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Cis–trans isomerization in the syntheses of ruthenium cyclam complexes with nitric oxide

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ABSTRACT

The *cis* to *trans* isomerizations during the syntheses of *trans*-[Ru(NO)(OH)(cyclam)]$(PF_6)_2$, from *cis*-[$RuCl_2$(cyclam)]Cl, and [Ru(NO)Cl(cyclam)] $(PF_6)_2$, from *cis*-[$RuCl_2(dmso)_4$], are reported. The novel *trans*-[Ru(NO)(OH)(cyclam)]$(PF_6)_2$ complex was characterized by X-ray crystallography and vibrational infrared and nuclear magnetic resonance spectroscopies. The Ru–N–O bond angle (176.75º) and ν(NO) (1835 cm^{-1}) suggest a nitrosonium character for this hydroxo complex. The crystal and molecular structure of *trans*-[Ru(NO)Cl(cyclam)]$(ClO_4)_2 \cdot 2\ H_2O$ is also reported. Results presented here support the *cis–trans* isomerization observed for the first time with ruthenium cyclam complexes.

Complexes of cyclam (1,4,8,11-tetraazacyclotetradecane) with several transition metals, such as Cr, Ni, Fe, Cu, Co, Mn, Rh, and Ru, have been reported [1–12]. The interest on these complexes and their analogous relies, at least in part, on the potential applications in fields such as catalysis, photochemistry, and medicine [2,12–21]. In general, metal complexes with cyclam adopt *cis* or *trans* configuration, and *cis* to *trans* isomerization has been reported for the first transition series with known examples for Fe, Cr, Mn, Ni and Co [4,7,22–25]. In solution, pH dependent *cis* to *trans*, as well as *trans* to *cis*, isomerization of $[Ni(cyclam)(OH_2)_2]^{2+}$ has been reported [22,23]. An increase in the *cis* to *trans* isomerization rate constant value (k_{obs}) with the increase of pH has been observed for *cis*-[Ni(cyclam)$(OH_2)_2]^{2+}$[23]. At pH 7, *cis*-$[CrCl_2(cyclam)]^+$ and *cis*-[$CoCl_2$(cyclam)]$^+$ hydrolyze to *cis*-$[M(OH)(OH_2)(cyclam)]^{2+}$ (M = Cr or Co) that undergoes isomerization to the *trans* form [24,26]. For *cis*-[$MnCl_2$(cyclam)]Cl, in addition to *cis* to *trans* isomerization, a less common *trans* to *cis* isomerization have been reported upon electrochemical reduction [25]. *cis*-$[Ru(NO)X(pyca)_2]^{n+}$ (pyca = 2-pyridine carboxylate; X = Cl^-, NO_2^-, or H_2O) complexes react with OH^-, N_3^-, and OCH_3^- anions and undergo *cis–trans* isomerization upon reduction, without release of NO [27,28].

Although $[Ru(cyclam)LL']^{n+}$ complexes can be obtained by different synthetic routes, *cis* or *trans* [$RuCl_2$(cyclam)]Cl are often used as the starting material [9,29]. The $[Ru(mac)LL']^{n+}$ (mac = tetraazamacrocycle) complexes exhibit different properties that depend on the nature of the L ligands, the size of the macrocycle, and the configuration, *cis* or *trans* [9]. For instance, substitution reactions of the *cis* complexes are usually faster than those of the *trans* ones, especially after reduction of Ru^{III} to Ru^{II}[9]. For $[RuCl_2(cyclam)]^{n+}$, chloride aquation rates, in general, increase from Ru(III) to Ru(II) and from *trans* to *cis* complexes [9]. The reduction of the Ru(III) center is followed by fast aquation of both chloro ligands in the *cis* complex while loss of the second chloride in *trans*-[$RuCl_2$(cyclam)] is too slow [9,30] to make the synthesis of *trans*-[Ru(cyclam)LL']$^{n+}$ feasible. Therefore, such properties have been explored to synthesize a wide variety of $[Ru(cyclam)LL']^{n+}$ complexes. For instance, the *cis*-$[Ru(cyclam)LL']^{2+}$ (LL' = bpy, phen, or py_2) (bpy = 2,2′-bipyridine; phen = o-phenantroline; py = pyridine) complexes were prepared following the reduction of *cis*-[$RuCl_2$(cyclam)]Cl with amalgamated zinc in neutral aqueous solution [29].

Because nitric oxide plays key roles in several biological processes that depend on its local concentration [31–33], development of controlled NO releasing pro-drugs has been subject of efforts. In this context, our group has been focused on the chemistry, photochemistry, and biological activity of ruthenium nitrosyl complexes [9,11,15–17,34] and also on the synthesis, chemical and photochemical properties of ruthenium complexes with cyclam and related

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ligands, $[Ru(mac)LL']^{n+}$ [9,12,16,19,34–36]. As far as we know, no *cis* to *trans* isomerization has been reported for ruthenium cyclam complexes. The *trans*-$[Ru(NO)Cl(cyclam)]^{2+}$ complex has been reported to have potential applications as a nitric oxide (NO) donor because it has low toxicity, is stable, water soluble, and releases NO only after reduction ($k_{-NO} = 6.1 \times 10^{-4}\ s^{-1}$) or photochemically [16,34]. Thus, considering the outstanding properties of *trans*-$[Ru(NO)Cl(cyclam)](PF_6)_2$ and the biological importance of NO, and aiming potential biological applications, we decided to synthesize the analogous *cis*-$[Ru(NO)Cl(cyclam)]^{2+}$ that is expected to release NO at a larger rate.

In this communication we report the *cis–trans* isomerizations observed during the syntheses of *trans*-$[Ru(NO)(OH)(cyclam)](PF_6)_2$ (complex **I**) from *cis*-$[RuCl_2(cyclam)]^+$ and *trans*-$[Ru(NO)Cl(cyclam)](PF_6)_2$ (complex **II**) from *cis*-$[RuCl_2(dmso)_4]$, and the crystal and molecular structure of the novel complex **I**. Also reported is the crystal and molecular structure of *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2 \cdot 2H_2O$ (complex **III**), grown from **II** in perchlorate solution. The orthorhombic complex **III** obtained from this new route, is basically the same as the monoclinic non-hydrated phase previously obtained by the synthesis through reaction of $K_2[RuNOCl_5]$ with cyclam [34].

Complex **I** was prepared by reduction of *cis*-$[RuCl_2(cyclam)]^+$ with amalgamated zinc in water/ethanol/chloroform (10:5:5 v/v) followed by reaction with nitrite and acidification (see supplementary information). After recrystallization of some amount of the complex, yellow crystals suitable for X-ray analysis were obtained. Complex **II** was prepared by modification of a previously described procedure for the synthesis of $[Ru(L^{py})NO](PF_6)_3$, (L^{py} = N-(2-methylpyridyl) cyclam) [37] in an one-pot reaction (see supplementary information). Elemental analysis, % calculated and (% found) for $C_{10}H_{24}N_5OClRuP_2F_{12}$ (656 g mol^{-1}): C = 18.29 (18.16); N = 10.67 (10.35); H = 3.68 (3.56). Crystals suitable for X-ray analysis were obtained when 20 mg of this complex was dissolved in minimum amount of HCl 0.1 mol L^{-1} saturated with $LiClO_4$. During crystallization PF_6^- counter ions were exchanged by ClO_4^- yielding of *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2 \cdot 2H_2O$ (**III**).

Because *cis*-$[RuCl_2(cyclam)]Cl$ was synthesized from *cis*-$[RuCl_2(dmso)_4]$ that may undergo *cis–trans* isomerization, *trans*-$[RuCl_2(cyclam)]Cl$ was also synthesized in order to check for the identity and purity of the *cis* complex. The UV–vis spectra and redox potentials of *cis*-$[RuCl_2(cyclam)]Cl$, as determined by cyclic voltammetry and differential pulse voltammetry match with reported values (see supplementary information, Figure SI7), eliminating any possibility of contamination of the *cis* complex with some *trans*.

Fig. 1 is an ORTEP plot of **I**. Listing of atomic coordinates and equivalent isotropic displacement parameters, full intramolecular bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters are available from the authors and were deposited at the Cambridge Crystallographic Data Centre, reference number CCDC 843698.

Bond distances and angles show that the molecular structure of **I** is similar to those of the closely related tetraazamacrocycle complexes *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2$[34] and *trans*-$[Ru(NO)(OH)(tmc)](ClO_4)_2$ (tmc = 1,5,9,13-tetramethyltetraazacyclohexadecane) [38]. The Ru atom is coordinated to the four N atoms of the cyclic amine and is placed essentially on the best least squares plane through them [at 0.092(2)Å]; one hydroxo and one nitrosyl groups complete the six coordination sites. The average $Ru–N_{cyclam}$ interatomic distance of the coordinated nitrogens in **I** (see table SI2 in supplementary information) of 2.086 Å is close to the average interatomic distance exhibited by the closely related *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2$ and *trans*-$[RuCl(cyclam)(4\text{-acpy})](BF_4)$ (4-acpy = 4-acethylpyridine) that show average $Ru–N_{cyclam}$ interatomic distances of 2.092(4) Å and 2.097(2) Å, respectively, which are shorter than those shown by Ru(II) ammines and close to those of Ru(III) complexes [9,34,35]. However, in *trans*-$[RuCl(cyclam)(4\text{-acpy})](BF_4)$, the shortening of

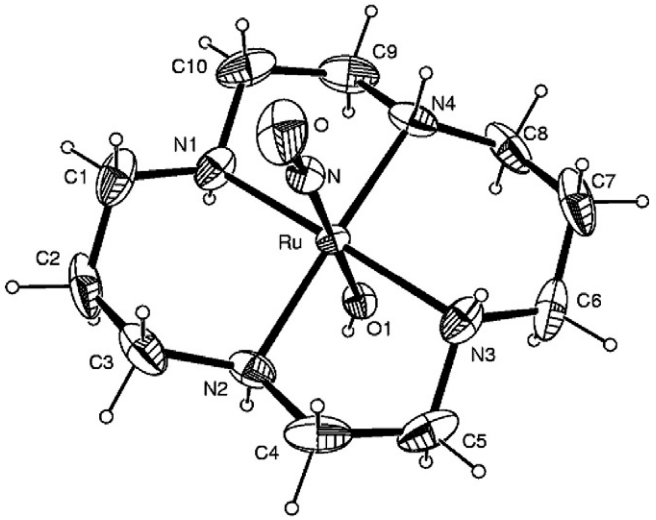

Fig. 1. ORTEP plot of the complex with anisotropic displacement ellipsoids shown to 20% probability. The two PF_6^- anions were not included for clarity. Selected bond lengths [Å] and angles [°] are as follows: Ru–N, 1.771(5); Ru–O, 1.935(4); O–N, 1.081 (7); O(1) –H, 0.887(4); Ru–N(1), 2.080(5); Ru–N(2), 2.069(5); Ru–N(3), 2.094(5); Ru–N(4), 2.099(5); O–N–Ru, 176.7(5); Ru–O(1)–H, 158.3(4); N–Ru–O(1), 179.67 (18); N–Ru–N(2), 91.5(2); O(1)–Ru–N(2), 88.8(2); N–Ru–N(1), 90.9(2); O(1)–Ru–N (1), 88.8(2); N(2)–Ru–N(1), 96.3(3); N–Ru–N(3); 94.1(2); O(1)–Ru–N(3), 86.1(2); N (2)–Ru–N(3), 83.8(3); N(1)–Ru–N(3), 174.9(2); N–Ru–N(4), 93.6(2); O(1)–Ru–N(4), 86.2(2); N(2)–Ru–N(4), 174.96(19); N(1)–Ru–N(4), 83.4(3), N(3)–Ru–N(4), 96.1(3).

$Ru–N_{cyclam}$ bond was attributed to annular constraint imparted by the rigidity of the macrocycle what would also be expected to occur for *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2$ (average $Ru–N_{cyclam}$ interatomic distance of 2.092 Å), and, similarly, for *trans*-$[Ru(NO)(OH)(cyclam)](PF_6)_2$. The Ru–OH distance (1.935 Å) of **I** is very close to that of *trans*-$[Ru(NO)(OH)(NH_3)_4]Cl_2$ (1.961 Å) [39], while the Ru–NO distance (1.771 Å) falls in the range of other ruthenium nitrosyl ammines [9,40]. The OH and NO ligands are in the same axis; the N–Ru–OH angle is 179.67º and the O–N–Ru angle is 176.75º. This last angle suggests a nitrosonium character for NO.

At variance with the monoclinic non-hydrated phase previously obtained by the synthesis through reaction of $K_2[RuNOCl_5]$ with cyclam [34], complex **III** crystallizes in the orthorhombic space group, Pnma, with the complex sited on a crystallographic symmetry plane which contains the Cl–Ru–NO line (see Figure SI1, Table SI3 and Table SI4, supplementary information). Also, there are two H_2O molecules in the crystal lattice, whereas crystals of *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2$ are monoclinic, space group, P21/c, and the complex is located on a general position. Crystallographic data for complex **III** have been deposited at the Cambridge Crystallographic Data Centre, reference number CCDC 843636.

The infrared absorption spectrum of mono crystals of **I** (see Fig. SI2, supplementary information) shows band characteristic of the macrocycle, the PF_6^- stretching band at 839 cm^{-1}, and the ν_{NO} band at 1830 cm^{-1}, in the range generally associated with nitrosyl metal complexes and consistent with a nitrosonium character and the linearity of the RuNO moiety [9,40,41]. For *trans*-$[Ru(NO)Cl(cyclam)](ClO_4)_2$, the ν_{NO} band appears at 1875 cm^{-1}, [9,34] so, there is a consistent shift of this frequency to lower energy for the hydroxo complex. This is similar to what occurs for *trans*-$[Ru(NO)Cl(NH_3)_4]Cl_2$ and *trans*-$[Ru(NO)(OH)(NH_3)_4]X_2$; for the chloro complex the ν_{NO} band appear at 1878 cm^{-1}[42] and for the OH complexes, it appears at 1855, 1850, and 1845 cm^{-1}, for X = Cl, Br, and I, respectively [42].

The assignment of the NMR spectra was done by comparing the ^1H and ^{13}C chemical shift (δ) values of the spectra of complex **I** to those of related species [34,35] and mainly on the correlations observed in the 2D spectra ($^1H–^1H$ COSY, $^1H–^{13}C$ HMQC _ J^1–J^1 coupling,

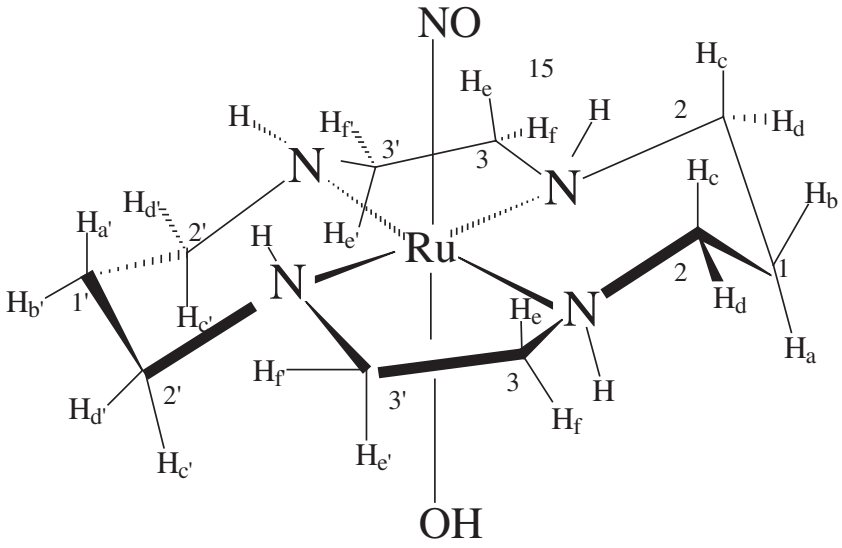

Fig. 2. Pictorial view of the structure of **I** with NMR labels.

and $^{1}H–^{13}C$ HMBC _ J^{1}–J^{2} and J^{1}–J^{3} coupling, see nuclear magnetic resonance section in Supporting Information). The N–H protons were not observed due to the fast exchange with deuterium atoms from the D_2O solvent, as occurs for similar complexes [11,34,35].

The spectra profile is rather simple, displaying signals with the expected multiplicity. In the case of the cyclam macrocycle the coupling pattern is dictated by the non-equivalence of axial and equatorial methylenic hydrogen atoms and by the fact that, in the *trans*–ruthenium complex, the two faces of the macrocycle are distinguishable due to differences in the inductive effect promoted by the nitrosyl and hydroxyl axial ligands (Fig. 2). Thus, the quartets observed between 2.0 and 1.5 ppm are assigned to the Ha,a′, split by the coupling with protons Hb,b′, Hc,c′ and Hd,d′. In turn, the duplets observed between 2.5 and 2.0 are ascribed to protons Hb,b′. Hc appears as a triplet due to the coupling with protons Hd and Ha and finally, protons Hd,d′ appears as duplets between 3.5 and 3.0 ppm (coupled with Hc,c′) (Table 1).

The $^{1}H–^{13}C$ correlations experiments (Fig. 3) (for the HMBC spectrum, see Figure SI5) were particularly useful in the assignment of the two multiplets centered at 2.84 and 3.61 ppm, which are the superposition of the Hc,e,e′ and Hf,f′ signals, respectively. Table 1 summarizes the ^{1}H and ^{13}C δ values. It is worth mentioning that the sum of the experimental integral values (20,8) matches pretty well the expected value (20).

Therefore, NMR results are consistent with the X-ray structure, giving further support to the *trans* configuration, and also indicating that the structure in the solid state is maintained in solution.

Table 1
^{1}H and ^{13}C NMR data for complex **I**, collected from D_2O solution.

^{13}C	δ (ppm)	^{1}H	δ (ppm)
1	28.6	a	1.70, q[a]
1′	28.5	a′	1.96, q
2	48.6	b	2.16, d
2′	51.5	b′	2.40, d
3	52.3	c	2.90, t
3′	54.4	c′, e, e′	2.84, m
		d	3.24, d
		d′	3.45, d
		f, f′	3.61, m

[a] q = quartet, d = duplet, t = triplet, m = multiplet.

In summary, this paper reports the *cis–trans* isomerization during the syntheses of *trans*-$[Ru(NO)(L)(cyclam)]^{2+}$ (L = Cl^- or OH^-) from *cis* ruthenium(II) complexes. In general, the syntheses of ruthenium ammine and tetraazamacrocycle complexes reported so far undergo with retention of configuration [9,29] . This is the case for cyclam complexes such as *cis*-$[Ru(cyclam)(py)_2]^{2+}$ and *cis*-[Ru(cyclam)(bpy)]$^{2+}$ which were obtained from *cis*-$[RuCl_2(cyclam)]Cl$ [29]. The *cis*-$[Ru(NO)X(pyca)_2]^{n+}$ complexes undergo *cis–trans* isomerization upon reduction [27,28]. In the present case, the *cis–trans* isomerization should be occurring after the addition of nitrite. The evidences so far do not allow establishing if it is the nitrite or the resulting nitrosyl group that is inducing the isomerisation. It is conceivable that after the fast conversion of the coordinated nitrite into nitrosyl, as reported for other ammine complexes [11], NO would induce, through its well known *trans* effect, the labilization of the N cyclam atom. This effect would result in a transient species that leads to the *trans* isomer. In order to understand this further studies are needed.

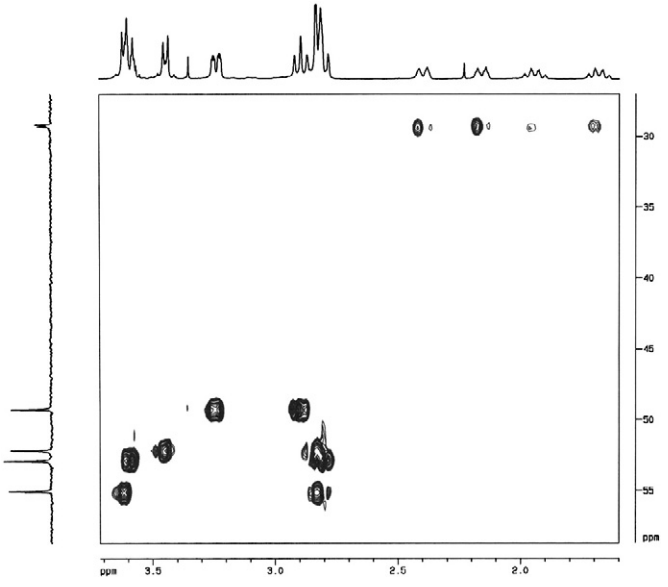

Fig. 3. HMQC NMR spectrum of *trans*-$[Ru(NO)(OH)(cyclam)](PF_6)_2$ (D_2O solution).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.09.046.

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