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Ruthenium nitrosyl complexes with 1,4,7-trithiacyclononane and 2,2'-bipyridine (bpy) or 2-phenylazopyridine (pap) coligands. Electronic structure and reactivity aspects[†]

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The present article describes ruthenium nitrosyl complexes with the $\{RuNO\}^6$ and $\{RuNO\}^7$ notations in the selective molecular frameworks of $[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}$ (4^{3+}), $[Ru^{II}([9]aneS_3)(pap)$ $(NO^{+})^{3+}$ (8³⁺) and $[Ru^{II}([9]aneS_{3})(bpy)(NO^{+})]^{2+}$ (4²⁺), $[Ru^{II}([9]aneS_{3})(pap)(NO^{+})]^{2+}$ (8²⁺) ([9]aneS₃ = 1,4,7-trithiacyclononane, bpy = 2,2'-bipyridine, pap = 2-phenylazopyridine), respectively. The nitrosyl complexes have been synthesized by following a stepwise synthetic procedure: $\{Ru^{II}-Cl\} \rightarrow$ $\{Ru^{II}-CH_3CN\} \rightarrow \{Ru^{II}-NO_2\} \rightarrow \{Ru^{II}-NO^+\} \rightarrow \{Ru^{II}-NO^+\}$. The single-crystal X-ray structure of 4^{3+} and DFT optimised structures of 4^{3+} , 8^{3+} and 4^{2+} , 8^{2+} establish the localised linear and bent geometries for {Ru–NO⁺} and {Ru–NO⁺} complexes, respectively. The crystal structures and $^{1}H/^{13}C$ NMR suggest the [333] conformation of the coordinated macrocyclic ligand ([9]ane S_3) in the complexes. The difference in π -accepting strength of the co-ligands, bpy in 4^{3+} and pap in 8^{3+} (bpy < pap) has been reflected in the v(NO) frequencies of 1945 cm⁻¹ (DFT: 1943 cm⁻¹) and 1964 cm⁻¹ (DFT: 1966 cm⁻¹) and $E^{\circ}(\{Ru^{II}-NO^{+}\}/\{Ru^{II}-NO^{+}\})$ of 0.49 and 0.67 V versus SCE, respectively. The v(NO) frequency of the reduced {Ru–NO[•]} state in 4^{2+} or 8^{2+} however decreases to 1632 cm⁻¹ (DFT: 1637 cm^{-1}) or 1634 cm^{-1} (DFT: 1632 cm^{-1}), respectively, with the change of the linear {Ru^{II}-NO⁺} geometry in 4^{3+} , 8^{3+} to bent {Ru^{II}-NO[•]} geometry in 4^{2+} , 8^{2+} . The preferential stabilisation of the eclipsed conformation of the bent NO in 4^{2+} and 8^{2+} has been supported by the DFT calculations. The reduced $\{Ru^{II}-NO^{\bullet}\}\$ exhibits free-radical EPR with partial metal contribution revealing the resonance formulation of $\{Ru^{II}-NO^{*}\}(major) \leftrightarrow \{Ru^{I}-NO^{*}\}(minor)$. The electronic transitions of the complexes have been assigned based on the TD-DFT calculations on their DFT optimised structures. The estimated second-order rate constant $(k, M^{-1} s^{-1})$ of the reaction of the nucleophile, OH⁻ with the electrophilic {Ru^{II}-NO⁺} for the bpy derivative (4^{3+}) of 1.39×10^{-1} is half of that determined for the pap derivative (8^{3+}), 2.84 × 10⁻¹ in CH₃CN at 298 K. The Ru–NO bond in 4^{3+} or 8^{3+} undergoes facile photolytic cleavage to form the corresponding solvent species {Ru^{II}-CH₃CN}, 2^{2+} or 6^{2+} with widely varying rate constant values, $(k_{\text{NO}}, \text{ s}^{-1})$ of 1.12×10^{-1} $(t_{1/2} = 6.2 \text{ s})$ and 7.67×10^{-3} $(t_{1/2} = 90.3 \text{ s})$, respectively. The photo-released NO can bind to the reduced myoglobin to yield the Mb-NO adduct.

Introduction

The relevance of nitrogen monoxide (NO) in biological processes including its role in neuro-signaling,¹ cardiovascular control,²

or in defence mechanisms against microorganisms and tumor cells³ makes it an attractive small molecule. At the cellular level, NO is known to be produced from L-arginine catalysed by the heme-containing enzyme NO synthase (NOS)⁴ and its deficiency facilitates a wide range of physiological disorders.⁵ The interaction of NO with the transition metal ions in biological fluids and its redox non-innocent features as cationic NO⁺, radical NO⁻, or anionic NO⁻ in the complex molecules have initiated an intense renewed research interest from the broader perspective of inorganic chemistry.⁶ This indeed has instigated the designing of newer nitrosyl complexes, especially iron nitrosyls, as the natural metal-binding centres.⁷ Though a large number of ruthenium nitrosyl derivatives are known for a long time in the literature,⁸ it has drawn considerable research interest in recent years primarily

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[†] Electronic supplementary information (ESI) available: Crystallographic materials, DFT data set and NMR, UV-vis. and EPR spectra (Tables S1–S15 and Fig. S1–S10). CCDC reference numbers 823376–823380. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10761e

due to their fascinating coordination chemistry,^{8a} and potential application as antitumor, and antiseptic agents,⁹ in catalysis¹⁰ and in photochemical processes.¹¹

In this context ruthenium nitrosyl complexes with the selective molecular frameworks of $[Ru^{II}(trpy)(AL)(NO^{+'})]^{n-12}$ and $[Ru^{II}(tpm)(AL)(NO^{+'})]^{n-13}$ incorporating meridionally and facially oriented tridentate ligands, 2,2':6',2"-terpyridine (trpy) and tris(1-pyrazolyl)methane (tpm), respectively, in combination with other ancillary ligands (AL) with varying electronic properties have been reported recently. The detailed studies reveal the significant contribution of the ancillary ligands, trpy/AL or tpm/AL in tuning the (i) electronic structural aspects, (ii) extent of electrophilicity of the coordinated NO⁺, (iii) accessibility of different redox states of NO (NO⁺, NO⁻, NO⁻), (iv) photolability of the Ru–NO⁺' bond and (v) reactivities of {Ru–NO⁺} and {Ru–NO⁺} with OH⁻ and O₂.

This indeed has initiated the present programme of dealing with the newer molecular frameworks of $[Ru^{II}([9]aneS_3)(bpy)(NO)]^n$ (**4**^{*n*}) and $[Ru^{II}([9]aneS_3)(pap)(NO)]^n$ (**8**^{*n*}) involving facially coordinated 1,4,7-trithiacyclononane ([9]aneS_3) and moderately π -accepting 2,2'-bipyridine (bpy) and strongly π -accepting 2phenylazopyridine (pap), respectively.



4ⁿ, **8**ⁿ

The present report describes the detailed synthetic and structural aspects of the nitrosyl derivatives, $\mathbf{4}^n$ and $\mathbf{8}^n$ including their precursor complexes. The electronic structures and subsequent reactivity aspects of $\mathbf{4}^n$ and $\mathbf{8}^n$ have been investigated by experimental and DFT studies. The specific effect of [9]aneS₃ in combination with bpy ($\mathbf{4}^n$) or pap ($\mathbf{8}^n$) on the {Ru–NO} moiety has been highlighted in relation with analogous reported systems.

It should be noted that the interaction of thiamacrocycle, 1,4,7-trithiacyclononane ([9]aneS₃) with various transition metal ions¹⁴ including ruthenium¹⁵ has been well studied from various perspectives of coordination chemistry. However, to the best of our knowledge there are only two reports till date, $[Re([9]aneS_3)(CO)_2(NO)](OTf)_2^{16a}$ and $[Ru(phpy)([9]aneS_3)(L)]BF_4^{16b}$ (phpy = phenylpyridine) which deal with the metal-nitrosyl chemistry in combination with [9]aneS₃.

Results and discussion

Synthesis, characterization and structural aspects

The nitrosyl complexes with the Enemark-Feltham notations¹⁷ of {RuNO}⁶ and {RuNO}⁷ involving the selective molecular frameworks of [Ru^{II}([9]aneS₃)(bpy)(NO⁺)]³⁺ (**4**³⁺), [Ru^{II}([9]aneS₃)(pap)-(NO⁺)]³⁺ (**8**³⁺) and [Ru^{II}([9]aneS₃)(bpy)(NO⁺)]²⁺ (**4**²⁺), [Ru^{II}([9]aneS₃)(bpy)(NO⁺)]



Scheme 1 Representation of complexes with their corresponding numerical notations.

The nitrosyl complexes $(4^{3+}/4^{2+})$ and $(8^{3+}/8^{2+})$ are synthesized by following the stepwise general synthetic procedure $[Ru^{II}([9]aneS_3)(AL)(Cl)]^+ \rightarrow [Ru^{II}([9]aneS_3)(AL)(CH_3CN)]^{2+} \rightarrow [Ru^{II}([9]aneS_3)(AL)(NO_2)]^+ \rightarrow [Ru^{II}([9]aneS_3)(AL)(NO^+)]^{3+} \rightarrow [Ru^{II}([9]aneS_3)(AL)(NO^-)]^{2+}$ (AL = bpy or pap, Scheme 1). The synthesis of the precursor bipyridine complex, $[Ru^{II}([9]aneS_3)(bpy)(Cl)]^+$ (1⁺) has been performed by following the reported procedure^{15m} and its electronic and ¹H NMR spectra match fairly well with those reported in the literature. The complexes have been isolated in the solid state as their perchlorate salts. It may be noted that attempts to synthesize the nitrosyl derivatives, 4^{3+} and 8^{3+} directly from the precursor chloro or solvate by using either NO gas or [NO]BF₄ proved unsuccessful.^{16b}

The complexes have been characterized by their satisfactory microanalytical, electrical conductivity and mass, IR, NMR spectral data (see the Experimental section). The single-crystal X-ray structures of selective derivatives have also been determined.

The crystal structures of the newly synthesized precursor complexes, bpy derivative: [**3**](ClO₄) (X = NO₂) and pap derivatives: [**5**](ClO₄) (X = Cl), [**6**](ClO₄)₂ (X = CH₃CN), [**7**](ClO₄) (X = NO₂) in Scheme 1 are shown in Fig. S1–S4 in the Electronic Supplementary Information (ESI†). Selected crystallographic parameters and bond distances and angles are listed in Tables S1 and S2 in the ESI,† respectively. The single-crystal X-ray structure of the nitrosyl complex, [Ru^{II}([9]aneS₃)(bpy)(NO⁺)](ClO₄)₃ ([**4**](ClO₄)₃) has also been determined (Fig. 1 and Tables 1 and 2). In each case the asymmetric unit consists of one independent molecule. The endocyclic torsion angles, S–C–C–S, C–S–C–C and C–C–S– C involving the coordinated macrocyclic [9]aneS₃ (Table S3†) in the complexes reveal the [333] conformation in the Dale nomenclature in each case.^{15m}

	[4](ClO ₄) ₃ .0.5 H ₂ O
Empirical formula	$C_{16}H_{20}Cl_3N_3O_{13}RuS_3 \cdot 0.5H_2O$
$M_{\rm r}$	773.95
Temperature/K	150(2)
Crystal symmetry	Monoclinic
Space group	$P2_1/n$
a/Å	16.7231(7)
b/Å	10.3071(3)
c/Å	17.4570(9)
α (°)	90
β (°)	116.828(6)
γ (°)	90
$V/Å^3$	2685.13(19)
Ζ	4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.915
μ/mm^{-1}	1.186
F(000)	1552
2θ range (°)	6.56 to 50
Data/restraints/parameters	4730/0/361
GOF	1.037
$R_1, WR_2 [I > 2\sigma(I)]$	0.0429, 0.1159
R_1 , w R_2 (all data)	0.0596, 0.1202
Largest diff. Peak, hole/e Å ⁻³	1.261, -1.069



Fig. 1 Molecular structure of the cation of $[Ru^{II}([9]aneS_3)(bpy)(NO)]-(ClO_4)_3$ in the crystal structure of $[4](ClO_4)_3$. Ellipsoids are drawn at 50% probability. Hydrogen atoms and solvent of crystallisation are omitted for clarity.

The tridentate [9]aneS₃ ligand binds to the ruthenium ion *via* the three sulfur donors in tris-*endo*dentate fashion with the expected staggered conformation about the C–C bonds. The average Ru^{II}– S bond distances and average S–Ru–S angles in the complexes (Table S2† and Table 2) are close to those reported in analogous ruthenium complexes.¹⁵ The reasonably shorter *cis* angles involving the coordinated bidentate bpy and pap with respect to the idealised 90° imply a distorted octahedral environment around the ruthenium ion in the complexes. The interligand *trans* angles, N1–Ru1–S2, N2–Ru1–S1, S3–Ru1–X (X = Cl or CH₃CN or NO₂ or NO) are close to 180° except the appreciably shorter N1–Ru1–S2 *trans* angle of 169.09(12)° in the nitrosyl complex ([4](ClO₄)₃). Ru–N(pyridine or CH₃CN or NO₂) and Ru–Cl distances match well with those of analogous complexes.¹² The average Ru–N2 (azo, pap) distance of 2.022(4) Å is shorter than the

	X-ray	DFT	
	[4](ClO ₄) ₃	4 ³⁺	4 ²⁺
Ru(1)–N(1)	2.083(4)	2.118	2.123
Ru(1) - N(2)	2.082(4)	2.119	2.124
Ru(1)-S(1)	2.3780(13)	2.461	2.408
Ru(1)-S(2)	2.3722(14)	2.455	2.409
Ru(1) - S(3)	2.3964(14)	2.466	2.459
Ru(1) - N(3)	1.766(4)	1.789	1.939
N(3) - O(1)	1.127(5)	1.135	1.168
S(1)-Ru(1)-S(2)	87.12(5)	85.25	85.94
S(1)-Ru(1)-S(3)	86.76(5)	85.10	86.45
S(2)-Ru(1)-S(3)	86.70(5)	85.07	86.29
N(1)-Ru(1)-S(2)	169.09(12)	170.1	174.0
N(1)-Ru(1)-S(1)	97.63(11)	97.86	98.13
N(2)-Ru(1)-S(1)	173.89(12)	171.9	175.5
N(1)-Ru(1)-S(3)	83.78(12)	85.83	89.60
N(2)-Ru(1)-S(2)	95.55(12)	97.55	98.10
N(2)-Ru(1)-S(3)	87.91(12)	87.64	91.77
N(1)-Ru(1)-N(2)	78.82(16)	78.15	77.67
N(1)-Ru(1)-N(3)	94.88(18)	94.14	91.37
N(2)-Ru(1)-N(3)	94.69(18)	93.15	89.68
S(1)-Ru(1)-N(3)	90.55(14)	94.09	92.13
S(2)-Ru(1)-N(3)	94.90(15)	95.00	92.82
S(3)-Ru(1)-N(3)	176.79(14)	179.2	178.4
Ru(1)-N(3)-O(1)	176.5(4)	179.5	140.4

average Ru–N1(pyridine, pap) distance, 2.069(4) Å in [5](ClO₄), [6](ClO₄)₂, [7](ClO₄) due to $(d\pi)Ru^{II} \rightarrow \pi^*(N=N, pap)$ backbonding effect¹⁸ which has also been reflected in the longer N=N bond distances of 1.287(5), 1.287(6) and 1.284(5) Å, respectively, as compared to the N=N distance of free [Hpap]⁺, 1.258(5) Å.¹⁹ The significantly shorter Ru^{II}–N3(NO) distance of 1.766(4) Å and the triple bond feature of N3–O1(NO) (1.127(5) Å) along with an almost linear Ru–N3–O1(NO) bond angle of 176.5(4)° reveal the π -acceptor character of the coordinated nitrosonium (NO⁺) ion in [4](ClO₄)₃.^{12b-d,g,j,k,13a,b} Consequently, the Ru–S3 bond (2.3964(14) Å) *trans* to the Ru–NO bond in [4](ClO₄)₃ is slightly longer than the other two Ru–S bonds (Ru–S1, 2.3780(13), Ru–S2, 2.3722(14) Å).

The DFT optimised structures of $[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}$ (4^{3+}) (Fig. 2, Table 2) and $[Ru^{II}([9]aneS_3)(pap)(NO^+)]^{3+}$ (8^{3+}) at the B3LYP level with SDD basis set for Ru and 6-31G* for other atoms (Fig. 3, Table S4†) also reveal the almost linear geometry of the {Ru–NO⁺} group in 4^{3+} and 8^{3+} with Ru–N–O angles of 179.5 and 179.2°, respectively, and the same N=O distance of 1.135 Å. On the other hand, the DFT optimised structures of the reduced $[Ru^{II}([9]aneS_3)(bpy)(NO^*)]^{2+}$ (4^{2+}) (Fig. 2, Table 2) and $[Ru^{II}([9]aneS_3)(pap)(NO^*)]^{2+}$ (8^{2+}) at the (U)B3LYP level (Fig. 3, Table S4†) predict the bent {Ru–N=O^*} geometry: Ru–N–O, 140.4,139.4° and N=O, 1.168, 1.165 Å, respectively.^{121,13c,20} On moving from NO⁺ in 8^{3+} to NO⁻ in 8^{2+} the DFT calculated Ru– N2(azo, pap) bond distance slightly decreases from 2.162 Å to 2.136 Å due to the difference in π -accepting strength of the NO⁺ and NO⁺ states.

The bent geometry of {Ru–NO}⁷ in the distorted octahedral environment introduces splitting in the degenerate *e*-level of {Ru– NO}⁶ leading to a non-degenerate state in {Ru–NO}⁷ which in effect yields eclipsed and staggered conformations with S_{trans}–Ru– N–O dihedral angles (θ) of 0° and 45°, respectively, at the two extreme cases.^{6I,m,12m} The geometry optimisation of **4**²⁺ or **8**²⁺ at



Eclipsed ($\theta = 0^{\circ}$)

Staggered ($\theta = 45^{\circ}$)

Optimised ($\theta = 4.45^{\circ}$)



Fig. 2 DFT-optimised structures of (a) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{3+}$ (4³⁺) and (b) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{2+}$ (4²⁺).

the G03/(U)B3LYP level reveals that eclipsed conformation is favoured in both the cases. In the case of 4^{2+} , the optimised geometry with the dihedral angle, $\theta = 4.45^{\circ}$ is calculated to be energetically more favourable by 83.8 cm⁻¹ (0.2396 kcal mol⁻¹) and 260 cm⁻¹ (0.7434 kcal mol⁻¹) with respect to the idealised eclipsed ($\theta = 0^{\circ}$) and staggered ($\theta = 45^{\circ}$) conformations in *vacuo* (Table S5†). The slight deviation from the idealised $\theta = 0^{\circ}$ in the optimised geometry ($\theta = 4.45^{\circ}$) could be attributed to the interaction between the nearby sulfur (S(1) of [9]aneS₃) and oxygen (O1) atoms.

Unlike the bpy complex 4^{2+} , for 8^{2+} four different eclipsed as well as staggered conformations are theoretically feasible due to the unsymmetrical nature of the pap ligand. The optimised geometry of 8^{2+} reveals an almost eclipsed conformation (aligned parallel to Ru–N(1) bond) with dihedral angle, $\theta = 0.41^{\circ}$ which is energetically lowered by 266 cm⁻¹ (0.7606 kcal mol⁻¹) and 391 cm⁻¹ (1.1179 kcal mol⁻¹), respectively, with regard to the idealised eclipsed form ($\theta = 0^{\circ}$) and staggered conformation with $\theta = 45^{\circ}$ in *vacuo* (Table S5[†]).

Though the eclipsed conformer is calculated to be more stable, both eclipsed and staggered forms are energetically probable at



Fig. 3 DFT-optimised structures of (a) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{3+}$ (8³⁺) and (b) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{2+}$ (8²⁺).

room temperature due to their minor difference in energy (Table S5[†]). The observed broad as well as slightly splitted profile of the v(NO) band in the IR spectra of 4^{2+} and 8^{2+} (Fig. 4, see later) could be rationalised on the basis of existence of both the conformers at the IR time scale.

Spectral aspects

¹H NMR spectra of the diamagnetic nitrosyl complexes, 4^{3+} and 8^{3+} in CD₃CN are shown in Fig. S5[†] and chemical shift values for all the complexes are set in Table S6.[†] In the aromatic region bpy complexes, 2^{2+} , 3^+ , 4^{3+} exhibit four distinct proton signals (two doublets and two triplets) in the range of δ , 7–9 ppm corresponding to one pyridine ring of bpy due to the internal





symmetry and the chemical shift values vary slightly depending on the electronic nature of the monodentate ligands, $X = CH_3CN$, NO₂, NO⁺ (Scheme 1). The twelve methylene protons associated with the three connecting $(CH_2)_2$ units of coordinated [9]aneS₃ in 2^{2+} , 3^+ and 4^{3+} appear as multiplets in the chemical shift range of δ , 2–4 ppm due to geminal and vicinal couplings. On the other hand the calculated number of nine aromatic protons of the unsymmetrical pap ligand in 5^+ , 6^{2+} , 7^+ , 8^{3+} appear as partially overlapping signals in the chemical shift range of δ , 7–9 ppm where the δ value differs slightly based on the monodentate ligands (X, Scheme 1). The unsymmetrical nature of pap introduces more complexities particularly in the CH₂ proton signals where the proton resonances are essentially distributed in the chemical shift range of δ , 1.3–4.2 ppm. The clearly resolved four or nine aromatic proton resonances associated with the half of the symmetric bpy or full molecule of unsymmetric pap, respectively, imply that one conformation of the macrocyclic ligand, [9]aneS₃ exists in the solution state as well. Furthermore, ¹³C NMR spectra of the representative nitro and nitroso derivatives, bpy $(3^+, 4^{3+})$ and pap (7⁺, 8³⁺), Fig. S6, Fig. S7, Table S7[†]) exhibit five, nine aromatic and

three, six aliphatic carbon signals, respectively, which essentially justifies the single isomeric identity of the complexes in the solution state. $^{\rm 15g,m}$

The IR data involving $v(ClO_4)$, $v(NO_2)$ and v(NO) vibrations of the respective complexes are given in the Experimental section. The v(NO) stretching frequencies of [4](ClO₄)₃ and [8](ClO₄)₃ at 1945 cm⁻¹ (DFT: 1943 cm⁻¹) and 1964 cm⁻¹ (DFT: 1966 cm⁻¹), respectively, (Fig. 4) suggest that the electrophilic character of the coordinated NO⁺ group increases with the increase in π -accepting character of the ancillary ligands, pap > bpy.²¹ A similar trend of v(NO) frequency based on the difference in π -accepting nature of bpy and pap has also been observed in analogous nitrosyl complexes with meridionally oriented 2,2':6',2"-terpyridine (trpy): bpy, 1952 cm⁻¹;^{12h} pap, 1960 cm⁻¹ ^{12a} and facially oriented tris(1pyrazolyl)methane (tpm): bpy, 1959 cm⁻¹;^{13a} pap, 1962 cm⁻¹.^{13c} The v(NO) band however shifts substantially ($\approx 300 \text{ cm}^{-1}$) to the lower energy region on reduction of 4^{3+} (1945 cm⁻¹) to 4^{2+} (1632 cm⁻¹, DFT: 1637 cm⁻¹) or 8³⁺ (1964 cm⁻¹) to 8²⁺ (1634 cm⁻¹, DFT: 1632 cm⁻¹) (Fig. 4). This implies predominantly NO centred reduction, $\{Ru^{II}-NO^{+}\}$ in $4^{3+}/8^{3+}$ to $\{Ru^{II}-NO^{-}\}$ in $4^{2+}/8^{2+}$ with the change in localised geometry from sp-hybridised (N of NO⁺) linear {Ru- NO^+ to close to sp²-hybridised (N of NO[•]) bent { Ru^{II} -NO[•]} as has also been revealed by the DFT optimised geometries (Fig. 2 and 3).

Ruthenium(II) based MLCT transition energy of the complexes systematically varies with the change in ligand field strength of the monodentate ligand (X) in $[Ru^{II}([9]aneS_3)(bpy)(X)]^n$ or $[Ru^{II}([9]aneS_3)(pap)(X)]^n$ and it follows the order: $X = Cl^- < NO' \le$ $NO_2 < CH_3CN$ (Fig. S8 and Fig. S9, Table S8†).¹²

The nitrosyl complexes with { $Ru^{II}-NO^+$ } configuration in 4^{3+} and 8^{3+} show one moderately intense absorption near 300 nm with weak shoulders at the lower energy region around 400 nm and multiple transitions in between 500–300 nm, respectively, in CH₃CN (Fig. S9†). The transitions are assigned based on the TD-DFT calculations as ligand-to-ligand charge-transfer (LLCT) and ligand-to-ligand/metal charge-transfer (LLMCT) transitions (Table S9†). Ligand based higher energy HOMOs and the mixed ligand and metal based lower energy LUMOs are primarily involved in the observed transitions.

The charge-transfer transitions in the reduced nitrosyl complexes with {Ru^{II}-NO[•]} configuration in 4^{2+} and 8^{2+} appear in the relatively lower energy region near 400 and 500 nm, respectively (Fig. S9†). The TD-DFT calculations on the optimised 4^{2+} and 8^{2+} predict multiple near by transitions in the above region which are essentially mixed metal/ligand-to-ligand charge-transfer (MLLCT), ligand-to-ligand charge-transfer (LLCT) and metal-to-ligand charge-transfer (MLCT) in nature (Table S10†). The Ru^{II}/Ru^{III} potentials of the precursors in [Ru^{II}([9]aneS₃)(bpy)(X)]^{*n*} or [Ru^{II}([9]aneS₃)(pap)(X)]^{*n*} with X = Cl⁻ (**5**⁺), CH₃CN (**2**²⁺, **6**²⁺), NO₂ (**3**⁺, **7**⁺) vary systematically in each set: X = Cl⁻ < NO₂ < CH₃CN¹² (Table S11[†]). The stronger π -accepting feature of pap relative to bpy enhances the stability of the Ru(II) state in **6**²⁺ (X = CH₃CN) and **7**⁺ (NO₂) as compared to the corresponding **2**²⁺ and **3**⁺. Furthermore, successive two and three ligand based reductions are observed for bpy and pap derivatives, respectively, within -2.0 V *versus* SCE (Table S11[†]). The diimine (N=C-C=N) and azo (N=N) functions of coordinated bpy and pap, respectively, are known to undergo successive two-step one-electron reductions²² and [9]aneS₃ also shows one irreversible reduction at -1.09 V *versus* SCE in CH₃CN.²³

Besides ancillary ligand (bpy, [9]aneS₃, pap) based reductions, the nitrosyl complexes, $\mathbf{4}^{3+}$ and $\mathbf{8}^{3+}$ exhibit additional one quasireversible reduction at 0.49 V and 0.67 V, followed by an irreversible reduction at 0.07 V and 0.03 V versus SCE, respectively (Fig. 5, Table S11[†]). These two reductions at relatively higher positive potential region are assigned to the successive NO based redox processes, $NO^+ \rightarrow NO^-$ (response I) and $NO^- \rightarrow NO^-$ (response II). The DFT calculations on optimised 4^{3+} and 8^{3+} also predict that in both the cases LUMO and LUMO+1 are dominated by NO⁺ based orbitals (~70%) (Tables S12 and S13[†]) along with ~20% contribution from ruthenium due to $(d\pi)Ru(II)$ $\rightarrow \pi^*(NO^+)$ back-bonding. The primarily nitrosyl based first reduction of $\{Ru^{II}-NO^{+}\} \rightarrow \{Ru^{II}-NO^{+}\}$ has also been revealed by the NO dominated SOMO (~50%) in the MOs (α -spin) of the reduced 4^{2+} or 8^{2+} (Tables S14 and S15⁺). The appreciable contribution of Ru (30%) in the SOMO implies that the electronic structure of 4^{2+} or 8^{2+} can be best represented as a mixed situation of {Ru^{II}-NO[•]}(major)/{Ru^I(NO⁺)}(minor). The dominating contribution of NO in the LUMO (β -spin, >50%) for the reduced 4^{2+} or 8^{2+} signifies that the second reduction corresponds to $\{Ru^{II}-NO^{-}\}(major)/\{Ru^{I}(NO^{+})\}(minor) \rightarrow \{Ru^{II}-NO^{-}\}$. The subsequent reductions at the more negative potentials (Table S11†) are associated with the ancillary ligands, bpy or [9]aneS₃ or pap.

The stronger electrophilicity of the NO⁺ centre in **8**³⁺ has been reflected in the 100–200 mV positive shift of NO reductions relative to those in **4**³⁺. The separation in potential of the two successive NO based redox processes leads to the large comproportionation constant (K_c) ($RT \ln K_c = nF(\Delta E)$)²⁴ values of 10^{7.1} and 10^{11.8} for the intermediate **4**²⁺ and **8**²⁺, respectively, which indeed has facilitated the isolation of the radical {Ru^{II}–NO⁺} derivatives.

The reduced {Ru^{II}-NO[•]} displays a free radical EPR ($g \sim 2.0$) (Fig. S10[†]) with slight metal based anisotropy as reported in numerous analogous systems.^{25,26} The spin-density plots of 4²⁺ and 8^{2+} (Fig. 6) also predict that NO is the primary spin-bearing centre with Mulliken spin densities of NO = 0.826, Ru = 0.100, [9]aneS₃ = 0.057, bpy = 0.016 and NO = 0.820, Ru = 0.118, [9]aneS₃ = 0.057, pap = 0.005, respectively. The SOMO of 4^{2+} or 8^{2+} indicates σ donation from the π^* orbital of NO to the dz²(Ru) centre which reveals {Ru^{II}-NO[•]} as the predominant valence formulation along with the considerable mixing of $\{Ru^{I}-NO^{+}\}$ configuration due to the presence of ~30% metal contribution (Tables S14 and S15[†]).^{12d} Moreover, σ -interaction between Ru and NO as revealed by the SOMO and the spin density at the axial position result in significant hyperfine splitting in the EPR spectrum due to $^{14}NO(I =$ 1). The observed slight g anisotropy in the EPR spectrum develops due to the bending mode of Ru-N-O (Fig. 2 and 3) and partial mixing of ruthenium frontier orbitals with the close lying singly occupied molecular orbital (SOMO) of NO'. The anisotropy of the g factor in the EPR of $\{Ru-NO'\}$ species including the modelling aspects and spin Hamiltonian of metal bound NO' have been discussed at length in earlier publications.8a,25



Fig. 5 Cyclic voltammograms (nitrosyl based reductions) of (a) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{3+}$ (4³⁺) and (b) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{3+}$ (8³⁺) in CH₃CN/0.1 M Et₄NClO₄ *versus* SCE, scan rate: 100 mV s⁻¹. Responses I and II correspond to NO⁺ \rightarrow NO⁻ and NO⁻ \rightarrow NO⁻ redox processes, respectively.



Fig. 6 Spin density plots of (a) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{2+}$ (4²⁺) and (b) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{2+}$ (8²⁺).



Unlike the precursor chloro (5⁺), solvate (2²⁺, 6²⁺) and nitro (3⁺, 7⁺) derivatives, nitrosyl complexes, 4³⁺ and 8³⁺ do not exhibit ruthenium(II) \rightarrow ruthenium(III) oxidation (Table S11†) since HOMOs are primarily composed of bpy and pap based orbitals, respectively (Tables S12 and S13†). This can be attributed to the effect of multiple strong π -acceptor ligands, bpy/pap, [9]aneS₃ and NO⁺ in the molecular frameworks of 4³⁺ and 8³⁺. Appreciable ruthenium contributions of 40% and 35% are predicted only in the much lower HOMO-7 and HOMO-10 levels in 4³⁺ and 8³⁺, respectively, revealing that the better π -accepting ability of pap introduces greater stability of Ru(II) state in 8³⁺ as has also been reflected in the experimental results.

Reactivity aspects

Reaction of {Ru^{II}–NO⁺} with the Nucleophile OH⁻. The ruthenium nitrosyls 4³⁺ and 8³⁺ are stable in the solid state. However, 4³⁺ and 8³⁺ quickly transform to the corresponding nitro derivatives, 3⁺ and 7⁺, respectively, in H₂O even with such a low concentration of OH⁻ of 10⁻⁷ M. This indeed had prevented us following the reaction of 4³⁺ or 8³⁺ with the nucleophile OH⁻ in aqueous medium using the conventional spectrophotometric technique. However, acetonitrile solutions of 4³⁺ and 8³⁺ are reasonably stable to follow the reaction with 100 fold excess OH⁻ under pseudo first-order conditions (pseudo pH, 9.2) which leads to the formation of the corresponding nitro complexes, 3⁺ and 7⁺, eqn (i) (AL = bpy or pap). On the other hand, the reverse process

$$[Ru^{II}([9]aneS_{3}(AL)(NO)]^{3+}+2OH^{-} \rightarrow [Ru^{II}([9]aneS_{3}(AL)(NO_{2})^{+}+H_{2}O + 4^{3+} or 8^{3+} 3^{+} or 7^{+}$$
(i)

i.e. {Ru^{II}-NO₂} \rightarrow {Ru^{II}NO⁺} is triggered by the H⁺ ion as stated before. The conversion of {Ru^{II}-NO⁺} to {Ru^{II}-NO₂} proceeds through distinct isosbestic points (Fig. 7) implying the presence of only {Ru^{II}-NO₂} and {Ru^{II}-NO⁺} species in the equilibriated solution. The rate constant value for the reaction (eqn (i)) has been determined by following the increase in absorbance of the product, {Ru^{II}-NO₂} with the progress of the reaction (Table 3). The pseudo first-order rate constant values at different concentrations of OH⁻ exhibit a linear relationship (Fig. 7), therefore the second order rate constant values are estimated simply by dividing the pseudo first-order rate constant value with the used base concentration. The second-order rate constant values at different experimental temperatures for the bpy complex in 4³⁺ are almost half to those obtained for the pap complex, 8³⁺ (Table 3) due to the difference in the π -accepting features of bpy and pap.



Fig. 7 Time evolution of the electronic spectra (time intervals: 5 min) of (a) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{3+}$ (4^{3+}), (concentration: 0.59×10^{-5} M in CH₃CN) in the presence of aqueous OH⁻ (concentration of 2.44 × 10⁻³ M) at 298 K and (b) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{3+}$ (8^{3+}), (concentration: 0.59×10^{-5} M in CH₃CN) in the presence of aqueous OH⁻ (concentration: 0.59×10^{-3} M) at 298 K. Insets show the plots of pseudo-first order rate constants (k, s⁻¹) at different OH⁻ concentrations at 298 K.

The negative ΔS^{\ddagger} values of -136 and -144 J K⁻¹ mol⁻¹ (eqn(i)) for **4**³⁺ and **8**³⁺, respectively, (Table 3) reveal that the reaction of {Ru^{II}-NO⁺} with OH⁻ proceeds through an associatively activated process involving the bound {Ru^{II}-NO₂H} intermediate followed by a rapid deprotonation step as shown by eqn (ii) and (iii) (AL = bpy or pap).^{13a} The estimated second-order rate constant value of ~10⁻¹ M⁻¹ s⁻¹ for the present

$$[\operatorname{Ru}^{II}(\operatorname{aneS}_{3})(\operatorname{AL})(\operatorname{NO}^{+})]^{3+} + \operatorname{OH}^{-} \rightarrow [\operatorname{Ru}^{II}([9]\operatorname{aneS}_{3})(\operatorname{AL})(\operatorname{NO}_{2}\operatorname{H})]^{2+}$$
(ii)

$[Ru^{II}(aneS_3)(AL)(NO_2H)]^{2+} \rightarrow [Ru^{II}([9]aneS_3)(AL)(NO_2)]^{+} + (iii)$ H^+

set of nitrosyl complexes (4^{3+} and 8^{3+}) in CH₃CN is much lower than that reported for the analogous complex involving the facially coordinated tris(1-pyrazolyl)methane (tpm) in combination with bpy, [Ru^{II}(tpm)(bpy)(NO⁺)]³⁺ in H₂O of ~10⁶ M⁻¹ s⁻¹. The much lower rate constant value for 4^{3+} or 8^{3+} can be attributed to the effect of using non-aqueous CH₃CN solvent instead of water. Incidentally, the k, M⁻¹ s⁻¹ of 2.03 × 10⁻¹ at 298 K for [Ru^{II}(tpm)(pap)(NO⁺)]³⁺ in CH₃CN ^{13c} is close to 2.84 × 10⁻¹ determined for the analogous 8^{3+} in acetonitrile and both the complexes exhibit similar v(NO) frequencies of 1964 and 1962 cm⁻¹, respectively.

 Table 3
 Rate constant and activation parameters

Complex (concentration)	Temp./K	$[OH^{-}] M^{-1}$	$k \mathrm{s}^{\scriptscriptstyle -1}$	$k \mathrm{M}^{-1} \mathrm{s}^{-1}$	$\Delta H^{\ddagger} \mathrm{kJ} \mathrm{mol}^{-1}$	$\Delta S^{\ddagger} \mathrm{J} \mathrm{K}^{-1} \mathrm{mol}^{-1}$	K ₂₉₈
4 ³⁺ (0.59×10 ⁻⁵ M in CH ₃ CN)	298	2.44×10^{-3}	3.41×10^{-4}	1.39×10^{-1}	52.11 ± 0.03	-136.51 ± 0.05	44.5
		4.88×10^{-3}	6.67×10^{-4}				
		7.32×10^{-3}	10.34×10^{-4}				
		9.76×10^{-3}	13.56×10^{-4}				
	308	2.44×10^{-3}	6.75×10^{-4}	2.77×10^{-1}			
	318	2.44×10^{-3}	13.67×10^{-4}	5.60×10^{-1}			
8 ³⁺ (0.59 × 10 ⁻⁵ M in CH ₃ CN)	298	0.59×10^{-3}	1.68×10^{-4}	2.84×10^{-1}	51.49 ± 0.02	-144.43 ± 0.07	2.04
		1.18×10^{-3}	3.35×10^{-4}				
		1.77×10^{-3}	5.02×10^{-4}				
		2.36×10^{-3}	$6.67 imes 10^{-4}$				
	308	0.59×10^{-3}	3.32×10^{-4}	5.63×10^{-1}			
	318	0.59×10^{-3}	6.63×10^{-4}	11.24×10^{-1}			

Photocleavage of the $\{Ru^{II}-NO\}$ bond

Under ambient light the nitrosyl complexes $[Ru^{II}([9]-aneS_3)(bpy)(NO^+)]^{3+}$ (4^{3+}) and $[Ru^{II}([9]aneS_3)(pap)(NO^+)]^{3+}$ (8^{3+}) are stable in CH₃CN. However, on exposure to radiation from a Xenon 350 W light source the deoxygenated acetonitrile solutions of 4^{3+} and 8^{3+} spontaneously transform the corresponding solvent species, $[Ru^{II}([9]aneS_3)(bpy)(CH_3CN)]^{2+}$, 2^{2+} and $[Ru^{II}([9]aneS_3)(pap)(CH_3CN)]^{2+}$, 6^{2+} via the photocleavage of the Ru–NO bond. The transformation of the nitrosyl complex, 4^{3+} or 8^{3+} to the corresponding solvate, 2^{2+} or 6^{2+} under photolytic conditions occurs with the distinct change in colour as well as the change in electronic spectral profile (Fig. 8).

The cleavage of the {Ru^{II}–NO⁺} bond in **4**³⁺ or **8**³⁺ via the photoirradiation process proceeds through the formation of the intermediate excited S = 1 state in {Ru^{III}–NO⁺}* as shown in eqn (iv).^{11a-c} The formation of {Ru^{II}–CH₃CN} instead of {Ru^{III}–CH₃CN} as the final metal-solvent fragment in the photolytic solution has been established by comparing its electronic spectral feature with the isolated solvent species, [Ru^{II}([9]aneS₃)(bpy)(CH₃CN)]²⁺, **2**²⁺ or [Ru^{II}([9]aneS₃)(pap)(CH₃CN)]²⁺, **6**²⁺ (Fig. 8).

$$\{\operatorname{Ru}^{II}-\operatorname{NO}^{+}\} + h\nu \rightarrow \{\operatorname{Ru}^{III}-\operatorname{NO}^{\bullet}\}^{*} \rightarrow \{\operatorname{Ru}^{II}\operatorname{-solvent}\} + \operatorname{NO}^{\bullet} (iv)$$

The electronic effect of π -accepting ancillary ligands (bpy or pap and [9]aneS₃) certainly facilitates the stabilisation of the {Ru^{II}-CH₃CN} species in the ground state.

It should be noted that the selective photolytic cleavage of the M–NO bond, $\{(AL)M^{II}-NO\} \rightarrow \{(AL)M^{II}(solvent)\}$ maintaining the integrity of the rest of the molecule is known to be biologically significant.¹¹

The rate of first-order photorelease of NO (k_{NO}) has been determined to be $1.12 \times 10^{-1} \text{ s}^{-1} (t_{1/2} = 6.2 \text{ s})$ or $7.67 \times 10^{-3} \text{ s}^{-1} (t_{1/2} = 90.3 \text{ s})$ for 4^{3+} or 8^{3+} , respectively. Thus, under identical experimental conditions the rate of photocleavage of the {Ru^{II}– NO⁺} bond (k_{NO} , s⁻¹) for the pap derivative (8^{3+}) is about 700 times slower than that for the bpy complex (4^{3+}).

The liberated NO from the photolysed acetonitrile solution of 4^{3+} or 8^{3+} could easily be trapped as {Mb-NO} adduct as evident from the emergence of a new band at $\lambda_{max} = 424$ nm corresponding to the standard absorption of {Mb-NO} (Fig. 8).²⁷

Hence, the newly designed molecular frameworks of $[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}$ (4³⁺) and $[Ru^{II}([9]aneS_3)(pap)-(NO^+)]^{3+}$ (8³⁺) extend a unique feature of photoreleasing "NO" at quite different rates under identical experimental conditions

primarily based on the difference in electronic nature of the ancillary ligands, bpy and pap.

Conclusion

The important features of the work are highlighted below:

– The nitrosyl function can be stabilised both in NO⁺ and NO[•] redox states in the newly designed molecular frameworks of $[Ru^{II}([9]aneS_3)(bpy)(NO)]^n$ (4^{*n*}) and $[Ru^{II}([9]aneS_3)(pap)(NO^n)]^n$ (8^{*n*}).

– The facially coordinated 1,4,7-trithiacyclononane ([9]aneS₃) in combination with the π-accepting bpy in 4^{3+} and pap in 8^{3+} develop strongly electrophilic coordinated NO⁺ centres as revealed by their high v(NO) frequencies and $E^{\circ}({Ru^{II}-NO^+}-{Ru^{II}-NO^+})$ (Table 4). The difference in the π-accepting strength of bpy and pap has been reflected in the electronic features of the molecules.

- The reduced {Ru-NO'} species in 4^{2+} and 8^{2+} can be best described by a resonance formulation of {Ru^{II}(NO')}(major) \leftrightarrow {Ru^I(NO')}(minor).

– The electrophilic NO⁺ centres in **4**³⁺ and **8**³⁺ react with the nucleophile OH⁻ to yield the corresponding {Ru^{II}-NO₂} derivatives, **3**⁺ and **7**⁺, respectively. However, the rate of the reaction (k, M⁻¹ s⁻¹) for **8**³⁺ is almost double that of **4**³⁺.

– On exposure to light both 4^{3+} and 8^{3+} undergo the photocleavage reaction of the Ru^{II}–NO bond to form the corresponding solvent species, 2^{2+} and 6^{2+} , respectively, but the rate of photorelease of "NO" (k_{NO} , s⁻¹) is 700 times faster in the case of 4^{3+} as compared to 8^{3+} .

Experimental

Materials

The ligand 2-phenylazopyridine $(pap)^{12a}$ and the starting complexes $[Ru([9]aneS_3)(dmso)Cl_2]$ ²⁸ $[Ru^{II}([9]aneS_3)(bpy)-(Cl)](ClO_4)^{15m}$ were prepared as described in the literature. The ligands 1,4,7-trithiacyclononane ([9]aneS_3) and 2,2'-bipyridyl were purchased from Aldrich. Other chemicals and solvents were reagent grade and used as received. For spectroscopic and electrochemical studies HPLC grade solvents were used.

Physical measurements

Infrared spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. ¹H NMR and ¹³C NMR spectra

Complex	$v(NO)cm^{-1a}$	$E^{\circ}/V(Ru^{II}-NO^{+}/Ru^{II}-NO^{-})^{b}$	$E_{\rm pc}/\rm V(Ru^{II}-NO^{\bullet}/Ru^{II}-NO^{-})^{b,c}$	Ref.
$[Ru^{II}(trpy)(bpy)(NO^+)]^{3+}$	1952	0.45	-0.20	12h
$[Ru^{II}(trpy)(pap)(NO^+)]^{3+}$	1960	0.72	0.07	12a
$[Ru^{II}(tpm)(bpy)(NO^{+})]^{3+}$	1959	0.55	-0.24	13a
$[Ru^{II}(tpm)(pap)(NO^{+})]^{3+}$	1962	0.60	-0.07	13c
$[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}(4^{3+})$	1945	0.49	0.07	Present work
$[Ru^{II}([9]aneS_3)(pap)(NO^+)]^{3+}$ (8 ³⁺)	1964	0.67	0.03	Present work

 Table 4
 IR vibrational frequencies and redox potentials

^a As KBr disk. ^b In CH₃CN versus SCE. ^c E_{pc} value for the irreversible process.



Fig. 8 Time evolution of the electronic spectra of (a) $[Ru^{II}([9]aneS_3)(bpy)(NO)]^{3+}$ (4^{3+}), (concentration: 0.63×10^{-5} M in CH₃CN, time intervals: 5 s) and (b) $[Ru^{II}([9]aneS_3)(pap)(NO)]^{3+}$ (8^{3+}), (concentration: 0.63×10^{-5} M in CH₃CN, time intervals: 2 s) under exposure to light (Xe lamp, 350 W). Insets show the (a) absorbance *versus* time plot at 384 nm corresponding to the solvent species $[Ru^{II}([9]aneS_3)(bpy)(CH_3CN)]^{2+}$ (2^{2+}) and (b) absorbance *versus* time plot at 480 nm corresponding to the solvent species $[Ru^{II}([9]aneS_3)(pap)(CH_3CN)]^{2+}$ (2^{2+}) and (b) absorbance *versus* time plot at 480 nm corresponding to the solvent species $[Ru^{II}([9]aneS_3)(pap)(CH_3CN)]^{2+}$ (6^{2+}). (c) Absorption spectra of met-Mb, reduced Mb and Mb-NO adduct in water.

were recorded using a 300 MHz Varian FT NMR spectrometer and a 400 MHz Bruker AV III FT NMR spectrometer with CD₃CN as solvent. Solution electrical conductivity was checked using a Systronic conductivity bridge 305. Cyclic voltammetric and coulometric measurements were carried out using a PAR model 273A electrochemistry system. A platinum wire working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used in a standard three-electrode configuration. Tetraethylammoniumperchlorate (TEAP) was used as the supporting electrolyte and the solution concentration was *ca.* 10^{-3} M; the scan rate used was 100 mV s⁻¹. A platinum gauze working electrode was used in the coulometric experiments. All electrochemical experiments were carried out under dinitrogen atmosphere. UV-vis. spectral studies were performed on a Perkin Elmer Lambda 950 spectrophotometer. The EPR measurements were made with a Varian model 109 C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K. The elemental analyses were carried out with a Perkin-Elmer 240 C elemental analyser. Electrospray mass spectra were recorded on a Micromass Q-ToF mass spectrometer.

Synthesis

Synthesis of $[Ru^{II}(9]aneS_3)(bpy)(CH_3CN)](ClO_4)_2$ [2](ClO₄)₂. The precursor chloro complex $[Ru^{II}([9]aneS_3)(bpy)(Cl)](ClO_4)$ (100 mg, 0.17 mmol) and an excess of AgNO₃ (287 mg, 1.7 mmol) were taken in CH₃CN (25 cm³) and heated at reflux for 2 h. The colour of the solution gradually changed from orange to yellow. The solution was cooled to room temperature and the precipitated AgCl was separated by filtration through a sintered glass crucible (G-4). The volume of the filtrate was reduced to 5 cm³ and an excess saturated aqueous solution of NaClO₄ was added. The solid $[2](ClO_4)_2$ thus obtained was filtered off and washed thoroughly with ice-cold water and dried in vacuo over P₄O₁₀. Yield: 78 mg (66%). Anal. Calcd. for $C_{18}H_{23}Cl_2N_3S_3O_8Ru$ (Mol. wt. 676.91): C, 31.91; H, 3.42; N, 6.21. Found: C, 31.86; H, 3.48; N, 6.34%. Molar conductivity $[\Lambda_{\rm M} (\Omega^{-1} \, {\rm cm}^2 \, {\rm M}^{-1})]$ in acetonitrile: 215. ESI(+) Mass spectrum in CH₃CN (m/z): 536.76 corresponding to { $[Ru^{II}([9]aneS_3)(bpy)](ClO_4)$ } + (calcd. 536.93). IR (KBr, cm⁻¹): $v(ClO_4^{-})$, 1087, 623. λ [nm] (ε [M⁻¹ cm⁻¹]) in acetonitrile: 384(2280), 315(4080), 307(4680), 278(13010), 240(6400).

Synthesis of $[Ru^{II}([9]aneS_3)(bpy)(NO_2)](CIO_4)$ [3](CIO_4). Ru^{II}([9]aneS_3)(bpy)(CH₃CN)](CIO₄)₂ [2](CIO₄)₂ (100 mg, 0.15 mmol) and an excess of NaNO₂ (103.5 mg, 1.5 mmol) were taken in 25 cm³ water and the mixture was heated under reflux for 5 h. The yellow colour of the solution darkened during the course of the reaction. While cooling the solution to room temperature pure crystalline nitro complex precipitated out. The solid [3](CIO₄) thus obtained was filtered off, washed several times with ice-cold water and dried *in vacuo* over P₄O₁₀. Yield: 65 mg (76%). Anal. Calcd for C₁₆H₂₀CIN₃S₃O₆Ru (Mol. wt. 582.92): C, 32.94; H, 3.46; N 7.21. Found: C, 32.87; H, 3.53; N, 7.45%. Molar conductivity [$\Lambda_{\rm M}$ (Ω⁻¹ cm² M⁻¹)] in acetonitrile: 129. ESI(+) Mass spectrum in CH₃CN (*m*/*z*): 482.92, corresponding to {[Ru^{II}([9]aneS₃)(bpy)(NO₂)]}⁺ (calcd. 483.98). IR (KBr, cm⁻¹): ν (ClO₄⁻¹), 1085, 622; ν (NO₂⁻¹), 1343, 1297. λ [nm] (ε [M⁻¹ cm⁻¹]) in acetonitrile: 408(1300), 316(2120), 283(12450), 241(7690).

Synthesis of $[Ru^{II}(9]aneS_3)(bpy)(NO)](ClO_4)_3$ [4](ClO₄)₃. Nitric acid (2 cm³) was added drop wise to the solid $[Ru^{II}([9]aneS_3)(bpy)(NO_2)](ClO_4)$ [3](ClO₄) (100 mg, 0.17 mmol) under constant stirring at 273 K to form a pasty mass followed by the addition of ice-cold $HClO_4$ (3 cm³) under continuous mechanical stirring using a glass rod. Then saturated aqueous NaClO₄ solution was added which resulted in a yellow solid product. The precipitate was filtered off immediately, washed with a little ice-cold water and then dried in vacuo over P_4O_{10} . Yield: 92 mg (70%). Anal. Calcd for $C_{16}H_{20}Cl_3N_3S_3O_{13}Ru$ (Mol. wt. 764.83): C, 25.10; H, 2.64; N, 5.49. Found: C, 25.24; H, 2.45; N, 5.42%. Molar conductivity $[\Lambda_M (\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})]$ in acetonitrile: 324. ESI(+) Mass spectrum in CH₃CN (m/z): 536.92, corresponding to { $[Ru^{II}([9]aneS_3)(bpy)](ClO_4)$ } + (calcd. 536.93). IR (KBr, cm⁻¹): $v(ClO_4^{-})$, 1090, 624; $v(Ru^{II}-NO^+)$, 1945. λ [nm] (ε [M⁻¹ cm⁻¹]) in acetonitrile: 306(6490), 226(17580).

Synthesis of [Ru^{II}([9]aneS₃)(bpy)(NO)](CIO₄)₂ [4](CIO₄)₂. The nitroso complex, [4](CIO₄)₃ (100 mg, 0.13 mmol) was taken in 5 cm³ acetonitrile and an excess of hydrazine hydrate was added to it. The solution was stirred magnetically for 0.5 h under a dinitrogen atmosphere. The solution of [4](CIO₄)₃ changed to dark yellow. The solid mass thus obtained after removal of the solvent under reduced pressure was washed with a little icecold water and then dried *in vacuo* over P₄O₁₀. Yield: 73 mg (84%). Anal. Calcd for C₁₆H₂₀Cl₂N₃S₃O₉Ru (Mol. wt. 665.88): C, 28.83; H, 3.03; N, 6.31. Found: C, 28.71; H, 2.92; N, 6.22%. Molar conductivity [$\Lambda_{\rm M}$ (Ω^{-1} cm² M⁻¹)] in acetonitrile: 223. ESI(+) Mass spectrum in CH₃CN (*m*/*z*): 537.0, corresponding to {[Ru^{II}([9]aneS₃)(bpy)](CIO₄)}⁺ (calcd. 536.93). IR (KBr, cm⁻¹): ν (CIO₄⁻), 1087, 626; ν (Ru^{II}–NO⁺), 1632. λ [nm] (ε [M⁻¹ cm⁻¹]) in acetonitrile: 407(1790), 315(3400), 285(10760), 242(7260).

Synthesis of $[Ru^{II}(9]aneS_3)(pap)(CI)](CIO_4)$ [5](CIO₄). The ligand 2-phenylazopyridine (42 mg, 0.23 mmol) was added to a 25 cm³ ethanolic solution of $[Ru^{II}([9]aneS_3)(dmso)Cl_2]$ (100 mg, 0.23 mmol). The mixture was heated under reflux for 5 h under dinitrogen atmosphere. The solid residue thus obtained on removal of solvent under reduced pressure was redissolved in a minimum volume of acetonitrile followed by the addition of excess saturated aqueous solution of NaClO₄ which resulted in a dark precipitate. The precipitate was filtered off and washed several times with icecold water and dried *in vacuo* over P_4O_{10} . The purification of the dried precipitate using a silica gel column and CH₂Cl₂: CH₃CN (5:1) mixture as eluant yielded the purple coloured complex [Ru^{II}([9]aneS₃)(pap)Cl](ClO₄). Yield: 106 mg (76%). Anal. Calcd for C₁₇H₂₁Cl₂N₃S₃O₄Ru (Mol. wt. 598.91): C, 34.06; H, 3.53; N, 7.01. Found: C, 34.16; H, 3.55; N, 7.13%. Molar conductivity $[\Lambda_{\rm M}(\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})]$ in acetonitrile: 132. ESI(+) Mass spectrum in CH₃CN: 500.13 m/z, corresponding to {[Ru^{II}([9]aneS₃)(pap)Cl]}+ (calcd. 499.96) IR(KBr disk) (cm⁻¹): $v(ClO_4^{-})$, 1087, 623. λ [nm] (ε $[M^{-1} \text{ cm}^{-1}]$) in acetonitrile: 534(4180), 367(4120), 316(8760).

Synthesis of $[Ru^{II}([9]aneS_3)(pap)(CH_3CN)](ClO_4)_2$ [6](ClO₄)₂. The chloro complex $[Ru^{II}([9]aneS_3)(pap)(Cl)](ClO_4)$ [5](ClO₄) (100 mg, 0.17 mmol) was taken in a 1:1(v/v) mixture of CH₃CN-H₂O (25 cm³) and heated at reflux for 10 min. Excess AgNO₃ (287 mg, 1.7 mmol) was added to the above hot solution and the heating was continued for another 4 h. On cooling the solution to room temperature the liberated AgCl precipitated out which was then filtered off using a sintered glass crucible (G-4). The volume of the filtrate was reduced to 5 cm³ under reduced pressure. The solid mass of $[6](ClO_4)_2$ was obtained on addition of saturated aqueous solution of NaClO₄ to the above filtrate. The solid thus obtained was filtered off and washed thoroughly with icecold water. The product was dried in vacuo over P_4O_{10} . Yield: 96 mg (82%). Anal. Calcd for C19H24S3Cl2N4O8Ru (Mol. wt. 703.92): C, 32.39; H, 3.44; N, 7.96. Found: C, 32.32; H, 3.35; N, 8.14%. Molar conductivity $[\Lambda_{\rm M} (\Omega^{-1} \, {\rm cm}^2 \, {\rm M}^{-1})]$ in acetonitrile: 198. ESI(+) Mass spectrum in CH₃CN (m/z): 563.92, corresponding to $\{[Ru^{II}([9]aneS_3)(pap)](ClO_4)\}^+$ (calcd. 563.94). IR(KBr disk) (cm⁻¹): $v(ClO_4^{-})$, 1084, 622. λ [nm] (ε [M⁻¹ cm⁻¹]) (CH₃CN): 480(5450), 369(7260), 306(6700), 278(7940).

Synthesis of [Ru^{II}([9]aneS₃)(pap)(NO₂)](CIO₄) [7](CIO₄). The mixture of [Ru^{II}([9]aneS₃)(pap)(CH₃CN)](CIO₄)₂ [6](CIO₄)₂ (100 mg, 0.14 mmol) and an excess of NaNO₂ (97 mg, 1.4 mmol) in 25 cm³ water was heated at reflux for 4 h. The pure crystalline nitro complex [7](CIO₄) precipitated out on cooling the solution to room temperature. The solid [7](CIO₄) was filtered off, washed with ice-cold water and dried *in vacuo* over P₄O₁₀. Yield: 64 mg (74%). Anal. Calcd for C₁₇H₂₁S₃ClN₄O₆Ru (Mol. wt. 609.93). C, 33.45; H, 3.47; N, 9.18. Found: C, 33.38; H, 3.56; N, 9.26%. Molar conductivity [$A_{\rm M}$ (Ω^{-1} cm² M⁻¹)] in acetonitrile: 130. ESI(+) Mass spectrum in CH₃CN: 510.81 *m/z*, corresponding to {[Ru^{II}([9]aneS₃)(pap)(NO₂)]}⁺ (calcd. 510.99) IR (KBr disk) (cm⁻¹): *v*(CIO₄⁻), 1084, 622; *v*(NO₂⁻), 1359, 1265. λ [nm] (ε [M⁻¹ cm⁻¹]) (CH₃CN): 498(5190), 363(7160), 309(9330), 281(8360).

Synthesis of $[Ru^{II}(9]aneS_3)(pap)(NO)](ClO_4)_3$ [8](ClO₄)₃. Concentrated nitric acid (2 cm³) was added to the solid nitro complex [Ru^{II}([9]aneS₃)(pap)(NO₂)](ClO₄), [7](ClO₄) (100 mg, 0.16 mmol) under constant stirring at 273 K. The slow addition of ice-cold $HClO_4$ (5 cm³) to the resulting paste under mechanical stirring using a glass rod followed by the addition of saturated aqueous NaClO₄ solution resulted in a yellowish brown solid product. The precipitate was filtered off immediately, washed with a little ice-cold water and then dried *in vacuo* over P_4O_{10} . Yield: 102 mg (79%). Anal. Calcd for $C_{17}H_{21}S_3Cl_3N_4O_{13}Ru$ (Mol. wt. 791.84): C, 25.76; H, 2.67; N, 7.07. Found: C, 25.67; H, 2.59; N, 7.08%. Molar conductivity $[\Lambda_{M} (\Omega^{-1} \text{ cm}^{2} \text{ M}^{-1})]$ in acetonitrile: 315. ESI(+) Mass spectrum in CH₃CN: 563.97 m/z, corresponding to { $[Ru^{II}([9]aneS_3)(pap)](ClO_4)$ } + (calcd. 563.94) IR (KBr disk) (cm⁻¹): $v(ClO_4^{-})$, 1089, 625; $v(Ru^{II}-NO^+)$, 1964. λ [nm] (ε [M⁻¹ cm⁻¹]) (CH₃CN): 444(2750), 358(4370), 311(4190), 275(4370).

Synthesis of $[Ru^{II}([9]aneS_3)(pap)(NO)](CIO_4)_2$ [8](CIO₄)₂. Excess hydrazine hydrate was added to a 5 cm³ acetonitrile solution of the nitroso complex [8](CIO₄)₃ (100 mg, 0.13 mmol) and the solution was stirred for 0.5 h under dinitrogen atmosphere. The yellow solution of [8](CIO₄)₃ immediately changed to reddish yellow. On removal of solvent under reduced pressure a dark solid mass was obtained which was washed with little ice-cold water and then dried *in vacuo* over P₄O₁₀. Yield: 59 mg (66%). Anal. Calcd for C₁₇H₂₁S₃Cl₂N₄O₉Ru (Mol. wt. 692.89): C, 29.44; H, 3.05; N, 8.08.

Found: C, 29.34; H, 3.01; N, 8.13%. Molar conductivity $[\Lambda_{\rm M} (\Omega^{-1} \text{ cm}^2 \text{ M}^{-1})]$ in acetonitrile: 210. ESI(+) Mass spectrum in CH₃CN (m/z): 563.93, corresponding to { $[\text{Ru}^{II}([9]\text{aneS}_3)(\text{pap})](\text{CIO}_4)$ }⁺ (calcd. 563.94). IR (KBr disk) (cm⁻¹): $v(\text{CIO}_4^{-})$,1079, 624; $v(\text{Ru}^{II} - \text{NO}^{-})$, 1634. λ [nm] (ε [M⁻¹ cm⁻¹]) (CH₃CN): 500(3260), 343(5590), 315(5920), 282(5090).

CAUTION! Perchlorate salts of metal complexes are generally explosive. Care needs to be taken while handling such complexes.

Kinetic experiments

The pseudo first-order rate constant values (k, s^{-1}) for the transformations of $[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}$ (4^{3+}) (0.59 × 10⁻⁵ M in CH₃CN) $\rightarrow [Ru^{II}([9]aneS_3)(bpy)(NO_2)]^+$ (3^+) and $[Ru^{II}([9]aneS_3)(pap)(NO^+)]^{3+}$ (8^{3+}) (0.59 × 10⁻⁵ M in CH₃CN) $\rightarrow [Ru^{II}([9]aneS_3)(pap)(NO_2)]^+$ (7^+) in the presence of aqueous sodium hydroxide solution of concentrations 2.44 × 10⁻³ and 0.59 × 10⁻³ M, respectively, were determined by following the increase in absorbance (A_1) at 408 nm and 498 nm corresponding to λ_{max} of the nitro complexes 3^+ and 7^+ , respectively, as a function of time (*t*) at three different temperatures, 298, 308, 318 K. A_{α} values were measured when the intensity changes at 408 nm or 498 nm completely leveled off. The pseudo first-order rate constant (k, s^{-1}) at each temperature was calculated from the slope of linear least-squares plot of $-ln(A_{\alpha} - A_t)$ versus *t*. The activation parameters ΔH^{\ddagger} and ΔS^{\ddagger} were determined from the Eyring plots.²⁹

The first order rate constant values (k, s^{-1}) for the photorelease of "NO" from $[Ru^{II}([9]aneS_3)(bpy)(NO^+)]^{3+}$ (4^{3+}) and $[Ru^{II}([9]aneS_3)(pap)(NO)]^{3+}$ (8^{3+}) in acetonitrile were determined from the single-exponential fittings of the plots of change in absorbance against time under photolysis condition at $\lambda_{max} = 384$ nm and 480 nm, respectively.

Trapping of photoreleased "NO" by myoglobin

The acetonitrile solution of 4^{3+} or 8^{3+} (3.0 cm³) was taken in a quartz cuvette of optical path length 1 cm which was then covered by a rubber septum. The solution in the cuvette was thoroughly deoxygenated by purging it with dinitrogen gas. The photolysis was carried out for 10 min using a Xe 350 W lamp. The photoreleased free "NO" was allowed to pass through a freshly prepared aqueous solution of reduced myoglobin (Mb) using a cannula and the instantaneous formation of {Mb-NO} adduct was authenticated by its characteristic UV-vis. spectrum.

Crystallography

Single crystals of [3](ClO₄), [4](ClO₄)₃, [5](ClO₄), [6](ClO₄)₂ and [7](ClO₄) were grown by slow evaporation of the respective acetonitrile solutions. X-ray data were collected using an OX-FORD XCALIBUR-S CCD single crystal X-ray diffractometer. The structures were solved and refined by full-matrix least-squares techniques on F^2 using the SHELX-97 program.³⁰ The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement process as per the riding model.

Computational details

Full geometry optimisations of 4^{3+} , 4^{2+} and 8^{3+} , 8^{2+} were carried out using the density functional theory method at the B3LYP and (U)B3LYP level, respectively³¹ with Gaussian 03 program package.32 All elements except ruthenium were assigned the 6-31G(d) basis set. The SDD basis set with effective core potential was employed for the ruthenium atom.³³ The vibrational frequency calculations were performed to ensure that the optimised geometries represent the local minima and there are only positive eigenvalues. The frequencies calculated using the B3LYP functional were scaled by a factor of 0.98. Vertical electronic excitations based on B3LYP/(U)B3LYP optimised geometries were computed for the time-dependent density functional theory (TD-DFT) formalism³⁴ in acetonitrile using conductor-like polarizable continuum model (CPCM).³⁵ GaussSum³⁶ was used to calculate the fractional contributions of various groups to each molecular orbital.

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