Nitro–ruthenium(II)–arylazoimidazoles: synthesis, spectra, crystal structure and electrochemistry of dinitro-bis{1-alkyl-2-(arylazo)imidazole}ruthenium(II). Nitro–nitroso derivatives and reactivity of the electrophilic {Ru-NO}[6] system

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Silver ion assisted aquation of blue *cis,trans,cis*-$RuCl_2(RaaiR')_2$ (**4–6**) leads to solvento species, blue–violet *cis,trans,cis*-$[Ru(OH_2)_2(RaaiR')_2](ClO_4)_2$ [$RaaiR'$ = *p*-R–C_6H_4–N=N–C_3H_2–NN-1-R' (**1–3**), abbreviated as N,N'-chelator where N(imidazole) and N(azo) represent N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**1/4/7/10**), CH_2CH_3(**2/5/8/11**), CH_2Ph (**3/6/9/12**)] that have been reacted with NO_2^- in warm ethanol resulting violet dinitro complexes of the type, $Ru(NO_2)_2(RaaiR')_2$ (**7–9**). The structure in one case, $[Ru(NO_2)_2(HaaiCH_2Ph)_2]$ (**9a**), has been established by X-ray diffraction as the *cis*-$Ru(NO_2)_2$ motif along with *trans*-N,N and *cis*-N',N' dispositions of the chelator N atoms around the coordination sphere. The nitrite complexes are useful synthons of electrophilic nitrosyls, and on triturating the compounds **7b–9b** with conc. $HClO_4$ nitro–nitrosyl derivatives, $[Ru(NO_2)(NO)(MeaaiR')_2](ClO_4)_2$ (**10b–12b**), are isolated. The solution structure and stereoretentive transformation in each reaction step have been established by ^{1}H NMR results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centred oxidation and successive ligand-based reductions. The redox potentials of $Ru(III)/Ru(II)$ ($E_{1/2}^M$) of **10b–12b** are anodically shifted by ∼0.2 V as compared to those of dinitro precursors **7b–9b**. The $v(NO) > 1900$ 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 (**12b**) by reacting with a bicyclic ketone, camphor, containing an active methylene group and an arylhydrazone with an active methine group, and the heteroleptic tris-chelates thus formed are characterised.

Introduction

For the last few years, nitric oxide (NO) has been the focus of discussion because of the discovery of its role in the immune defense mechanism, neuronal signaling process, cardiovascular system and in environmental chemistry.[1,2] The chemistry of transition metal nitrosyl complexes[3] in general and group 8 metal nitrosyls[4,5] in particular is of great interest in this regard. The search for suitable precursors to synthesize NO-complexes is a challenging domain[3] and nitrite compounds are found to be useful.[6]

Recently, we have developed the arylazoimidazole chemistry of ruthenium and synthesised dichloro componds $RuCl_2(RaaiR')_2$ (**4–6**)[7] and diaquo species[8] $[Ru(OH_2)_2(RaaiR')_2]^{2+}$ [$RaaiR'$ = *p*-R–C_6H_4–N=N–C_3H_2–NN-1-R' (**1–3**), R = H, Me, Cl and R' = Me, CH_2CH_3, CH_2Ph abbreviated as N,N'-chelator where N(imidazole) and N(azo) represent N and N', respectively]. Syntheses of hetero-tris-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}](ClO_4)_2$ [bpy = 2,2'-bipyridine; *n* = 2,[9] *n* = 1[8]) from the solvento complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$/ $[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres are reported by us.[8] In this paper, we examine the reactivity of NO_2^- towards $[Ru(OH_2)_2(RaaiR')_2]^{2+}$ and the reactions of the complexes derived therefrom. The nitrites $Ru(NO_2)_2(RaaiR')_2$ (**7b–9b**) are useful synthons of nitrosyls, and mono-nitrosyl compounds of type $[Ru(NO_2)(NO)(MeaaiR')_2](ClO_4)_2$ (**10b–12b**) are afforded in perchloric acid medium. The electro-

philicity of bound NO has been established by reacting with nucleophiles such as camphor (cmp), a bicyclic ketone with an active methylene group and an arylhydrazone (ahz) having an active methine group. The details of synthesis and characterisation are presented below.

Experimental

Measurements

UV–VIS (in MeCN) and IR (KBr discs, 4000–300 cm^{-1}) spectra were run with JASCO UV–VIS–NIR model V-570 and JASCO FTIR model 420 spectrophotometers, respectively. Electrical conductivities (in MeCN, solute concentration ∼10^{-3} M) were recorded using a Systronics conductivity bridge. Magnetic susceptibilities were measured with a PAR 155 vibrating sample magnetometer. The ^{1}H NMR spectra in CDCl₃ were carried on a Brucker 300 and 500 MHz FTNMR spectrometer using $SiMe_4$ as internal standard. Microanalyses (C, H and N) were done with a Perkin–Elmer 2400 CHNS/O elemental analyser. Electrochemical studies (in MeCN) were performed with a PARC electrochemistry system as described elsewhere.[9] In cyclic voltammetry (CV) the following parameters and relation were used: scan rate, 50 mV s^{-1}; formal potential $E^0 = 0.5(E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively;

ΔE_p is the peak–to–peak separation. For differential pulse voltammetry (DPV): scan rate, 10 mV s^{-1}; modulation amplitude (ΔE), 25 mV; $E^0 = E_p + 0.5(\Delta E)$ where E_p is the DPV peak potential. The agreement between E^0 data obtained by the two techniques was good (within ±5 mV). In constant potential coulometry experiments (oxidation done at potential $E^0 + 200$ mV); $n = Q/Q'$ where Q' is the calculated coulomb count for 1e transfer and Q is coulomb count found after exhaustive electrolysis of 0.01 mmol of solute. All experiments were done under a dry N$_2$ atmosphere at 295(2) K in a three electrode configuration by using a Pt-disk milli working electrode and a Pt-wire auxiliary electrode. The potentials are referenced to a saturated calomel electrode (SCE) and are uncorrected for the junction contributions.

Materials

Published methods were used to prepare RaaiR′,[7] ctc-RuCl$_2$(RaaiR′)$_2$,[7] ctc-[Ru(OH)$_2$)$_2$(RaaiR′)$_2$](ClO$_4$)$_2$,[8] alkylidenearylhydrazone, ArCH=NNHPh (Ar = Ph, p-MeC$_6$H$_4$),[10] arylazooxime ArN=NC(=NOH)Ph (Ar = Ph, phaaoH; Ar = p-MeC$_6$H$_4$, taaoH)[10] and camphorquinone monoxime (cmpoH).[10] All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, India). The purification of MeCN and preparation of tetrabutylammonium perchlorate [Bu$^n_4$N][ClO$_4$], respectively, used as solvent and supporting electrolyte in electrochemical experiments were done following a literature method.[8]

Preparation of the complexes

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

Cis,trans,cis-Dinitrobis{1-methyl-2-(*p*-tolylazo)imidazole}ruthenium(II), *ctc*-Ru(NO$_2$)$_2$(MeaaiMe)$_2$ (7b). Three independent methods were employed to synthesise **7b**.

Method (a). To an ethanolic blue–violet solution (15 ml) of *ctc*-[Ru(OH)$_2$)$_2$(MeaaiMe)$_2$](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. A violet solution that resulted was concentrated (4 ml) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with water 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 suspension of *ctc*-RuCl$_2$(MeaaiMe)$_2$ (**4b**) (0.1 g, 0.18 mmol) in ethanol (25 ml) was added an aqueous solution of AgNO$_3$ and the reaction mixture stirred at room temperature (300 K) for 2 h. AgCl so precipitated was filtered through a G-4 sintered crucible. An ethanolic solution of NaNO$_2$ (0.025 g, 0.35 mmol) was added to the filtrate, and the resulting mixture was stirred at room temperature for 8 h under a nitrogen atmosphere. The violet solution was concentrated by slow evaporation and the precipitate was processed as in method (a); yield, 0.047 g (45%).

Method (c). To a CH$_2$Cl$_2$–Me$_2$CO (1:1, v/v, 30 ml) solution of *ctc*-RuCl$_2$(MeaaiMe)$_2$ (**4b**) (0.1 g, 0.18 mmol) was added an H$_2$O–Me$_2$CO solution of NaNO$_2$ (0.024 g, 0.35 mmol). The mixture was stirred at 343–353 K for 30 h. The violet solution was processed as in method (a) to give analytically pure **7b**; yield, 0.021 g (20%).

The high yield in method (a) has prompted us to follow this route for syntheses of the other complexes **7a**, **7c**, **8a–8c** and **9a–9c**. The yields varied in the range 65–85%. Calc. for

C$_{20}$H$_{20}$N$_{10}$O$_4$Ru (**7a**): C, 42.47; H, 3.54; N, 24.77. Found: C, 42.34; H, 3.41; N, 24.98%. Calc. for C$_{22}$H$_{24}$N$_{10}$O$_4$Ru (**7b**): C, 44.51; H, 4.05; N, 23.60. Found: C, 44.34; H, 3.95; N, 23.68%. Calc. for C$_{20}$H$_{18}$N$_{10}$O$_4$Cl$_2$Ru (**7c**): C, 37.85; H, 2.84; N, 22.08. Found: C, 37.64; H, 2.75; N, 22.17%. Calc. for C$_{22}$H$_{24}$N$_{10}$O$_4$Ru (**8a**): C, 44.51; H, 4.05; N, 23.60. Found: C, 44.46; H, 3.99; N, 23.56%. Calc. for C$_{24}$H$_{28}$N$_{10}$O$_4$Ru (**8b**): C, 46.37; H, 4.51; N, 22.54. Found: C, 46.48; H, 4.58; N, 22.49%. Calc. for C$_{22}$H$_{22}$N$_{10}$O$_4$Cl$_2$Ru (**8c**): C, 39.87; H, 3.32; N, 16.92. Found: C, 40.14; H, 3.21; N, 16.78%. Calc. for C$_{32}$H$_{28}$N$_{10}$O$_4$Ru (**9a**): C, 53.55; H, 3.90; N, 19.52. Found: C, 53.39; H, 3.85; N, 19.59%. Calc. for C$_{34}$H$_{32}$N$_{10}$O$_4$Ru (**9b**): C, 54.76; H, 4.29; N, 18.69. Found: C, 54.64; H, 4.35; N, 18.58%. Calc. for C$_{32}$H$_{26}$N$_{10}$O$_4$Cl$_2$Ru (**9c**): C, 48.85; H, 3.31; N, 17.81. Found: C, 48.74; H, 3.45; N, 17.63%.

Ctc-[Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (10b). *ctc*-Ru(NO$_2$)$_2$-(MeaaiMe)$_2$ (**7b**) (0.1 g, 0.17 mmol) and conc. HClO$_4$ (3 ml) were taken in a small beaker, and the mixture was triturated with a glass rod for 1 h. The colour of the mixture immediately changed from violet to deep red. The pasty mass was extracted with CH$_2$Cl$_2$ (4 × 5 ml) and concentrated under reduced pressure. The dark red crystalline product was separated by filtration, washed with chilled water containing a few drops of dil. HClO$_4$ and dried *in vacuo* over P$_4$O$_{10}$ to yield analytically pure **10b**. The yield was 0.092 g (70%). **11b** [yield, 0.078 g (60%)] and **12b** [yield 0.081 g (65%)] were prepared similarly starting with **8b** (0.1 g, 0.16 mmol) and **9b** (0.1 g, 0.13 mmol), respectively. Calc. for C$_{22}$H$_{24}$N$_{10}$O$_{11}$Cl$_2$Ru (**10b**): C, 34.02; H, 3.09; N, 18.04. Found: C, 34.14; H, 3.20; N, 18.16%. Calc. for C$_{24}$H$_{28}$N$_{10}$O$_{11}$Cl$_2$Ru (**11b**): C, 35.82; H, 3.48; N, 17.41. Found: C, 35.74; H, 3.61; N, 17.36%. Calc. for C$_{34}$H$_{32}$N$_{10}$O$_{11}$Cl$_2$Ru (**12b**): C, 43.96; H, 3.45; N, 15.08. Found: C, 43.64; H, 3.56; N, 15.24%.

Interconversion: [Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (10b) → Ru(NO$_2$)$_2$(MeaaiMe)$_2$ (7b). To an aqueous solution of **10b** (0.1 g, 0.13 mmol) was added an equivalent amount of KOH in the same solvent. The orange–red solution immediately turned violet, which was extracted with CH$_2$Cl$_2$. The solvent was removed by evaporation under reduced pressure and the pasty mass, dissolved in a minimum volume of dichloromethane, was chromatographed on an alumina (neutral) column. A deep violet band was eluted by toluene–acetonitrile (4:1, v/v). The identity of the product as **7b** was checked by comparing its properties with an authentic sample. The yield is almost quantitative.

[Ru(cmpo)(MeaaiMe)$_2$]ClO$_4$ (13). *Method (a): coupling with nitroso derivative.* To a solution of [Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (0.2 g, 0.26 mmol) in 20 ml MeOH were added 0.032 g (0.26 mmol) camphor (cmp) and NaOMe (0.015 g, 0.26 mmol), and the mixture was refluxed 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 water followed by Et$_2$O and dried *in vacuo* over P$_4$O$_{10}$. The dry mass was dissolved in a minimum volume of CH$_2$Cl$_2$ and was chromatographed through 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 **13** was obtained after drying *in vacuo* over P$_4$O$_{10}$. The yield was 0.14 g (70%).

Method (b): direct reaction with diaquo complex. 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$_2$)$_2$-(MeaaiMe)$_2$](ClO$_4$)$_2$ (0.2 g, 0.27 mmol) in 20 ml MeOH, and the mixture was refluxed for 4 h. The solution was cooled and processed as in method (a). The yield was 0.16 g (75%).

The product from methods (a) and (b) gave same analytical results. Calc. for $C_{32}H_{38}N_9O_6ClRu$ (**13**): C, 49.17; H, 4.87; N, 16.13. Found: C, 49.08; H, 4.74; N, 15.99%.

[Ru(taao)(MeaaiMe)₂]ClO₄ (14b). *Method (a): Coupling with nitroso derivative.* To a methanolic solution (20 ml) of [Ru(NO₂)(NO)(MeaaiMe)₂](ClO₄)₂ (0.2 g, 0.26 mmol) equivalent amounts of *p*-Me–C₆H₄–CH=NNHPh (0.054 g, 0.26 mmol) and NaOMe (0.015 g, 0.26 mmol) were added, and 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 its original and cooled. A saturated aqueous solution of NaClO₄ was added to it. The precipitate that resulted was filtered and dried. Analytically pure **14b** was obtained by column chromatography as described in **13**. The yield was 0.15 g (70%). [Ru(phaao)(MeaaiMe)₂]ClO₄ (**14a**) was prepared (yield, 75%) similarly using PhCH=NNHPh instead of *p*-Me–C₆H₄–CH=NNHPh.
Method (b): Direct reaction with diaquo complex. 0.065 g, (0.27 mmol) *p*-Me–C₆H₄–C(=NOH)N=NPh (taaoH) and 0.015 g (0.27 mmol) NaOMe were added to a methanolic solution (20 ml) of [Ru(OH₂)₂(MeaaiMe)₂](ClO₄)₂ (0.2 g, 0.27 mmol) and heated to reflux for 4 h. The reaction solution was processed as above to give **14b** [yield, 0.17 g (75%)]. **14a** was prepared [yield, 70%] similarly using PhC(=NOH)N=NPh (phaaoH) instead of *p*-Me–C₆H₄–C(=NOH)N=NPh (taaoH). Analyses from both methods are same. Calc. for $C_{35}H_{34}N_{11}O_5ClRu$ (**14a**): C, 50.77; H, 4.13; N, 18.89. Found: C, 50.68; H, 4.23; N, 18.94%. Calc. for $C_{36}H_{37}N_{11}O_5ClRu$ (**14b**): C, 51.49; H, 4.21; N, 18.36. Found: C, 51.32; H, 4.12; N, 18.21%.

X-Ray structure determination of Ru(NO₂)₂(HaaiCH₂Ph)₂ (9a)

Crystals suitable for the X-ray diffraction study of dinitrobis{1-benzyl-2-(phenylazo)imidazole}ruthenium(II), Ru(NO₂)₂(HaaiCH₂Ph)₂ (**9a**) were grown by slow diffusion of hexane into a dichloromethane solution of the complex at 298 K. X-Ray diffraction data were collected at 293 K with a Siemens SMART CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A summary of the crystallographic data and structure refinement parameters are given in Table 1. Data were corrected for Lorentzian polarization effects and for linear decay. Semi-empirical absorption corrections based on Ψ-scans were applied. The structure was solved by the direct method using SHELXS-86 and successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed geometrically and refined using a riding model. There is one water molecule per half of the complex. The solvate water was refined in three 1/3 occupancy sites; the oxygen positions were refined isotropically and water hydrogen-atoms were not included in the refinement.
CCDC reference number 190870. See http://www.rsc.org/suppdata/nj/b2/b204442k/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and formulation

The synthetic routes are shown in Scheme 1. Diaquo complexes, *ctc*-[Ru(OH₂)₂(RaaiR′)₂](ClO₄)₂, prepared by Ag⁺-assisted aquation of *ctc*-RuCl₂(RaaiR′)₂ (**4–6**), were reacted with NaNO₂ (excess amount > 3 mol) under stirring at 343–353 K in aqueous alcohol to give Ru(NO₂)₂(RaaiR′)₂ (**7–9**) in good yield [method (a), 65–85%]. The dinitrites **7–9** were also synthesized either directly on stirring RuCl₂(MeaaiMe)₂ with NaNO₂ in dichloromethane–acetone for 30 h [method (c); yield, 20%] or *in situ* synthesis of the aquo complex from

RuCl₂(MeaaiMe)₂ by AgNO₃ followed by the reaction with NaNO₂ [method (b); yield, 45%]. The low yield in method (c) may be due to the inertness of the Ru–Cl bond in such reaction conditions while Ag⁺-assisted halide displacement enhances the yield in method (b). The high yield in method (a) results from the use of the solvento complex containing labile reaction centres.[8] The composition of the complexes is supported by microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t_{2g}^6, $S = 0$). The structure of the dinitro derivative has been examined in one case (**9a**) by X-ray crystallography. Trituration[6] of solid Ru(NO₂)₂(MeaaiR′)₂ (**7b–9b**) in concentrated HClO₄ at ambient condition gives an orange–red solution from which the nitrosyl complexes [Ru(NO₂)(NO)(MeaaiR′)₂](ClO₄)₂ (**10b–12b**) are isolated. In alkaline media nitrosyl complexes, **10b–12b**, regenerate the corresponding nitrite precursors (**7b–9b**). The reaction of H⁺ with the coordinated NO₂ group in nitrite complexes and the nucleophilic attack of OH⁻ on the NO⁺ in nitrosyls are the key steps for such reactions.[11]
The violet dinitrites **7–9** are soluble in common organic solvents but insoluble in H₂O whereas the orange–red nitrosyls **10b–12b** are soluble in water and in a range of common organic solvents *viz.*, methanol, ethanol, acetone, acetonitrile, chloroform, dichloromethane. In MeCN, **10b–12b** behave as 1:2 electrolytes ($\Lambda_M = 140$–160 Ω⁻¹ cm² mol⁻¹) whereas non-electrolytic behaviour is seen for type **7–9** complexes as indicated by their very low Λ_M values (10–20 Ω⁻¹ cm² mol⁻¹).

Molecular structure

The single crystal X-ray structure of Ru(NO₂)₂(HaaiCH₂Ph)₂ (**9a**) is shown in Fig. 1, and the bond parameters are collected in Table 2. The structure shows a distorted octahedron around the metal centre with six N donor set (RuN₆) arising from two N(azo), two N(imidazole) and two N(nitro) donor centres. A crystallographic 2-fold rotation axis passes through Ru. Two atomic groups Ru, N(1a), N(6a), N(1), N(20a) (plane 1) and Ru, N(1a), N(20), N(1), N(6) (plane 2) constitute excellent

$RuCl_2(RaaiR')_2$ $\xrightarrow{(i)}$ $[Ru(OH_2)_2(RaaiR')_2](ClO_4)_2$ $\xrightarrow{(ii)}$ $Ru(NO_2)_2(RaaiR')_2$

(iii) ↓↑ (iv)

$[Ru(NO_2)(NO)(MeaaiR')_2](ClO_4)_2$

RaaiR'
1-3

R = H (**a**), Me (**b**), Cl (**c**);

R' = Me (**1/4/7/10b**), CH$_2$CH$_3$ (**2/5/8/11b**),

CH$_2$Ph (**3/6/9/12b**)

X = Y = Cl (**4 - 6**), n = 0; X = Y = NO$_2$ (**7 – 9**), n = 0

X = NO, Y = NO$_2$ (**10b – 12b**), n = 2
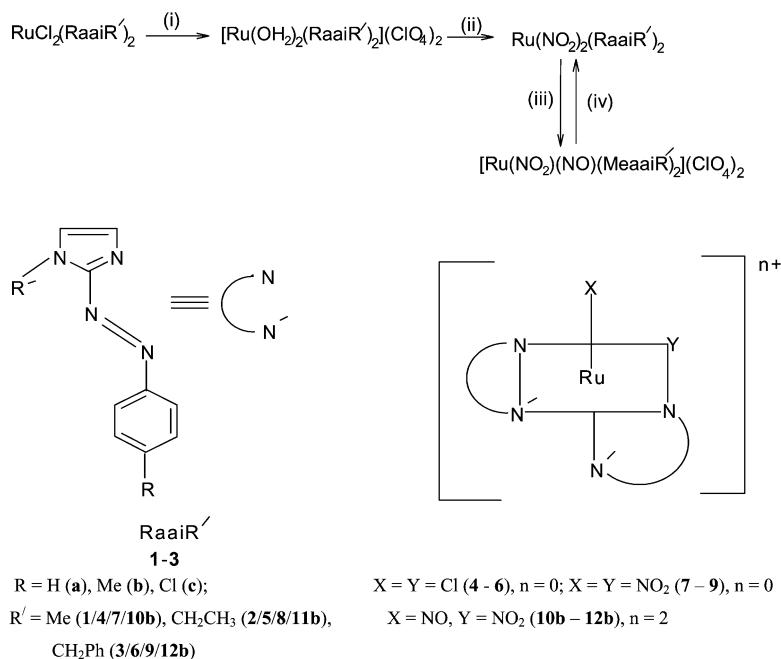
Scheme 1 *Reagents and conditions*: (i) AgNO$_3$, EtOH–H$_2$O (1:1, v/v), reflux, NaClO$_4$; (ii) NaNO$_2$, EtOH–H$_2$O, stir, 343–353 K; (iii) conc. HClO$_4$; (iv) KOH, MeCN.

planes (max. deviation from mean plane by $\leqslant 0.03$ Å). The atomic group Ru, N(20), N(20a), N(6), N(6a) (plane 3) constitutes a good plane and deviate by 0.13 Å from the mean plane. Planes 1 and 2 are orthogonal (88°) and plane 3 inclines at an angle 97° with other two planes separately. Two chelate planes constituting the set of atoms Ru, N(1a), C(2a), N(2a), N(6a), and Ru, N(1), C(2), N(2), N(6), respectively (mean deviation < 0.01 Å) are mutually orthogonal (86°) to each other. The pendant phenyl group to each chelate ring is no longer planar and makes dihedral angle of 54° with the respective chelate ring. The bite angle N(1)–Ru–N(6)/N(1a)–Ru–N(6a) is 76.2(3)° and is deviated from regular pentagonal angle. This may cause distortion to octahedral geometry. The angles N(6)–Ru–N(20)/N(6a)–Ru–N(20a), 170.91(4)° and N(1)–Ru–N(1a), 172.4(4)° are reduced from *trans* angular

values due to acute chelate bite angles.[7,9] The N–N distance is 1.293(9) Å and is longer than the free ligand value [1.250(1) Å].[12] The increase in bond length supports charge delocalisation, dπ Ru(II) $\rightarrow$ π* ligand (N=N). The coordination of N(azo) with Ru can lead to decrease in the bond order due to both σ-donor and π-acceptor character of the ligand—the latter having a more pronounced effect.[7,13] The Ru–N(azo) [N(6)/N(6a)] and Ru–N(imidazole) [N(1)/N(1a)] bond distances are equivalent at 2.035 Å which is unusual. In general, complexes of ruthenium(II)–1-alkyl-2-(arylazo)imidazoles[7] show shorter Ru–N(azo) distances than Ru–N(imidazole)—supporting metal-to-ligand charge transfer to be localized on the azo bond (N=N) (*vide infra*). This strengthens the π-acidic nature of the ligand system. The electron withdrawing *cisoid* NO$_2$ groups compete with azo N atoms to withdraw metal d-electrons. Again the azo groups lie *trans* to –NO$_2$ groups, thus they are in competition for the same metal dπ orbitals. This may cause elongation of the Ru–N(azo) distance and the accidentally equivalence to the Ru–N(imidazole) bond length, which is not[7–9] the case for RuCl$_2$(RaaiR')$_2$ and [Ru(bpy)$_n$(RaaiR')$_{3 - n}$](ClO$_4$)$_2$. The NO$_2$ groups display some disorder of the oxygen atoms—one oxygen [O(1)] was refined with 100% occupancy, the remaining two sites [O(2) and O(3), assigned in Fig. 2) were refined with 50% occupancies. Fig. 1 omits O(3) for clarity. There is one half molecule of water per molecule of the complex.

A molecular packing view is shown in Fig. 2. An interesting hydrogen bonded one-dimensional (1D) wave is observed where every molecular unit present as W or M motif. Two 1-CH$_2$Ph group act as two wings in the motif and two (N=N)-Ph groups cross each other. An intramolecular π–π interaction between two 1-CH$_2$Ph groups is noticed. Molecular units are hydrogen bonded to constitute one-dimentional (1D) chain. Imidazolyl-H(4) is hydrogen bonded with disordered O(2)/ O(3)–N and –CH$_2$– of 1-CH$_2$Ph forms hydrogen bonding with the O–N(NO$_2$) group of neighbouring molecule. Thus, H-bonding constructs a 1D chain. The pendant phenyl and (1-CH$_2$)Ph are in efficient C–H···π interaction with optimum distance between the centre of gravity of the phenyl ring and H(8a)/H(14a) (range of 2.94–3.27 Å).[14] The hydrogen bonding parameters are listed in Table 2.
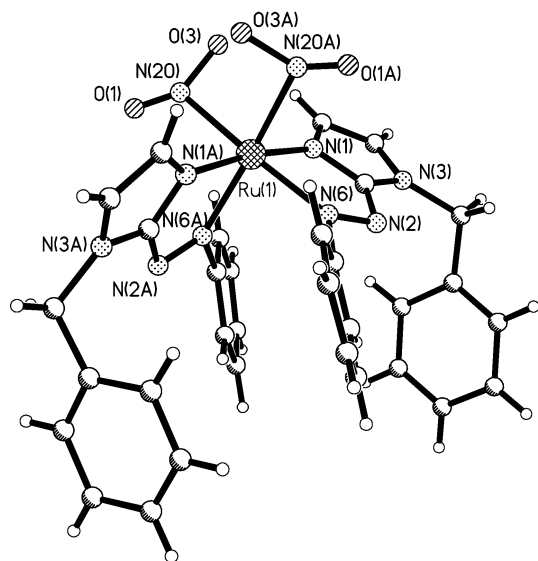
Fig. 1 Single crystal X-ray structure of Ru(NO$_2$)$_2$(HaaiCH$_2$Ph)$_2$ (**9a**).

Table 2 Selected bond distances (Å) and angles (°) for *ctc*-[Ru(NO₂)₂(HaaiCH₂Ph)₂]·0.5H₂O

Distances/Å		Angles/°	
Ru–N(1)	2.035(7)	N(1)–Ru–N(6)	76.2(3)
Ru–N(6)	2.035(6)	N(20)–Ru–N(20A)	89.8(8)
Ru–N(20)	2.137(13)	N(1)–Ru–N(1A)	172.4(4)
N(2)–N(6)	1.293(9)	N(1)–Ru–N(6A)	98.3(3)
N(20)–O(1)	1.01(2)	N(1)–Ru–N(20)	94.8(4)
N(20)–O(3)	1.32(4)	N(1A)–Ru–N(20)	90.6(4)
		N(1A)–Ru–N(20A)	94.8(4)
		N(6)–Ru–N(6A)	88.3(3)
		N(6A)–Ru–N(20)	91.6(4)
		N(6)–Ru–N(20)	170.9(4)

Hydrogen bonding parameters

Donor (D)	H	Acceptor (A)	D–H/Å	H–A/Å	D–A/Å	D–H–A/°
C(4)	H(4A)	O(1)	0.9300	2.4880	3.3771	160.05
C(4)	H(4A)	O(2)	0.9300	2.3882	3.1235	135.85
C(10)	H(10A)	O(3)	0.9300	2.3294	3.0621	135.41
C(12)	H(12A)	O(2)	0.9699	2.4872	3.3495	148.01

X–H···Cg (π-ring) interactions

	X–Cg/Å	H-perpendicular to Cg (π-ring)/Å	X–H···Cg/°
C(8)–H(8A)···(C-6)	3.2012	3.181	138.14
C(14)–H(14A)···(C-5)	2.9367	2.724	128.30
C(18)–H(18A)···(C-5)	3.2767	3.109	123.37

Cg = centroid of (C-5) or (C-6). The (C-5) plane contains C6C7C8C9C10C11; (C-6) plane contains C13C14C15C16C17C18; (C-4) plane contains N1C2N3C4C5. Distances among the planes (Å), (C-5)–(C-5) 5.535(3), (C-5)–(C-4) 4.269(2), (C-4)–(C-4) 3.890(1), (C-6)–(C-5) 5.151(5), (C-6)–(C-4) 5.683(6) Å.

Spectral studies

Infrared spectra of dinitro complexes, Ru(NO₂)₂(RaaiR′)₂ (**7–9**) show a 1:1 correspondence to the spectra of dichloro analogue, *ctc*-RuCl₂(RaaiR′)₂ except the appearance of intense stretching at 1300–1335 and 1250–1280 cm⁻¹ with concomitant loss of *v*(Ru–Cl) at 320–340 cm⁻¹. They are assigned to *v*(NO)ₐₛ and *v*(NO₂)ₛ, respectively.[5,6,15] The *v*(N=N) and *v*(C=N) appear at 1365–1380 and 1570–1600 cm⁻¹, respectively. Mono-nitro–nitroso–ruthenium(II), [Ru(NO₂)(NO)-

(MeaaiR′)₂](ClO₄)₂ (**10b–12b**) show a very strong stretch in the range 1910–1925 cm⁻¹ which is conspicuously absent in the spectra of Ru(NO₂)₂(MeaaiR′)₂. This is certainly due to the stretching mode of *v*(NO) of the coordinated nitrosyl group.[3,4,11] The stretching frequency *v*(NO) qualitatively indicates the stereochemistry of M–N–O bonding. Usually, *v*(NO) > 1700 cm⁻¹ has been assigned to linear M–N–O bond.[11,16,17] Thus this present series of Ru–NO complexes are assumed to be linear. Other important frequencies are *v*(H₂O) at 3350–3400 cm⁻¹ and *v*(ClO₄) at 1140–1145, 1110–1120 and 1080–1090 cm⁻¹ along with weak bands at 640 and 625 cm⁻¹. Triplet splitting pattern of ClO₄ may be due to some sort of hydrogen bonding interaction, Cl–O···H(O/C) (*vide supra*).[9,18]

The solution electronic spectra of these new complexes were recorded in dry acetonitrile. Dinitro complexes **7–9** exhibit multiple transitions in the UV–visible region (Table 3, Fig. 3). They display an intense MLCT transition in the range 550–560 nm along with weak longer wavelength absorption at 740–750 nm. The transitions are blue shifted by ~40 nm as compared with corresponding dichloro derivatives, RuCl₂(RaaiR′)₂. In the nitroso derivatives [Ru(NO₂)(NO)-(MeaaiR′)₂](ClO₄)₂ (**10b–12b**) the intense absorption bands are further shifted to shorter wavelength, 400–420 nm along with a weak band at 600–620 nm. This is attributed to strong dπ(Ruᴵᴵ) → π*(NO) back bonding which stabilizes the dπ level and consequently shifts the MLCT band to lower wavelength.[5,6,15] The nitrosyl complexes are found to be stable only in dry acetonitrile solutions. 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 (**7b**) isolation in one case (**10b**) and characterized comparing its properties with authentic sample.

The ¹H NMR spectra of Ru(NO₂)₂(RaaiR′)₂ (**7–9**) complexes were unambiguously assigned (Table 4) on comparing
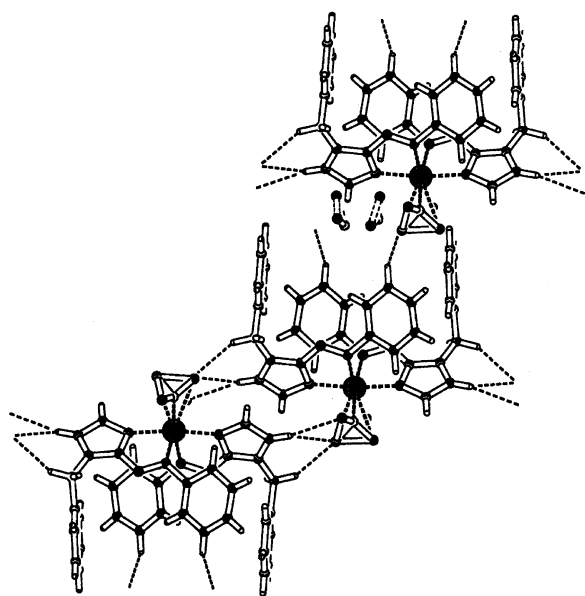

Fig. 2 Molecular packing view of **9a** along the *z*-axis showing hydrogen bonds and the 1-D chain.

Table 3 UV–VIS[a] and cyclic voltammetric[b] data

| Complex | UV-Vis spectral data,[a] λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1}) | Cyclic voltammetric data,[b] E/V (ΔE_P/mV) | | |
		E^{M1}	E^{M2}	$-E^{L}$
Ru(NO$_2$)$_2$(HaaiMe)$_2$ (**7a**)	741 (0.596),[d] 552 (8.379), 420 (8.914),[d] 371 (18.3)	1.184 (110)	0.531 (130)[e]	0.381 (80), 0.659 (130), 1.212[f]
Ru(NO$_2$)$_2$(MeaaiMe)$_2$ (**7b**)	746 (0.544),[d] 549 (6.773), 420 (12.271), 379 (17.791)	1.141 (115)	0.521 (100)[e]	0.407 (95), 0.691 (120), 1.282[f]
Ru(NO$_2$)$_2$(ClaaiMe)$_2$ (**7c**)	744 (0.906),[d] 556 (13.919), 424 (23.416),[d] 380 (40.721)	1.251 (107)	0.551 (110)[e]	0.344 (80), 0.673 (100), 1.201[f]
Ru(NO$_2$)$_2$(HaaiEt)$_2$ (**8a**)	745 (0.684),[d] 550 (8.796), 416 (10.081),[d] 376 (20.755)	1.198 (120)	0.551 (140)[e]	0.377 (80), 0.632 (75), 1.021[f], 1.251[f]
Ru(NO$_2$)$_2$(MeaaiEt)$_2$ (**8b**)	739 (0.717),[d] 547 (8.752), 423 (17.149),[d] 380 (23.694)	1.211 (80)	0.521 (130)[e]	0.383 (85), 0.647 (100), 1.131[f], 1.301[f]
Ru(NO$_2$)$_2$(ClaaiEt)$_2$ (**8c**)	746 (0.821),[d] 560 (12.017), 420 (21.796),[d] 379 (38.537)	1.268 (100)	0.601 (100)[e]	0.358 (80), 0.624 (100), 0.958 (130), 1.281[f]
Ru(NO$_2$)$_2$(HaaiCH$_2$Ph)$_2$ (**9a**)	744 (0.612),[d] 552 (9.296), 424 (10.944),[d] 376 (22.199)	1.252 (91)	0.561 (110)[e]	0.354 (80), 0.608 (100), 1.081[f], 1.351[f]
Ru(NO$_2$)$_2$(MeaaiCH$_2$Ph)$_2$ (**9b**)	746 (0.752),[d] 546 (7.281), 426 (11.984),[d] 382 (19.832)	1.213 (120)	0.531 (130)[e]	0.374 (65), 0.640 (100), 0.968,[f] 1.324[f]
Ru(NO$_2$)$_2$(ClaaiCH$_2$Ph)$_2$ (**9c**)	749 (0.578),[d] 562 (8.429), 425 (18.349),[d] 380 (25.782)	1.301 (125)	0.631 (140)[e]	0.334 (75), 0.588 (95), 0.935 (140), 1.292[f]
[Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (**10b**)[c]	552 (3.093),[d] 388 (8.719), 265 (9.021)[d]	1.390 (110)	0.521 (120)	0.173[f], 0.371 (85), 0.651 (130), 1.231[f]
[Ru(NO$_2$)(NO)(MeaaiEt)$_2$](ClO$_4$)$_2$ (**11b**)[c]	550 (3.996),[d] 408 (10.616), 258 (12.403)	1.410 (110)	0.501 (130)	0.134[f], 0.401 (80), 0.711 (120), 1.271[f]
[Ru(NO$_2$)(NO)(MeaaiCH$_2$Ph)$_2$](ClO$_4$)$_2$ (**12b**)[c]	555 (3.118),[d] 412 (13.016), 260 (14.469)[d]	1.532 (120)	0.581 (130)	0.212[f], 0.351 (85), 0.621 (120), 1.221[f]
[Ru(cmpo)(MeaaiMe)$_2$](ClO$_4$) (**13**)[c]	572 (6.461),[d] 531 (8.443), 385 (15.584), 278 (11.599)	1.342 (110)	0.651 (100)	0.350 (100), 0.657 (120), 1.171[f]
[Ru(phaao)(MeaaiMe)$_2$](ClO$_4$) (**14a**)[c]	783 (1.008)[d], 560 (3.997), 387 (18.987), 283 (13.765)	1.274 (140)		0.363 (100), 0.641 (110), 0.891 (140), 1.351[f]
[Ru(taao)(MeaaiMe)$_2$](ClO$_4$) (**14b**)[c]	772 (1.017)[d], 574 (4.257), 488 (6.886)[d], 391 (20.219), 282 (15.211)	1.164 (130)		0.384 (110), 0.691 (90), 0.931 (150), 1.444[f]

[a] In 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. $\sim$10^{-3} M, scan rate 50 mV s^{-1}, E^M. eqn. (3), E^L: ligand reductions, $\Delta E_P = |E_{pa} - E_{pc}|$V where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential. [c] Solvent super dry MeOH for UV-VIS spectra. [d] Shoulder [e] Half wave potential of the couple generated on second and subsequent scans for Ru(NO$_2$)$_2$(RaaiR')$_2$ as given in eqn. (4), E^{M2} = current height increases with number of cycles. [f] E_{pc}
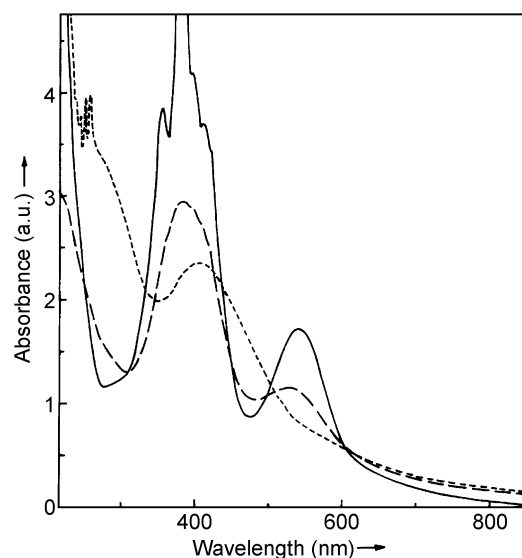
Fig. 3 Electronic spectra of Ru(NO₂)₂(MeaaiCH₂CH₃)₂ (**8b**) (——), [Ru(NO₂)(NO)(MeaaiCH₂CH₃)₂](ClO₄)₂ (**12b**) (···), [Ru(cpmo)-(MeaaiMe)₂]ClO₄ (**13**) (---) in dry acetonitrile.

with RuCl₂(RaaiR′)₂.[7] The aryl protons (7-H–11-H) of **7–9** are downfield shifted by 0.1–0.7 ppm as compared to those of the parent dichloro derivatives.[7–9] 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)-position. The aryl protons 7-(7′-)H and 11-(11′-)H resonate asymmetrically indicative of a magnetically anisotropic environment[7] even in the solution phase. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The 1-R′ (R′ = Me, CH₂CH₃, CH₂Ph) exhibit usual spin–spin interaction. 1-Me appears as a singlet at 4.2 ppm for Ru(NO₂)₂(RaaiMe)₂; the methylene protons, 1-CH_2(CH₃) show AB type sextet (*ca.* 4.4, 4.6 ppm, *J* = 10–12 Hz) and (1-CH₂)CH_3 gives a triplet at 1.5 ppm (8.0 Hz) for Ru(NO₂)₂(RaaiCH₂CH₃)₂; 1-CH_2(Ph) protons appear as AB type quartets (*ca.* 5.5, 5.7 ppm) with geminal coupling constant av. 18 Hz in Ru(NO₂)₂(RaaiCH₂Ph)₂ (Fig. 4). Imidazole 4-

and 5-H appear as a doublet at lower frequency side of the spectra (7.0–7.2 ppm for 4-H; 6.9–7.1 ppm for 5-H). The aryl-Me (R = Me) in Ru(NO₂)₂(MeaaiR′)₂ (**7b–9b**) appears as a single peak at 2.30 ppm and is in consonance with stereo-retentive reaction. Isomerisation of *ctc*-isomer may lead to *ccc*-configuration which belongs to C_1-symmetry and would give two equally intense Ar-Me signals.[7] The mononitrosyls, [Ru(NO₂)(NO)(MeaaiR′)₂](ClO₄)₂ show a similar pattern of signals in the aromatic region and the spectra have been shifted to higher field by 0.03–0.15 ppm from those of respective dinitro derivatives. This is presumably be due to better dπ(Ru) → π*(NO) charge transfer[3,4,11] which increases the hardness of Ru(II) leading to strong σ-interaction with the chelator, MeaaiR′. The transformation, Ru(NO₂)₂(MeaaiR′)₂ → [Ru(NO₂)(NO)(MeaaiR′)₂]²⁺ reduces the overall symmetry of the product ($C_2 \rightarrow C_1$) and is supported through the appearance of two Ar-Me signals at 2.4 and 2.2 ppm in **10b–12b**. This has been indirectly proved by conversion of [Ru(NO₂)(NO)-(MeaaiMe)₂](ClO₄)₂ (**10b**) to *ctc*-Ru(NO₂)₂(MeaaiMe)₂ on treating with KOH solution and the latter gives an identical spectrum as shown by **7b**.

Redox properties

The potential values of the complexes in dry acetonitrile solution are given in Table 3 and representative voltammograms are shown in Fig. 5. The dinitrites **7–9** exhibit a quasi-reversible ($\Delta E_P \geqslant 100$ mV) oxidative response in the potential range 1.1–1.3 V [Table 3, Fig. 5(a)]. This is assigned to the Ru(III)/Ru(II) couple [eqn. (1)].

$$[Ru(NO)_2)_2(RaaiR')_2]^+ + e \rightleftharpoons [Ru(NO_2)_2(RaaiR')_2]\text{.......}$$
(1)
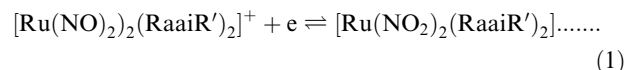
The one-electron stoichiometry of this couple is confirmed by constant potential electrolysis at 1.4 V *vs.* SCE in one case, Ru(NO₂)₂(HaaiMe)₂ (**7a**) and electron count ratio equals to 0.94. The potential $E_{1/2}^M$ is dependent on the substituent type R and R′. The present series of complexes show higher $E_{1/2}^M$ values than that of precursor dichloro derivatives **4–6** by ∼0.4 V. The better electron withdrawing property of NO₂⁻ over Cl⁻ stabilises the dπ shell of the metal and thus shifts the metal-centred redox process to more anodic values.[19] A similar com-

Table 4 ¹H NMR spectral data, δ/ppm (*J*/Hz) of the complexes in CDCl₃

Compound	9-Me	4-H[c]	5-H[c]	11-H[c]	7-H[c]	8,10-H	1-CH₃	1-CH₂	Others
7a[a]		7.15 (7.5)	7.06 (7.5)	8.03 (8.1)	7.80 (8.1)	7.45 (8.1)[d]	4.09[f]		
7b	2.31	6.98 (7.5)	6.86 (7.5)	8.17 (8.1)	8.04 (8.1)	7.34 (8.1)[c]	4.17[f]		
7c		7.13 (8.1)	7.02 (8.1)	8.15 (7.8)	7.95 (7.8)	7.55 (7.8)[c]	4.16[f]		
8a[a]		7.14 (7.5)	7.00 (7.5)	8.01 (7.8)	7.85 (7.8)	7.45 (8.1)[d]	1.52 (8.1)[d]	4.42, 4.55(10.0)[e]	
8b	2.30	7.02 (8.1)	6.94 (8.1)	8.11 (7.5)	8.04 (7.5)	7.12 (7.5)[c]	1.48(8.1)[d]	4.40,4.52 (11.0)[e]	
8c		7.13 (8.1)	7.06 (8.1)	8.14 (7.8)	8.06 (7.5)	7.61 (7.5)[c]	1.50 (8.1)[d]	4.45, 4.53 (11.0)[e]	
9a[a]		7.06 (7.8)	6.98 (7.8)	8.08 (8.1)	8.00 (8.1)	7.48 (8.1)[d]		5.48, 5.73 (15.0)[g]	7.2–7.4[h]
9b	2.30	6.97 (8.1)	6.85 (8.1)	8.21 (8.1)	8.10 (8.1)	7.10 (8.1)[c]		5.46, 5.73 (17.0)[g]	7.2–7.5[h]
9c		7.11 (7.8)	7.02 (7.8)	8.15 (8.1)	8.05 (8.1)	7.58 (8.1)[c]		5.44, 5.70 (18.0)[g]	7.2–7.6[h]
10b	2.44, 2.23	7.18 (8.1)	6.99 (8.1)	8.25 (8.1)	8.18 (8.1)	7.49 (8.1)[c]	4.36[f]		
11b	2.40, 2.16	7.15 (8.1)	7.02 (8.1)	8.19 (7.8)	8.09 (7.8)	7.44 (7.8)[c]	1.61(8.1)[d]	4.52, 4.65 (12.0)[e]	
12b	2.45, 2.21	7.20 (7.5)	7.01 (7.5)	8.27 (7.8)	8.20 (7.8)	7.52 (7.8)[c]		5.50, 5.74 (18.0)[g]	
13	2.29, 2.38	7.07 (7.8)	6.88 (7.8)	8.10 (7.5)	7.84 (7.5)	7.14 (8.1)[c]	4.03[b], 4.18[b]		1.02–1.20[i], 1.55–1.75[i]
14a	2.35, 2.39	6.96 (8.1)	6.72 (8.1)	8.17 (8.1)	7.95 (8.1)	7.20 (8.1)[c]	4.02[b], 4.11[b]		7.40–7.70[j]
14b[l]	2.33, 2.35, 2.39, 2.42	6.95 (7.5)	6.74 (7.5)	8.15 (8.1)	7.92 (8.1)	7.20 (8.1)[c]	3.98, 4.02, 4.06, 4.10		7.35–7.70[j], 2.48[k]

[a] δ(9-H) 7.60 ppm(m). [b] δ (9-Me). [c] Doublet. [d] Triplet. [e] AB type sextet, geminal coupling constant. [f] 1-Me, singlet. [g] AB type quartet, geminal coupling constant. [h] Phenyl-H. [i] camphor –CH₂– and –CH– signals. [j] Phenyl-H of Phaao. [k] Phenyl-Me of taao. [l] Four Ar-Me and 1-Me signals appear in the intensity ratio 2:2:1:1.

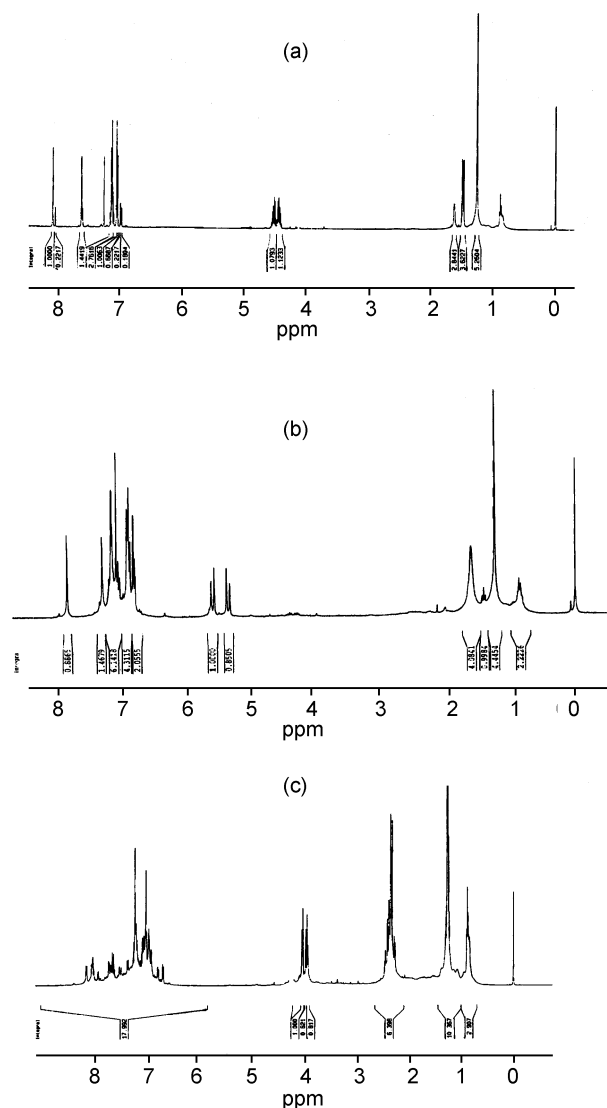**Fig. 5** Cyclic voltammogram of (a) Ru(NO$_2$)$_2$(MeaaiMe)$_2$ (**7b**) (——), repeat cycles show the generation of a new couple (· · ·) and (b) [Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (**10b**) in MeCN using a Pt-disk milli electrode at 298 K, SCE reference and TBAP (0.1 M) supporting electrolyte.

Fig. 4 ^{1}H NMR spectra of (a) Ru(NO$_2$)$_2$(ClaaiCH$_2$CH$_3$)$_2$ (**8c**), (b) Ru(NO$_2$)$_2$(HaaiCH$_2$Ph)$_2$ (**9a**) and (c) [Ru(taao)(MeaaiMe)$_2$]ClO$_4$ (**14b**) in CDCl$_3$ at 298 K.

plex with a diimine system, [Ru(NO$_2$)(py)(bpy)$_2$]$^+$ displays the Ru(III)/Ru(II) couple at ~1.0 V *vs.* SCE.[20,21] The stronger π-acidic nature of RaaiR′ compared to the α-diimine system leads to better stabilisation of Ru(II) in the present series of complexes. The cyclic voltammogram of Ru(NO$_2$)$_2$(RaaiR′)$_2$ exhibits some unusual behaviour on 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 [Fig. 5(a)]. The first primary redox process ($E_{1/2}^{MI}$ = 1.1–1.3 V) is assigned to the Ru(III)/Ru(II) couple [eqn. (1)] and the newly generated wave at ($E_{1/2}^{M2}$) 0.5–0.6 V may be assigned[20] to [Ru^{II}(NO$_2$)(NO)(MeaaiR′)$_2$]$^{2+}$/ [Ru^{II}(NO$_2$)(NO)(MeaaiR′)$_2$]$^+$. The nitrosyl complexes, [Ru(NO$_2$)(NO)(RaaiR′)$_2$](ClO$_4$)$_2$ exhibit multiple redox responses in the potential range +2.0 to −2.0 V *vs.* SCE. Two quasi-reversible reductive responses in the potential range 0.5 to 0.6 V and −0.1 to −0.2 V are seen (Fig. 5). 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 **10b**. 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–VI, Table 3) has been confirmed by differential pulse voltam-
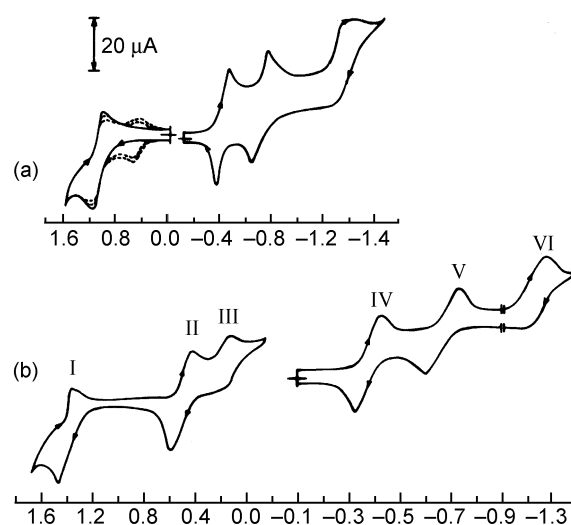
metry experiments. The couples IV and V are assigned to successive one-electron reductions of the coordinated NO$^+$ unit; [{Ru–NO}$^+$ → {Ru–NO} (couple II), {Ru–NO} → {Ru–NO}$^-$ (couple III). Couple III is irreversible indicating instability of the reduced species. The assignment is based on earlier observations of similar Ru–bipyridine[21] and Ru–azopyridine[11] systems. The potential values of the present set of complexes lie between those of analogous bipyridine and azopyridine complexes and follow the order azopyridine > azoimidazole > bipyridine. This is in line of π-acidity order of these different ligand systems.[22] The high potential voltammetric wave at 1.4–1.5 V (couple I) ($\Delta E_P \geqslant 120$ mV) [Fig. 5(b)] is assigned to the Ru(III)/Ru(II) couple. The one-electron stoichiometry of the couples is assigned by comparison of current heights in differential pulse voltammetry experiments. Successive reductions on the negative side of SCE were observable and their one-electron nature was confirmed by comparing the current heights of these process with that of the couple of eqn. (1) in the differential pulse voltammetry experiments and are assigned to the reduction of coordinated ligand. The azo group in RaaiR′ may accommodate two electrons[7] and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window only three reductions were observable.

Reactivity of [Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$

The nitrosyl complexes exhibit a high degree of electrophilic character[3,4,11,17] of the coordinated NO [v(NO) > 1900 cm^{-1}]. The electrophilic behaviour of these new complexes has been investigated by reacting camphor (cmp), a compound having an active methylene group and arylhydrazone (ahz), an organic substrate with active methine group. Methanolic solutions of [Ru(NO$_2$)(NO)(MeaaiMe)$_2$](ClO$_4$)$_2$ (**10b**) reacted smoothly with camphor (cmp) and arylhydrazone (ahz) in the presence of an organic base, *viz.*, NaOMe. The progress of the reaction was followed by monitoring the v(NO) decrease 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 reactions (2) and (3). These reactions

$$(2)$$

$$(3)$$
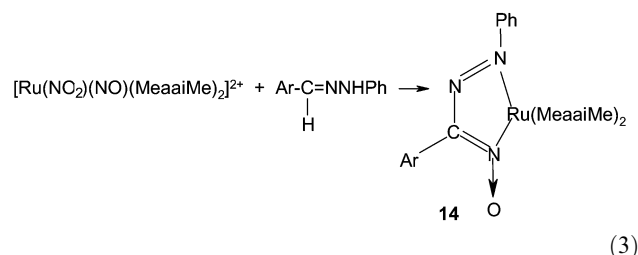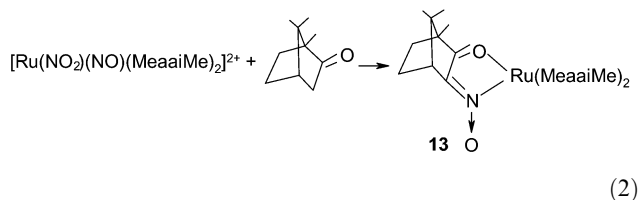
proceed very slowly in the absence of base. However, addition of a base, *viz.* NaOMe, to the reaction mixture changes the solution colour from orange–red to red–violet. The reaction involves electrophilic addition[17,20] of the coordinated nitrosyl to the activated methylene/methine group (formed by the added base) of the ketone/hydrazone forming a bound oxime (camphorquinone monoxime (**13**), phenylazooxime (**14a**) and *p*-tolylazooxime (**14b**). Deprotonation of active –CH$_2$–/ =CH– groups leads to the generation of a carbanion which subsequently attacks electrophilic NO$^+$ and results in camphorquinone monoxime (**13**) and arylazoxime (**14**) chelate rings, respectively, *via* expulsion of the –NO$_2$ group. Disappearance of ν(NO) at ~1910 cm^{-1} and the growth of ν(N→O) at 1280 cm^{-1} strongly support eqns. (2) and (3). To substantiate such nitrosation reaction a direct synthetic approach was adopted. The reaction of camphorquinone monoxime (cmpoH) and arylazooxime (aaoH) separately with the diaquo complex in boiling alcohol in presence of a base, respectively yielded **13** and **14** through solvolytic displacement followed by chelation of appropriate oximates. Microanalytical, spectroscopic and electrochemical results of **13** and **14** obtained in both methods match well. The heteroleptic tris-chelates **13**/**14** may exist in two isomeric forms with stereoretentive *ctc*-Ru(MeaaiMe)$_2$ geometry. However, we cannot separate these isomers by a chromatographic purification process. The ^{1}H NMR spectra of the complexes suggest a mixture of isomers. The aliphatic region (2–5 ppm) is particularly useful to support the chemical reaction. There are four Ar-Me signals at 2.33, 2.35, 2.39 and 2.42 in the intensity ratio 2:2:1:1 and 1-Me appear at 3.98, 4.06, 4.02 and 4.10 ppm in the intensity ratio of 2:2:1:1 for [Ru(MeaaiMe)$_2$-(taao)]ClO$_4$. Two signals of 2:2 intensity ratio may be due to Me of MeaaiMe and the signals corresponding to 1:1 intensity ratio may refer to the Me group of the coordinated taao group. The appearance of a pair of Me signals of either MeaaiMe or taao supports two isomeric molecules in the mixture. [Ru(phaao)(MeaaiMe)$_2$]ClO$_4$ gives a pair of Ar-Me at 2.35, 2.39 and N(1)-Me at 4.02 and 4.11 ppm of equal intensity. [Ru(cmpo)(MeaaiMe)$_2$]ClO$_4$ shows a very complex pattern of proton signals in the aliphatic region, 1.02–1.20; 1.55–1.70; 2.29; 2.38 and 4.03, 4.18 ppm. Camphor –CH$_2$– and –CH– may be assigned to 1.02–1.20 and 1.55–1.70 ppm signals. The 9-Me MeaaiMe is assignable to the signals at 2.29 and 2.38 ppm and 1-Me refers to 4.03 and 4.18 ppm. A pair of signals indicates an isomeric mixture of complexes in solution. The aromatic region gives a very complex splitting pattern and assignments of the signals are not made. Cyclic voltammetric studies show an Ru(III)/Ru(II) couple at 1.2–1.3 V and successive ligand reductions on the negative side of SCE.

Conclusion

Dinitro complexes of ruthenium(II)–azoimidazoles, *ctc*-Ru(NO$_2$)$_2$(RaaiR′)$_2$ have been synthesised by stereoretentive reaction of the diaquo complexes [Ru(OH$_2$)$_2$(RaaiR′)$_2$]$^{2+}$ with nitrite ion, and characterised by spectroscopic and X-ray crystallographic studies. They are useful synthons for electrophilic mono-nitrosyls, [Ru(NO$_2$)(NO)(RaaiR′)$_2$](ClO$_4$)$_2$. The electrophilic activity of bound NO has been established through C–N bond formation *via* reaction with organic substrates containing active methylene (camphor)/methine groups (arylhydrazone). The complexes exhibit strong MLCT transitions. Voltammetric studies show Ru(III)/Ru(II) couples along with successive ligand-based reductions and additionally metal-bound NO$^+$ reduction in nitrosyl derivatives.

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