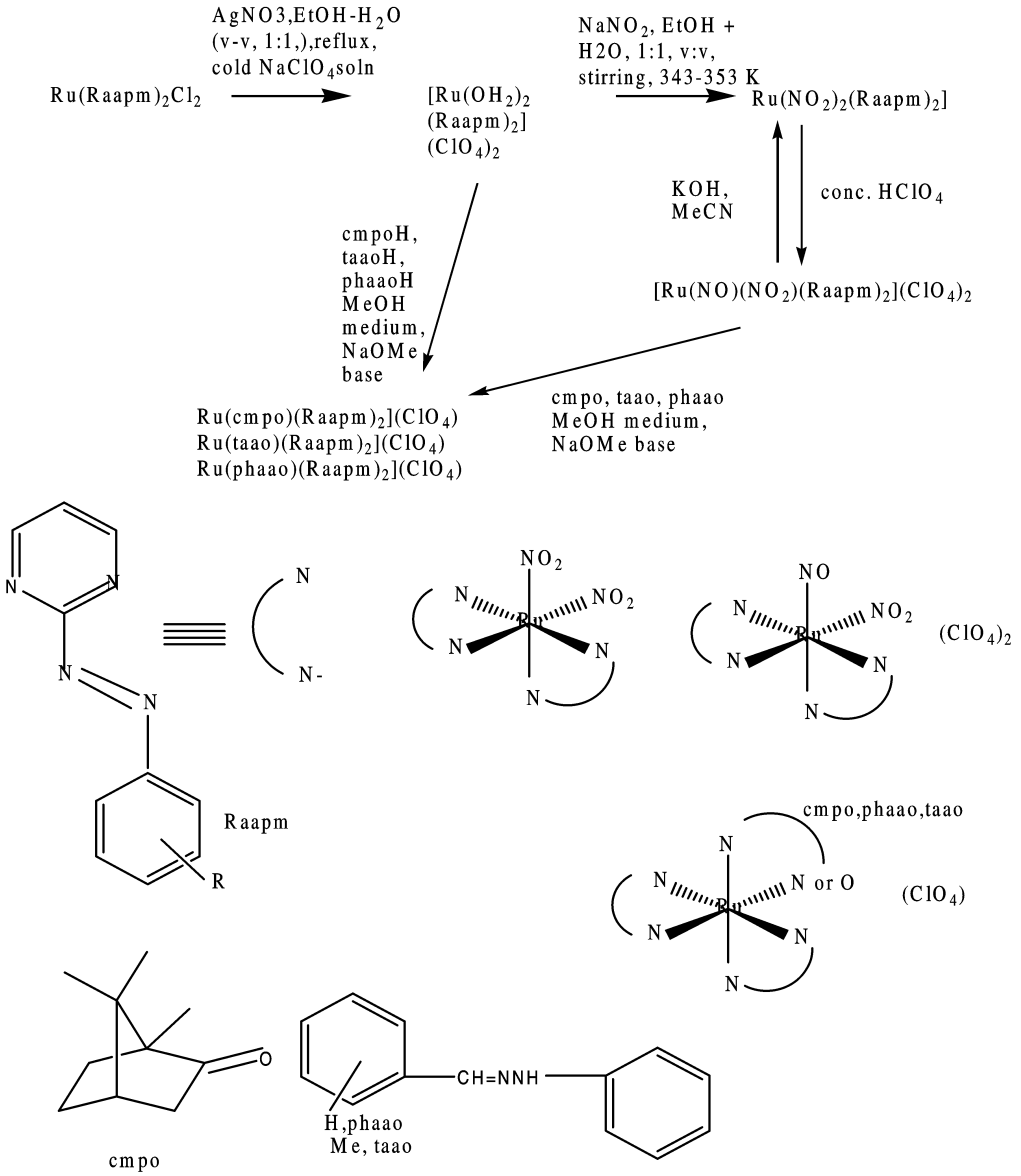
Method (b) – To a dichloromethane solution (20 cm^3) of $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (0·2 g, 0·26 mmol), an equivalent amount of aniline (0·054 g, 0·26 mmol) was added and the mixture was stirred for 30 min at room temperature and then evaporated to dryness using a vacuum pump. Brownish white needles of $[C_6H_5N][ClO_4]$ were collected. The residue was then extracted with 30 cc of ice-cold water and the aqueous solution collected by filtration. To the aqueous solution an aqueous solution of alkaline ***b***-naphthol was added with continu-

ous stirring over a period of 15 min. Red crystals of 1-phenylazo-2-naphthol were separated and recrystallised from methanol. The residue was dried and dissolved in dichloromethane and brown crystals of $[Ru(S)(NO_2)(Meaapm)_2]ClO_4.H_2O$ (S=H_2O) (**7a**–**7e**) were obtained. These were collected by filtration and dried *in vacuo* over P_4O_{10}.

3. Results and discussion

3.1 *Synthesis and formulation*

Di-aquo complexes *ctc*-$[Ru(OH_2)_2(Raapm)_2](ClO_4)_2$, prepared by Ag^+-assisted aquation of *ctc*-$RuCl_2(Raapm)_2$ (**1a–1e**), were reacted with $NaNO_2$ (excess amount >3 mol) under stirring at 343–353 K in aqueous alcohol to give $Ru(NO_2)_2(Raapm)_2$ (**3a–3e**) in good yields (65–85%). The synthetic routes are shown in scheme 1. The dinitrites were synthesised in low yields either directly on stirring $NaNO_2$ in ethanol–acetone mixture for 30 h or by *in situ* synthesis of the aquo complex with $AgNO_3$ followed by reaction with $NaNO_2$.[7–9] The composition of the complexes is supported by the microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t_{2g}^6, $S = 0$). Trituration of solid $Ru(NO_2)_2(Meaapm)_2$ in concentrated $HClO_4$ at ambient condition gives an orange-red solution from which the nitrosyl complexes $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$



Scheme 1.

(**4a–4e**) are isolated. In alkaline media, the nitrosyl complexes (**4a–4e**) regenerate the corresponding nitrite precursors (**3a–3e**). The reaction of H^+ with coordinated NO_2 group in nitrite complexes and the nucleophilic attack of OH^- on the NO^+ in nitrosyls are the key steps for such reactions. The violet dinitrites are soluble in common organic solvents but insoluble in H_2O, whereas the orange-red nitrosyls are soluble in H_2O and in a range of common organic solvents, viz. methanol, ethanol, acetone, acetonitrile, chloroform, dichloromethane. In MeCN (**4a–4e**) behave as 1 : 2 electrolytes (Λ_M = 140–160 Ω^{-1} cm^{-1} mol^{-1}) whereas non-electrolytic behaviour is found for type (**3a–3e**) complexes as indicated by their very low Λ_M values.

3.2 *Spectral studies*

IR spectra of dinitro complexes, $Ru(NO_2)_2(Raapm)_2$ (**3a–3e**) show a 1 : 1 correspondence to the spectra of the dichloro analogue, *ctc*-$RuCl_2(Raapm)_2$ except for the appearance of intense stretching at 1300–1335 and 1250–1280 cm^{-1} with concomitant loss of n(Ru–Cl) at 320–340 cm^{-1}. They are assigned to $n(NO_2)_{as}$ and $n(NO_2)_s$ respectively. The n(N=N) and n(C=N) appear at 1365–1380 and 1570–1600 cm^{-1}, respectively. Mono-nitro-nitroso-ruthenium(II), $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (**4a–4e**) show very strong stretching in the 1910–1925 cm^{-1} range which is conspicuously absent in the spectra of $Ru(NO_2)_2(Meaapm)_2$. This is certainly due to the stretching mode of n(NO) of the coordinated nitrosyl group. Nitric oxide formally acts as cationic donor (NO^+) and binds both in the linear and bent N–O fashion (table 1). The stretching frequency n(NO) qualitatively determines the stereochemistry of M–N–O bonding. Usually, n(NO) > 1700 cm^{-1} has been assigned to linear M–N–O bond. Thus, the present series of Ru–NO complexes are assumed to contain the linear NO group. Other important frequencies are n (H_2O) at 3350–3400 cm^{-1} and n (ClO_4) at 1140–1145, 1110–1120 and 1080–1090 cm^{-1} along with weak bands at 640 and 625 cm^{-1}. Triplet splitting pattern of ClO_4 may presumably be due to some sort of hydrogen bonding interaction, Cl...O·····H(O/C).

The solution electronic spectra of these new complexes were recorded in dry acetonitrile (table 2, figures 1 and 2). Dinitro complexes (**3a–3e**) exhibit multiple transitions in the UV-visible region. They display intense MLCT transition in the 550–560 nm range along with weak longer wavelength absorption near 750 nm. In nitroso derivatives $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$ (**4a–4e**), the intense absorption bands are further shifted to shorter wavelengths, near 420 nm along with a weak band near 600 nm. This is attributed to strong dp(Ru) → p(NO) back bonding which stabilizes the dp level and consequently shifts the MLCT band to the lower wavelength region. The nitrosyl complexes are found to be stable only in dry acetonitrile solution. In ordinary acetonitrile or in contact with water the spectrum spontaneously changes and levels off with the spectrum of precursor dinitro derivative. The transformation has been proved through product (**3b**) isolation in one case (**4b**), and characterized comparing of its properties with an authentic sample. The conversion from nitroso to the nitro complex is followed by the following mechanism, and kinetic investigation supports it (figure 2).

The ^1H NMR spectra of $Ru(NO_2)_2(Raapm)_2$ (**3a–3e**) complexes were unambiguously assigned on comparing with $RuCl_2(Raapm)_2$. The aryl protons (7-H–11-H) of (**3a–3e**) are shifted downfield by 0·1–0·7 ppm as compared to those of the parent dichloro derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9) and C(10)-position. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. Pyrimidine 4- and 6-H appear as doublet at the lower frequency side of the spectra (7·0–7·2 ppm for 4-H; 6·9–7·1 ppm for 6-H). The aryl-Me (R = Me) in $Ru(NO_2)_2(Meaapm)_2$ (**3a–3e**) appears as a single signal at 2·30 ppm and is in consonance with stereoretentive nucleophilic substitution during synthesis of dinitro complexes from *ctc*-

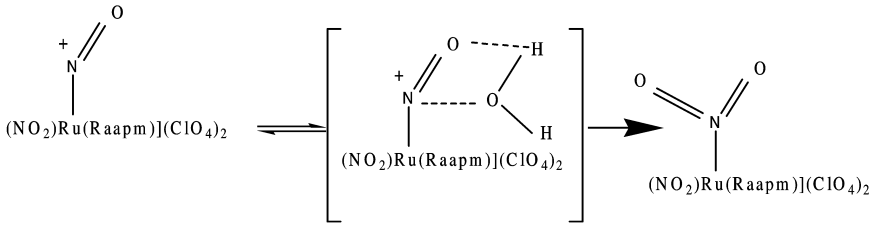


Table 1. Microanalytical (CHN)[a] and FT-IR spectroscopic[b] data.

Complexes	C	H	N	O	*n* (N=N), *n* (C=N), $n(NO_2)_{as}$, $n(NO_2)_s$, *n* (NO), $n(ClO_4)$
$Ru(NO_2)_2$(H-aapm)$_2$, **3a**	42·4 (42·3)	3·5 (3·4)	24·8 (24·7)	24·2 (24·1)	1365, 157,0 1300, 1250
$Ru(NO_2)_2$(*p*-Me-aapm)$_2$, **3b**	44·4 (44·5)	4·0 (4·1)	23·6 (23·7)	23·2 (23·1)	1367, 1580, 1320, 1270
$Ru(NO_2)_2$(*p*-Cl-aapm)$_2$, **3c**	37·8 (37·7)	2·84 (2·7)	22·1 (22·0)	23·7 (23·6)	1370, 1590, 1325, 1255
$Ru(NO_2)_2$(*m*-Me-aapm)$_2$, **3d**	44·3 (44·5)	4·2 (4·1)	23·5 (23·7)	23·3 (23·1)	1375, 1585, 1320, 1260
$Ru(NO_2)_2$(*m*-Cl-aapm)$_2$, **3e**	37·8 (37·7)	2·84 (2·7)	22·1 (22·0)	23·7 (23·6)	138,0 1590, 1310, 1265
$[Ru(NO_2)(NO)$(H-aapm)$_2](ClO_4)_2$, **4a**	34·1 (34·0)	2·3 (2·4)	19·9 (19·8)	25·0 (24·9)	1370, 1570, 1300, 1255, 1920, 1140, 1090, 640
$[Ru(NO_2)(NO)$(*p*-Meaapm)$_2](ClO_4)_2$, **4b**	34·0 (34·1)	3·1 (3·0)	18·0 (18·1)	23·2 (23·1)	1365, 1575, 1310, 1265, 1910, 1145, 1090, 645
$[Ru(NO_2)(NO)$(*p*-Claapm)$_2](ClO_4)_2$, **4c**	31·1 (31·2)	1·81 (1·82)	18·1 (18·2)	22·8 (22·7)	1380, 1570, 1320, 1260, 1920, 1140, 1080, 640
$[Ru(NO_2)(NO)$(*m*-Meaapm)$_2](ClO_4)_2$, **4d**	34·2 (34·1)	3·2 (3·0)	18·1 (18·1)	23·2 (23·1)	1370, 1575, 1310, 1255, 1930, 1145, 1090, 645
$[Ru(NO_2)(NO)$(*m*-Claapm)$_2](ClO_4)_2$, **4e**	31·3 (31·2)	1·80 (1·82)	18·1 (18·2)	22·8 (22·7)	1372, 1570, 1310, 1265, 1930, 1140, 1080, 640
[Ru(cmpo)(Meaapm)$_2](ClO_4)$, **5a**	49·2 (49·1)	4·8 (4·7)	16·1 (16·2)	22·0 (22·1)	1365, 1575, 1140, 1090, 640
[Ru(taao)(Meaapm)$_2](ClO_4)$, **5b**	51·5 (51·4)	4·2 (4·1)	18·4 (18·3)	23·0 (23·1)	1370, 1570, 1145, 1080, 645
[Ru(phaao)(Meaapm)$_2](ClO_4)$, **5c**	50·8 (50·7)	4·1 (4·0)	18·9 (18·8)	22·9 (22·8)	1375, 1570, 1140, 1090, 640
$[Ru(CH_3CN)(NO_2)$(Haapm)$_2]ClO_4·H_2O$, **6a**	42·9 (42·8)	3·4 (3·3)	16·7 (16·8)	20·6 (20·7)	1365, 1570, 1300, 1255, 1145, 1090, 645
$[Ru(CH_3CN)(NO_2)$(*p*-Meaapm)$_2]ClO_4·H_2O$, **6b**	42·2 (42·1)	3·6 (3·5)	17·2 (17·1)	20·9 (20·8)	1367, 1570, 1300, 1255, 1140, 1090, 640
$[Ru(CH_3CN)(NO_2)$(*p*-Claapm)$_2]ClO_4·H_2O$, **6c**	42·9 (42·8)	3·4 (3·3)	16·7 (16·8)	20·6 (20·7)	1365, 1570, 1300, 1255, 1145, 1090, 645
$[Ru(CH_3CN)(NO_2)$(*m*-Meaapm)$_2]ClO_4·H_2O$, **6d**	42·2 (42·1)	3·6 (3·5)	17·2 (17·1)	20·9 (20·8)	1367, 1570, 1300, 1255, 1140, 1090, 640
$[Ru(CH_3CN)(NO_2)$(Haapm)$_2]ClO_4·H_2O$, **6e**	42·9 (42·8)	3·4 (3·3)	16·7 (16·8)	20·6 (20·7)	1365, 1570, 1300, 1255, 1145, 1090, 645
$[Ru(H_2O)(NO_2)$ (Haapm)$_2]ClO_4·H_2O$, **7a**	41·0 (41·0)	3·5 (3·4)	15·1 (15·0)	17·7 (17·6)	1370, 1570, 1300, 1255, 1144, 1095, 640
$[Ru(H_2O)(NO_2)$(*p*-Meaapm)$_2]ClO_4·H_2O$, **7b**	41·6 (41·5)	3·6 (3·5)	16·0 (16·1)	17·9 (17·8)	1380, 1570, 1300, 1255, 1140, 1085, 640
$[Ru(H_2O)(NO_2)$(*p*-Cl-aapm)$_2]ClO_4·H_2O$, **7c**	41·0 (41·0)	3·5 (3·4)	15·1 (15·0)	17·7 (17·6)	1370, 1570, 1300, 1255, 1144, 1095, 640
$[Ru(H_2O)(NO_2)$(*m*-Meaapm)$_2]ClO_4·H_2O$, **7d**	41·6 (41·5)	3·6 (3·5)	16·0 (16·1)	17·9 (17·8)	1380, 1570, 1300, 1255, 1140, 1085, 640
$[Ru(H_2O)(NO_2)$(*m*-Cl-aapm)$_2]ClO_4·H_2O$, **7e**	41·0 (41·0)	3·5 (3·4)	15·1 (15·0)	17·7 (17·6)	1370, 1570, 1300, 1255, 1144, 1095, 640

[a]Calculated values are in parentheses; [b]as KBr disks

$RuCl_2$(Raapm)$_2$ via aquo derivatives. The mononitrosyls, $[Ru(NO_2)(NO)$(Meaapm)$_2](ClO_4)_2$, exhibit similar pattern of signals in the aromatic portion and the spectra have been shifted to higher fields by 0·03–0·15 ppm from those of respective dinitro derivatives. It may presumably be due to better

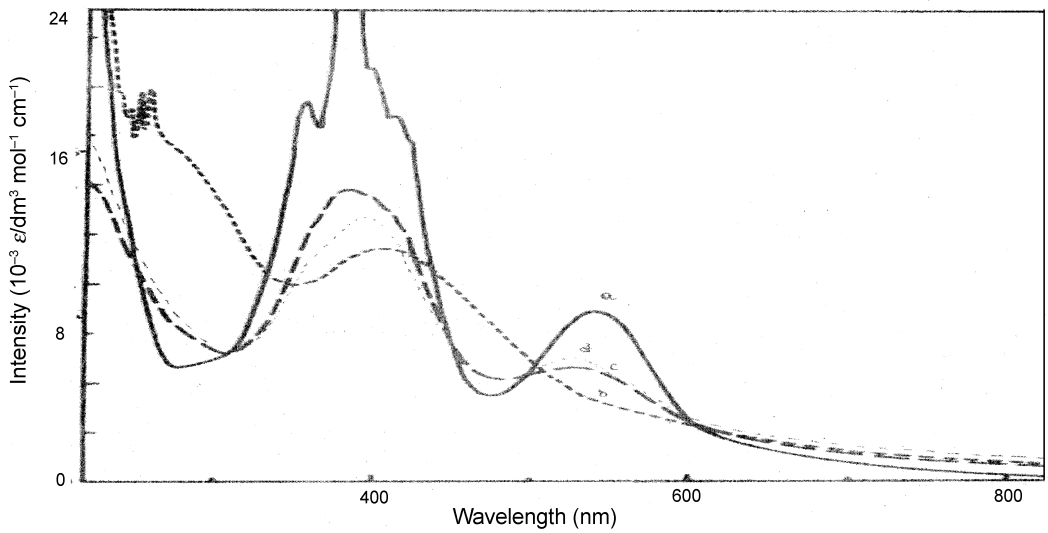


Figure 1. The solution electronic spectra of (a) $[Ru(NO_3)_3(Haapm)_2]$, (b) $[Ru(NO)(NO_2)$ (*p*-Meaapm$)_2](ClO_4)_2.H_2O$, (c) $[Ru(cmpo)(Haapm)_2]ClO_4.H_2O$, (d) $[Ru(CH_3CN)(NO_2)(Haapm)_2]ClO_4.H_2O$, complexes in dry acetonitrile.

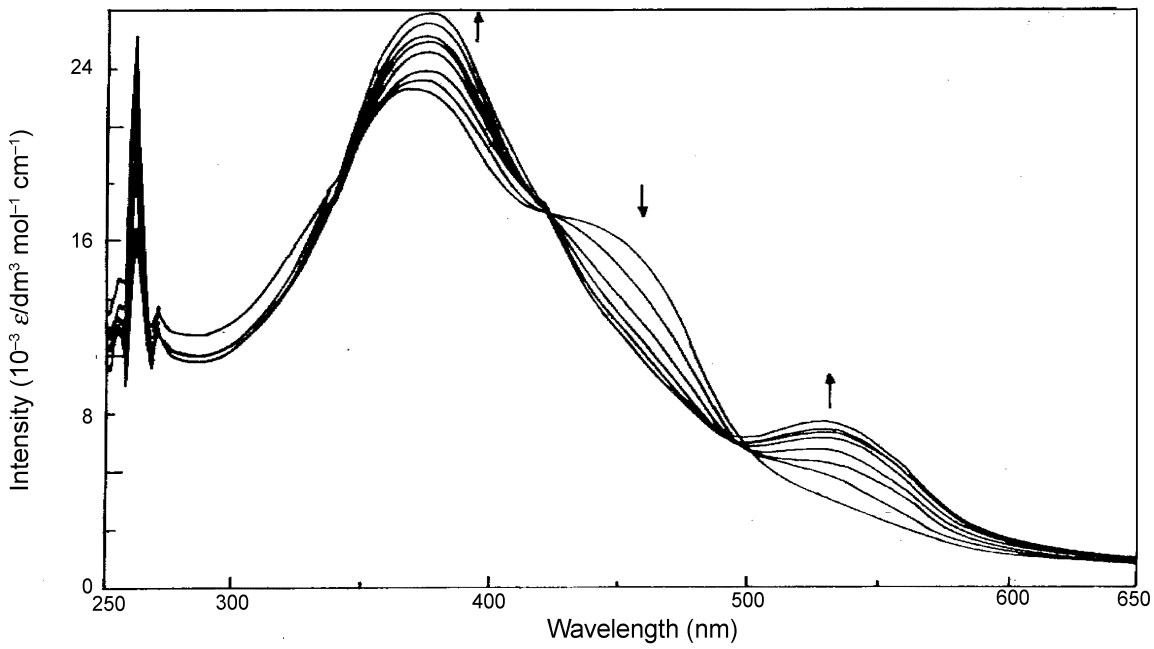
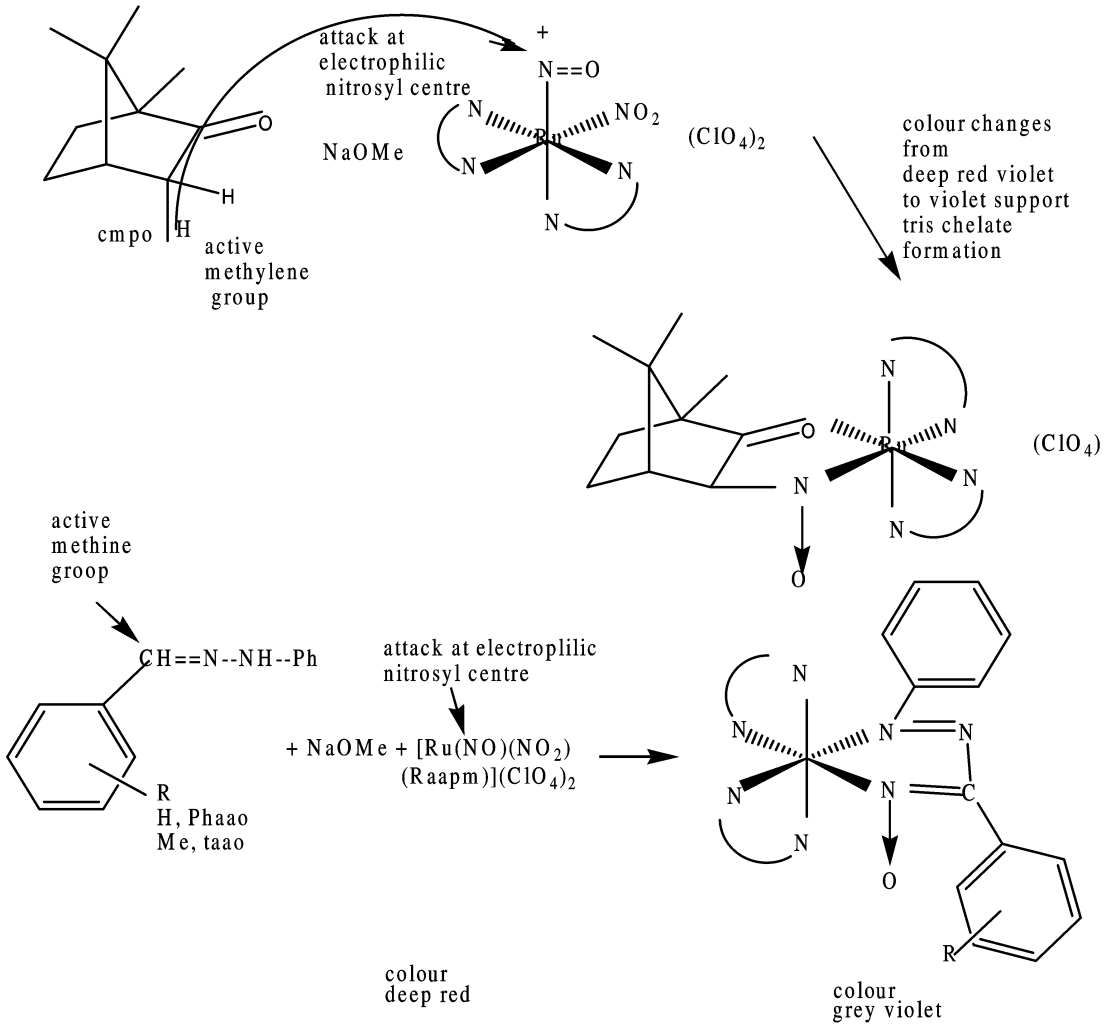


Figure 2. Time evolution of the electronic spectra of a changing solution of $[Ru^{II}(NO_2)(NO)(MeaaiMe)_2](ClO_4)_2$ (**10b**) → $[Ru^{II}(NO_2)_2(MeaaiMe)_2]$ (**7b**) in dry acetonitrile and in the presence of a 50 times excess of water at 300 K. The arrows indicate increase or decrease in band intensities.

dp(Ru) → *p**(NO) charge transfer which increases hardness of Ru(II) leading to strong *s*-interaction with the chelator, Meaapm.

3.3 *Redox properties*

The potential values of the complexes in dry acetonitrile solution are set out in table 2. The cyclic voltammograms of $Ru(NO_2)_2(Raapm)_2$ exhibit some unusual behaviour in repetitive cycles. The reduction sweep shows a new wave that has a counter oxidative wave on the second sweep. The second and consecutive cycles increase the peak height with subsequent decrease of the primary couple. The first primary redox process ($E_{1/2}^{MI}$ = 1·1–1·3 V) is assigned to Ru(III)/Ru(II) couple. The nitrosyl complexes



$[Ru(NO_2)(NO)\ (RaaiR)_2](ClO_4)_2$ exhibit multiple redox responses in the potential range +2·0 V to –2·0 V versus SCE. Two quasi-reversible reductive responses in the potential 0·5 to 0·6 V (**4b**), and –0·1 to –0·2 V, (**3b**), are seen. The one-electron stoichiometry of the reversible electron transfer process is established by constant potential coulometry locked at 0·3 V (n = 0·93) in the case of (**4b**). The reduced species is unstable even at 273 K, which has precluded its isolation and characterization. The one-electron nature of other couples (I and III to VI) has been confirmed by differential pulse voltammetry experiments. The couples IV and V are assigned to successive one-electron reductions of the coordinated NO^+ unit [Ru-NO^+ → Ru-NO (couple II), Ru-NO → Ru-NO^- (couple III)]. Couple III is irreversible, indicating instability of the reduced species. The assignment is based on earlier observations of similar Ru-bipyridine and Ru-azopyridine systems. High potential voltammetric wave at 1·4–1·5 V (couple 1) ($\Delta E_P \geq 120$ mV) is assigned to the Ru(III)/Ru(II) couple. Successive reductions on the negative side of SCE are observable and one-electron nature is confirmed by comparing the current heights of these process with that of couple II in the differential pulse voltammetry experiments and are assigned to the reduction of coordinated ligand. The azo group in RaaiR may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window three reductions were clearly observable.

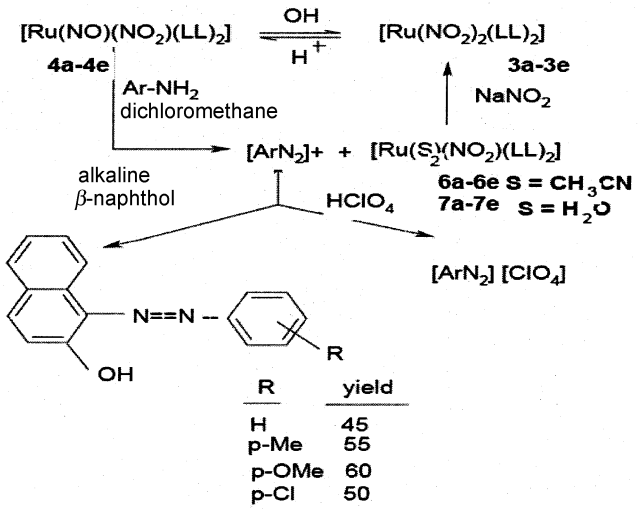
3.4 *Reactivity of $[Ru(NO_2)(NO)(Meaapm)_2](ClO_4)_2$*

The nitrosyl complexes exhibit a high degree of the electrophilic character of coordinated NO [n(NO) > 1900 cm]. The electrophilic behaviour of these new complexes has been investigated by reacting cam-

Table 2. UV–Vis[a] and cyclic voltammetric[b] data.

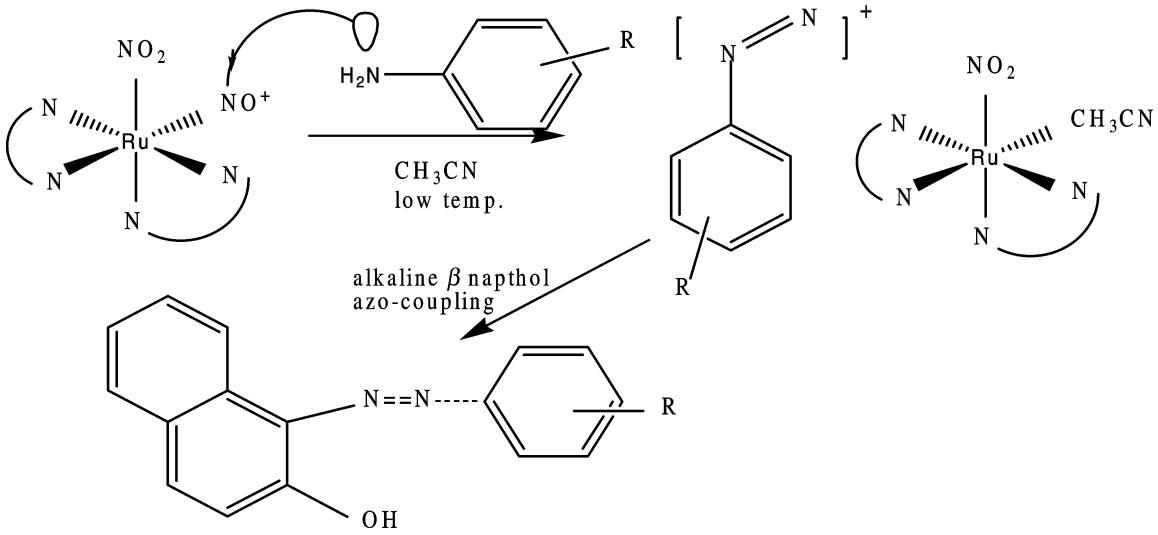
Compound	UV–Vis spectra l_{max} (nm) ($10^{-3}e$/dm^3 mol^{-1} cm^{-1})	Cyclic voltammetric data E/V (ΔE_P/mV)	
		E^M	$-E^L$
(**3a**)	551 (8·379),421 (8·914)[c]	0·533 (130)	0·388 (80), 0·651 (130), 1·216[d]
(**3b**)	548 (6·773), 421 (12·271)[c]	0·521 (100)	0·407 (95), 0·691 (120), 1·282[d]
(**3c**)	555 (13·919), 424 (23·416)[c]	0·551 (110)	0·344 (80), 0·673 (100), 1·201[d]
(**3d**)	550 (8·796), 416 (10·081)[c]	0·551 (140)	0·377 (80), 0·632 (75), 1·251[d]
(**3e**)	547 (8·752), 423 (17·149)[c]	0·521 (130)	0·383 (85), 0·647 (100), 1·301[d]
(**4a**)	550 (3·996)[c], 408 (10·616)	0·501 (130)	0·134[d], 0·401 (80), 0·711 (120), 1·271[d]
(**4b**)	555 (3·118)[c], 412 (13·016)	0·581 (130)	0·212[d], 0·351 (85), 0·621 (120), 1·221[d]
(**4c**)	550 (3·996)[c], 408 (10·616)	0·501 (130)	0·134[d], 0·401 (80), 0·711 (120), 1·271[d]
(**4d**)	555 (3·118)[c], 412 (13·016)	0·581 (130)	0·212[d], 0·351 (85), 0·621 (120), 1·221[d]
(**4e**)	550 (3·996)[c], 408 (10·616)	0·501 (130)	0·134[d], 0·401 (80), 0·711 (120), 1·271[d]
(**5a**)	531 (8·443), 385 (15·584)	0·651 (100)	0·350 (100), 0·657 (120), 1·171[d]
(**5b**)	560 (3·997), 387 (18·987)	0·363 (100)	0·641 (110), 0·891 (140), 1·351[d]
(**5c**)	574 (4·257), 391 (20·219)	0·384 (110)	0·691 (90), 0·931 (150), 1·444[d]
(**6a**)	517 (4·257), 359 (20·219)	0·46 (130)	0·69 (90), 0·90 (150)
(**6b**)	527 (4·200), 369 (19·219)	0·44 (130)	0·731 (90), 0·93 (150)
(**7a**)	534 (4·257), 359 (20·200)[c]	0·41 (140)	0·742 (90), 0·94 (140)
(**7b**)	527 (4·257), 359 (20·312)[c]	0·44 (130)	0·76 (70), 0·98 (130)

[a]Solvent dry MeCN; [b]solvent dry MeCN, supporting electrolyte [^{n}Bu$_4$N][ClO$_4$] (0·1 M), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute conc. ~10^{-3} M, scan rate 50 mVs^{-1}; [c]shoulder; [d]E^L: ligand reductions, $\Delta E_P = |E_{pa} - E_{pc}|V$ where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential



Scheme 2

phor (cmp), a compound having an active methylene group and arylhydrazone (ahz), an organic substrate with active methine group. MeOH solutions of [Ru(NO$_2$)(NO)(Meaapm)$_2$](ClO$_4$)$_2$ reacted smoothly with camphor (cmp) and arylhydrazone (ahz) in presence of an organic base viz. NaOMe. The progress of the reaction was followed by monitoring the n(NO) decreases at ~1910 cm^{-1}, and the composition of the reaction mixture was followed by thin-layer chromatography, collecting portions of the reaction solution from time to time. The product analyses are in accordance with the (phenylazooxime, phaao, **14a**); *p*-CHCH(p-tolylazooxime, taao, **14b**)]. The reactions proceed very slowly in the absence of base. However, addition of a base, viz. NaOMe to the reaction mixture changes the solution colour from orange-red to red-violet. This involves electrophilic adition of the coordinated nitrosyl to the activated methylene/methine group (formed by the added base) of the ketone/hydrazone forming a bound oxime [camphorquinone monoxime, phenylazooxime and *p*-tolylazooxime]. Deprotonation of the active –CH$_2$–/–CH– group leads to the generation of carbanion which subsequently attacks electrophilic NO and results in camphorquinone monoxime and an arylazooxime chelate ring via expulsion of the –NO group, respectively. To substantiate such nitrosation a direct synthetic approach was adopted. The reaction of camphorquinonemonoxime (cmpoH) and arylazooxime (aaoH) separately with the diaquo complex in boiling alcohol in presence of a base res-



pectively, yielded *tris*-chelates through solvolytic displacement followed by chelation of appropriate oximates. The heteroleptic *tris*-chelates may exist in two isomeric forms (i and ii) with stereoretentive *ctc*-Ru(OMeaaiMe)$_2$ geometry. However, we can not separate these isomers by chromatographic purification process. The H NMR spectra of the complexes suggest a mixture of isomers. The aliphatic region (2–5 ppm) is particularly useful to support the chemical composition. The 10-Me of Meaapm is assignable to the signals at 2·29 and 2·38 ppm. A pair of signals refers to the isomeric mixture of complexes in solution. Aromatic region gives very complex splitting pattern and assignments of the signals are not made. Cyclic voltammetric studies show Ru(III)/Ru(II) couple at 1·2–1·3 V and successive ligand reductions on the negative side of SCE. Reaction of the mononitrosyl complexes with primary amines were studied by the following sequence. To investigate the reaction mechanism it was studied in two solvents, in acetonitrile and in. This monoaquo complex produces the monoacetonitrile complex on treatment with acetonitrile. The results of the products are listed in table 2. One real advantage of such reaction is the possibility of developing analytical route for synthetic nitrosation of organic substrate using [Ru(NO$_2$)(NO)(Meaapm)$_2$](ClO$_4$)$_2$ as the source of NO$^+$ under mildly acidic condition.

4. Conclusions

Dinitro complexes of ruthenium(II)–azopyrimidine, *ctc*-Ru(NO$_2$)$_2$(Raapm)$_2$ have been synthesised by stereoretentive reaction of diaquo complex [Ru(OH$_2$)$_2$(Raapm)$_2$] with nitrite ion. The electrophilic activity of bound NO has been established through C–N bond formation via reaction with organic substrate containing an active methylene group (camphor)/methine group (arylhydrazone). The complexes exhibit strong MLCT transitions. Voltammetric study shows Ru(III)/Ru(II) couple along with successive ligand-based reductions and additionally NO$^+$ reductions in nitrosyl derivatives. Diazotization of ArNH$_2$ with strongly electrophilic ruthenium mononitrosyl complex was examined.

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