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Synthesis, crystal structure and acidic properties in aqueous solution of phosphate ammine complexes of ruthenium nitrosyl

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ABSTRACT

First examples of phosphate ammine complexes of ruthenium nitrosyl *trans*-$[Ru(NO)(NH_3)_4(H_xPO_4)](NO_3)_x\cdot(2-x)H_2O$ ($x = 0, 1, 2$) were obtained with good yields. Results of elemental analysis, X-ray, infrared, UV–Vis diffuse reflectance, and ^{31}P NMR spectroscopies fit well with the formulas $[Ru(NO)(NH_3)_4(PO_4)]\cdot 2H_2O$ (**1**), $[Ru(NO)(NH_3)_4(HPO_4)]NO_3\cdot H_2O$ (**2**), and $[Ru(NO)(NH_3)_4(H_2PO_4)](NO_3)_2$ (**3**). In all the complexes, the phosphate group is in a *trans*-position to NO and is monodentate coordinated to ruthenium by one of the oxygen atoms. The pK_a values 2.6 and 7.2 were calculated from potentiometric titration and ^{31}P NMR for the reactions: *trans*-$[Ru(NO)(NH_3)_4(H_2PO_4)]^{2+} + H_2O \leftrightarrows$ *trans*-$[Ru(NO)(NH_3)_4(HPO_4)]^+ + H_3O^+$ and *trans*-$[Ru(NO)(NH_3)_4(HPO_4)]^+ + H_2O \leftrightarrows$ *trans*-$[Ru(NO)(NH_3)_4(PO_4)] + H_3O^+$, respectively. The rate constant for the reaction *trans*-$[Ru(NO)(NH_3)_4(H_2O)]^{3+} + H_2PO_4^- \leftrightarrows$ *trans*-$[Ru(NO)(NH_3)_4(H_2PO_4)]^{2+} + H_2O$ was estimated as $k_{obs} = 7 \times 10^{-8}\ s^{-1}$ at 70 °C in a dilute solution of H_3PO_4 (~5 M).

1. Introduction

The interest in transition-metal nitrosyls is primarily due to the presence in their structure of a coordinated group NO. It is well-known that NO plays an important role in various physiological processes, including cardiovascular control, immunological responses, neuronal signaling and others [1–5]. A disfunction of the regulation in nitric oxide metabolism was implicated in several disease states. The control of local concentration of NO, which is essential for obtaining the therapeutic effect, can be achieved with exogenous sources of nitric oxide [6,7]. Due to high affinity of ruthenium to NO, ruthenium complexes are currently being investigated as potential therapeutic NO-scavengers and -deliverers. Generally this metal based drugs exhibit fewer toxicity problems than drugs based on other metals [8–10].

In addition to the prospects of using ruthenium nitrosyls as biologically active compounds, the ability of these complexes to form light-induced long-lived metastable linkage isomers is of interest as well [11–13]. In the isomers, the nitrosyl group is bound either through the oxygen atom (isonitrosyl, MS1) or through both oxygen and nitrogen in a bidentate side-on arrangement (η^2, MS2). Due to the differences in the method of coordination of NO, ruthenium nitrosyls can be used as molecular constructive blocks for the synthesis of bifunctional compounds that combine photochromic properties with magnetic, conducting properties, etc. [14,15].

The successful development of these promising areas requires novel methods of synthesis and the actual data of structure and reactivity of the precursor complexes. To date, there is no information about the structure and synthesis methods of ruthenium nitrosyl complexes with coordinated ammonia molecules and phosphate ions. In this paper, we describe synthesis, spectroscopic and structural characterization of the complexes with coordinated four molecules of ammonia and PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$ ions, estimate their acidic properties and kinetics of formation in aqueous solutions.

2. Experimental

2.1. General

All reagents and solvents were obtained from commercial sources and used as supplied. The complex *trans*-$[Ru(NO)(NH_3)_4(OH)]Cl_2$ was synthesized from $(NH_4)_2[Ru(NO)Cl_5]$ with a nearly quantitative yield (~95%) [16]. $(NH_4)_2[Ru(NO)Cl_5]$ was obtained from commercial ruthenium(III) chloride hydrate according to the literature [17]. ^{31}P NMR spectra were recorded on a Bruker Avance 500 spectrometer at 298 K, operating at 202.45 MHz.

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Chemical shifts ($\delta(^{31}P)$, ppm) were referenced to an 85% solution of H_3PO_4 as an external standard. FT-IR spectra were recorded on a Scimitar FTS 2000 Fourier spectrometer in the range 4000–375 cm^{-1}. The samples for recording were prepared via the standard procedure by pressing the compounds in KBr pellets. UV–Vis diffuse reflectance spectra in the solid state were collected with a Shimatzu UV-3101PC spectrophotometer over the spectral range of 240–800 nm at room temperature. Reflectance spectra were converted to absorbance ones by using the Kubelka–Munk equation [18,19]. The electronic spectra in aqueous solutions (see Figs. S1 and S2) were recorded on a SF-102 model in the 200–900 nm range at room temperature in a 1.0 cm quartz cell. Elemental analyses were performed on a EURO EA3000 (Euro Vector).

2.2. Synthesis of trans-[Ru(NO)(NH_3)$_4$(PO_4)]·2H_2O (**1**)

2.0 ml H_3PO_4 (85 %) was added under stirring to 0.5 g (1.7 mmol) solid *trans*-[Ru(NO)(NH_3)$_4$(OH)]Cl_2. After 24 h at room temperature, the mixture was being heated for 5 h on a water bath at 95 °C. Then, ~5 ml of concentrated HCl was added to the mixture at room temperature and a light yellow precipitate was formed a few minutes later. The precipitate was filtered, dissolved in a minimum volume of water (~2 ml), and ~0.5 ml of 5 M NaOH was added (until pH ~9). The complex **1** was precipitated after ~3 h. The precipitate of **1** was collected by filtration, washed with cold water (~1 ml), acetone and dried in air. The yield was ~90%. After a few days of standing at room temperature, the mother liquor yielded yellow crystals suitable for a single-crystal X-ray analysis. *Anal.* Calc. for $H_{16}N_5O_7PRu$: H, 4.88; N, 21.21. Found: H, 4.91; N, 21.15%. FT-IR (cm^{-1}): 3456 sh $\nu(H_2O)$; 3360–3120 bvs $\nu(NH_3)$; 1848 vs ν(NO); 1621 m, 1591 m $\delta(H_2O)$, $\delta_{as}(NH_3)$; 1343 m, 1321 s, 1282 m $\delta_s(NH_3)$; 1052 bvs, 971 vs $\nu_{as}(PO_4)$; 922 bs, 876 sh, 853 m, 734 bm $\rho_r(NH_3)$, $\nu_s(PO_4)$; 663 bm, 644 m, 621 s, 589 m, 551 s, 501 m ν(Ru–NO), $\delta_{as}(PO_4)$; 486 s $\nu(Ru–NH_3)$; 440 m $\delta_s(PO_4)$; 415 w δ(Ru–NO). UV–Vis: λ_{max} = 450, 350 and 260 nm.

2.3. Synthesis of trans-[Ru(NO)(NH_3)$_4$(HPO_4)]NO_3·H_2O (**2**)

0.1 g (0.3 mmol) of complex **1** was dissolved in 0.25 ml of 1.5 M HNO_3 at room temperature. The solution was evaporated to dryness in air. The dry residue was washed with acetone and dried in air. Yellow crystals suitable for a single-crystal X-ray analysis were obtained by the slow evaporation at room temperature of a part of the solvent from the reaction solution. *Anal.* Calc. for $H_{15}N_6O_9PRu$: H, 4.03; N, 22.40. Found: H, 4.08; N, 22.39%. FT-IR (cm^{-1}): 3460 sh $\nu(H_2O)$; 3260 bvs, 3100 sh $\nu(NH_3)$; 1879 vs ν(NO); 1655 sh, 1600 m $\delta(H_2O)$, $\delta_{as}(NH_3)$; 1384 vs, 1350 vs $\nu(NO_3)$; 1302 bs $\delta_s(NH_3)$; 1125 bs δ_{plane}(POH); 1046 s, 980 bvs $\nu_{as}(PO_4)$; 920 bs, 896 m, 864 bs, $\rho_r(NH_3)$, $\nu_s(PO_4)$; 775 sh, 715 w $\nu(NO_3)$; 640 m, 617 bm, 579 m, 520 bs ν(Ru–NO), $\delta_{as}(PO_4)$, $\delta(NO_3)$; 479 s $\nu(Ru–NH_3)$; 460 sh $\delta_s(PO_4)$; 400 w δ(Ru–NO). UV–Vis: λ_{max} = 435, 315 and 250 nm.

2.4. Synthesis of trans-[Ru(NO)(NH_3)$_4$(H_2PO_4)](NO_3)$_2$ (**3**)

The compound **1** (0.1 g, 0.3 mmol) reacted with 1 ml of 1.5 M HNO_3 via the same procedure described for **2** in order to give a yellow precipitate of **3**. Yellow crystals of **3** suitable for a single-crystal X-ray analysis were formed similarly to crystals of **2** after a few days. *Anal.* Calc. for $H_{14}N_7O_{11}PRu$: H, 3.36; N, 23.33. Found: H, 3.39; N, 23.38%. FT-IR (cm^{-1}): 3300 bvs, 3180 sh $\nu(NH_3)$; 1897 vs ν(NO); 1605 bm $\delta(H_2O)$, $\delta_{as}(NH_3)$; 1360 bvs, 1350 bvs $\nu(NO_3)$; 1320 sh, 1250 bs $\delta_s(NH_3)$; 1149 s δ_{plane}(POH); 1065 bvs, 973 vs $\nu_{as}(PO_4)$; 897 s, 861 bs, 829 s $\rho_r(NH_3)$, $\nu_s(PO_4)$; 727 w $\nu(NO_3)$; 695 m, 638 m, 610 bw, 576 m, 535 s, 504 s ν(Ru–NO), $\delta_{as}(PO_4)$, $\delta(NO_3)$; 474 m $\nu(Ru–NH_3)$; 411 m, $\delta_s(PO_4)$; 400 sh δ(Ru–NO). UV–Vis: λ_{max} = 430, 308 and 244 nm.

2.5. Evaluation of acidity constants

Samples for ^{31}P NMR were prepared by dissolving exact weighed portions of **1** (~4×10^{-3} M) and adding either concentrated hydrochloric acid or 5 M NaOH to adjust pH to an appropriate value (Table S1). The prepared solutions were placed into a tube and ^{31}P NMR spectra were recorded at room-temperature.

The acidic properties were also determined by potentiometric titration (Fig. S3) with 0.1 M HCl (μ = 1.0 M KCl). All measurements were run in triplicate.

2.6. Kinetics measurements

Trans-[Ru(NO)(NH_3)$_4$(H_2PO_4)]$^{2+}$ was analysed in dilute solutions of *o*-phosphoric acid at 70 ± 1 °C by ^{31}P NMR spectroscopy. The spectra were acquired using 300 scans at 24 ± 0.5 °C. The kinetic data were treated as a pseudo-first-order reaction, and thus, the rate constant (k_{obs}) was estimated from the plots of $\ln(A_0/A)$ vs. time (Fig. S4).

2.7. Single-crystal structure analysis

Diffraction data for **1**–**3** were collected on a Bruker X8 Apex CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. The crystallographic characteristics and main indicators of the refinement are presented in Table 1. The structures were solved by direct methods and refined by a full-matrix least-squares treatment against $|F|^2$ in an anisotropic-isotropic (for H) approximation with the SHELX-97 program set [20]. All non-H atoms of the main structural units were refined anisotropically. The H atoms were refined in their geometrically calculated positions; a riding model was used for this purpose. Further details may be obtained from the Cambridge Crystallographic Data Center upon quoting depository numbers CCDC 908557–908559.

3. Results and discussion

3.1. Synthetic aspects

Three ruthenium nitrosyl complexes with PO_4^{3-}, HPO_4^{2-} or $H_2PO_4^-$ ions have been prepared. Despite the apparent simplicity

Table 1
X-ray experimental details.

	1	**2**	**3**
Empirical formula	$H_{16}N_5O_7PRu$	$H_{15}N_6O_9PRu$	$H_{14}N_7O_{11}PRu$
Formula weight	330.22	375.22	420.22
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*Pbcm*	*C*2/*c*	$P\bar{1}$
a (Å)	9.3467(7)	28.0526(13)	7.4614(15)
b (Å)	9.9602(8)	6.6930(3)	7.6213(15)
c (Å)	10.7240(8)	13.8414(6)	13.346(3)
α (°)	90	90	84.39(3)
β (°)	90	115.810(1)	75.33(3)
γ (°)	90	90	62.29(3)
V (Å^3)	998.35(13)	2339.56(18)	649.8(2)
Z	4	8	2
μ (mm^{-1})	1.757	1.528	1.401
Measured reflections	10251	17028	9341
Unique reflections (R_{int})	1994 (0.0328)	4459 (0.0148)	6826 (0.012)2
Parameters	106	183	388
R_1 [$I \geqslant 2\sigma(I)$]	0.0182	0.0138	0.0145
wR_2 [$I \geqslant 2\sigma(I)$]	0.0421	0.0374	0.0390
Goodness-of-fit	1.016	1.058	1.055