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Cyclam κ^4 to κ^3 Ligand Denticity Change Upon Mono-N-Substitution with a Carboxypropyl Pendant Arm in a Ruthenium Nitrosyl Complex

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The complex *fac*-[Ru(NO)Cl$_2$(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl · H$_2$O (1-carboxypropyl)cyclam = 3-(1,4,8,11-tetraazacyclotetradecan-1-yl)propionic acid) was prepared in a one pot reaction by mixing equimolar amounts of RuNOCl$_3$ and (1-carboxypropyl)cyclam and was characterized by X-ray crystallography, electrospray ionization tandem mass spectrometry (ESI-MS/MS), elemental analysis, NMR, and electronic and vibrational (IR) spectroscopies. *fac*-[Ru(NO)Cl$_2$(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl · H$_2$O crystallizes in the triclinic, space group $P\bar{1}$, No. 2, with unit cell parameters of $a = 8.501(1)$ Å, $b = 9.157(1)$ Å, $c = 14.200(1)$ Å, $\alpha = 72.564(5)°$, $\beta = 82.512(5)°$, $\gamma = 80.308(5)°$, and $Z = 2$. The Ru−N interatomic distance and bond angle in the [Ru-NO] unit are 1.739(2) Å and 167.7(2)°, respectively. ESI-MS/MS shows characteristic dissociation chemistry that initiates by HCl or NO loss. The IR spectrum displays a ν(NO) at 1881 cm^{-1} indicating a nitrosonium character. The electronic spectrum shows absorptions bands at 264 nm (log $\varepsilon = 3.27$), 404 nm (log $\varepsilon = 2.53$), and 532 nm (log $\varepsilon = 1.88$). ^{1}H and ^{13}C NMR are in agreement with the proposed molecular structure, which shows a very singular architecture where the cyclam ring N (with the carboxypropyl pendant arm) is not coordinated to the ruthenium resulting in a κ^3 instead of the expected κ^4 denticity.

Introduction

Macrocycles are very important and powerful ligands in transition metal chemistry. These molecules frequently impart great stability and inertness to their metal complexes, as is the case of the azamacrocycles[1,2] that have been attracting attention because of their applications in biology and medicine.[1,3–8] Cyclam (1,4,8,11-tetraazacyclotetradecane) is probably the most studied polyazamacrocycle in coordination chemistry. Many complexes of cyclam with most transition metals, such as Cr, Ni, Fe, Cu, Co, Rh, and Ru, have been reported during the past four decades.[9–15] Cyclam is tetracoordinated in the great majority of complexes because of the chelate effect, although there is a very small number of

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examples of substituted cyclam and derivatives coordinated by less than four N, such as in Ge and Au complexes, where they present κ^2 and κ^3 denticity.[16,17] In the case of ruthenium complexes, as far as we could verify, only in a single, κ^6, complex three out of four cyclam ring nitrogens are coordinated.[18] Although extensive investigations have been performed on the chemistry of Cu, Ni, and Co complexes with mono-N-functionalized macrocycles,[19–23] and more recently with Cr,[24–26] very few reports exist on ruthenium complexes with this kind of ligands.[27–30] The only reported ruthenium nitrosyl complex with a mono N-functionalized cyclam displays a *cis* configuration where the *N*-(2-methylpyridyl)cyclam ligand is pentacoordinated to the RuNO core in a κ^5 mode.[30]

We have been devoting efforts to the synthesis and the study of the chemical and photochemical properties of Ru(II) and Ru(III) complexes with cyclam and related species.[13,29,31–34] Among these, the Ru(II) complexes showed, in addition to similarities, some differences from the analogous Ru(II) ammines, especially the pentaammines, with regard to properties such as UV–visible (UV–vis) spectra and reactivity.[12,13,31–33,35,36]

Metal complexes that are able to capture or release nitric oxide (NO) have gained considerable attention.[13,25,37–43] Part of this interest has surged from the biological functions of nitric oxide and the large number of physiological functions and pathologies in which NO is involved.[44] For instance, NO acts as a biological messenger responsible for vasodilatation, inhibits platelet aggregation, plays a role in the immune response, and acts as a neurotransmitter.[44–46] NO may also prove to be involved in cell apoptosis and tumor kills.[47,48] However, high or low concentrations (bioavailability) of NO may be either beneficial or harmful;[49] hence, there is a need for selective and site specific NO donors.

The chemistry, photochemistry, and potential biological applications of ruthenium nitrosyls such as *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$ (L = nitrogen heterocyclic bases) and the analogous *trans*-$[Ru(NO)(mac)L]^{n+}$ (mac = tetraazamacrocycles) (L = Cl^-, OH^-, H_2O) complexes have been investigated to some extent.[13,41,50] These complexes may also act as potential NO delivering agents since they release NO upon reduction or under irradiation with light.[13,41,50–52] Indeed, these complexes show a very rich potential as NO delivery agents in biological systems.[52–55] For ruthenium am(m)ines, in vitro and in vivo studies showed that they display, for example, blood pressure reduction effects[53,54] and antiproliferative and trypanocidal[55] activities. For example,[54] administration of the less toxic *trans*-$[Ru(NO)Cl(cyclam)]^{2+}$ to hypertensive male Wistar rats resulted in blood pressure reduction 26 times longer than sodium nitroprusside (SNP), a classical vasodilator. This effect was related[54] to the rate of NO release (6.1×10^{-4} s^{-1})[56] following the reduction of *trans*-$[Ru(NO)Cl(cyclam)]^{2+}$, which is lower than that of all other ruthenium nitrosyls such as *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$.[41,56] This relationship opens the possibility for this complex to be used as a controlled-release NO donor. We

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decided, therefore, to study Ru complexes with mono-N-substituted cyclam ligands containing an arm bearing amine or carboxy functional groups. These groups are versatile linkers because they can form amide bonds with a desired material or relevant biomolecules such as proteins or antibodies. Whereas complex-modified solid materials may lead, for example, to sensors with potential analytical applications, the attachment of such compounds to biomolecules may form NO carrier systems with an additional possibility of targeting improvement by the judicious choice of the biomolecule (an antibody, for instance). With this aim, our first results were achieved with *trans*-[RuCl(L)(1-(3-propylammonium)-cyclam)]$^{n+}$ (L = Cl^-, H_2O (tfms = trifluoromethanesulfonate))[29] which has a pendant amino group that can be used as a linker unit. This complex was found to exhibits *trans* configuration[29] with its metal center coordinated to the four nitrogens of the cyclam similar to the ruthenium nitrosyl tetraazamacrocyclic complexes *trans*-[Ru(NO)Cl(cyclam)]$^{2+}$ [56] and *trans*-[Ru(NO)-(OH)(tmc)]$(ClO_4)_2$, (tmc = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane).[57] The complex investigated herein, that is, *fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl·H_2O (**I**) ((1-carboxypropyl)cyclam = 3-(1,4,8,11-tetraazacyclotetradecan-1-yl)propionic acid) adopts an entirely different configuration as those of the analogous complexes by exhibiting a denticity κ^3 for the pentadentate and potentially κ^5 mono-N-substituted 1-(carboxypropyl)cyclam ligand instead of κ^4. As far as we know, this is the first example of a κ^3 denticity for a cyclam ligand in a Ru complex. The unusual coordination of only three cyclam nitrogens for a ruthenium complex appears to have been reported only once.[18] In this single previous example, a tetra-N-substituted cyclam with a *N*-(2-methylpyridyl) ligand is chelating a Ru(III) atom which is coordinated to three N atoms from the cyclam ligand and three nitrogen atoms from the *N*-(2-methylpyridyl) substituent, rendering the ligand denticity to κ^6. Besides this unexpected coordination mode, the presence of a free carboxyl group (that can be used as a linker) and a nitrosyl ligand (that could turn it into a potential NO donor) imparts very promising properties to this complex. In addition, the κ^3 N-coordinated **I** structure also resembles the one of ruthenium complexes obtained with 1,4,7-triazacyclononane ligands.[58–60] Several of these complexes have been found to exhibit catalytic properties including epoxidation of alkenes and selective oxidation of alcohol and ketones.[61,62] Herein we report therefore the synthesis and extensive characterization of **I**, obtained by reaction of the 3-(1,4,8,11-tetraazacyclotetradecan-1-yl)propionic acid ligand (Figure 1) with $RuNOCl_3$.

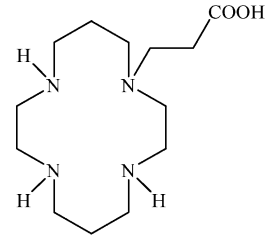

Figure 1. Structure of mono-N-substituted cyclam ligand [3-(1,4,8,11-tetraazacyclotetradecan-1-yl)propionic acid = (1-carboxypropyl)cyclam] with a carboxyl pedant arm.

Experimental Section

Chemicals and Reagents. Cyclam and $RuCl_3 \cdot nH_2O$ (40–45% Ru) were purchased from Strem Chemicals. $RuNOCl_3$ was prepared as described.[63] All other solvents and reagents were of analytical grade and used as supplied or purified when necessary, according to standard methods.[64] All the manipulations with air sensitive compounds were carried out following conventional techniques.[65] Deionized water was used throughout.

(1-Carboxypropyl)cyclam. This ligand was synthesized according to a published procedure[66] with slight modifications. Acrylic acid (0.38 g, 5.0×10^{-3} mol) was added dropwise to a solution of cyclam (1.00 g, 5.00×10^{-3} mol) in 20 mL of chloroform in the presence of the tip of a spatula of 2,4-di*tert*-butylphenol. The reaction mixture was stirred at room temperature for 1 h and heated to reflux for 4 days. The solvent was rotary-evaporated under reduced pressure. The crude product was chromatographed through silica gel (CH_3OH-NH_4OH, 6:4) to yield a colorless oil. Yield: 40% (0.56 g, 2.0×10^{-3} mol). IR: ν_{max} (cm^{-1}, nujol) 3500 (OH); 1560 (CH), 1640 (COO^-). ^{1}H NMR: δ_H (ppm; $CDCl_3$) 1.75–1.84 (m, 4H, $CH_2CH_2CH_2$), 2.35 (t, 2H, CH_2CO), 2.53–2.58 (m, 4H), 2.64 (t,2 H), 2.79–2.85 (m, 10H), 2.90(t, 2H). ^{13}C NMR: δ_C (ppm; $CDCl_3$) 24.42 e 26.38 ($CH_2CH_2CH_2$), 35.64 ($CH2CO$), 45.93, 46.06, 47.35, 48.75, 49.18, 50.09, 50.07, 52.04, 54.52 (CH_2N), 179.26 (CO). *m*/*z* (electrospray) = 271.22. These results agree with the reported values.[66]

***fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]Cl·H_2O (I).** $RuNOCl_3$ prepared using an amount of 1.00 g (4.10×10^{-3} mol) of $RuCl_3 \cdot nH_2O$ was dissolved in 250 mL of argon degassed ethanol in a three-necked round flask. To this solution was added dropwise 1.22 g (4.49×10^{-3} mol) of (1-carboxypropyl)cyclam dissolved in 100 mL of argon degassed ethanol. The resulting mixture was kept under reflux with continuous argon bubbling for 18 h. After filtration of the reaction mixture through a glass frit, the filtrate was rotary-evaporated to dryness. The resulting brown residue was dissolved in water and loaded onto a Sephadex SP-C25 cation exchange column 15 × 2 cm in size. The column was eluted sequentially with water, 0.1 and 0.2 mol L^{-1} HCl aqueous solutions. The light purple product band eluted with 0.1 mol L^{-1} HCl. From the yellow band eluted with 0.2 mol L^{-1} HCl attempts to isolate products were unsuccessful. The product containing fraction was rotary-evaporated to dryness and the light purple solid was dissolved in 0.5 mol L^{-1} HCl and left in the dark for ~3 weeks at room temperature for crystallization. Dark purple crystals suitable

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for X-ray crystallography were collected. Yield 13% (0.30 g, 0.59 × 10^{-3} mol). Anal. Calcd for $C_{13}H_{28}O_3N_5Cl_3Ru$: C, 29.56; H, 5.56; N, 13.27; Cl, 20.16. Found: C, 29.68; H, 5.52; N, 13.39; Cl, 20.90.

***trans*-[Ru(NO)Cl(cyclam)](PF$_6$)$_2$.** *trans*-[Ru(NO)Cl(cyclam)]-$(PF_6)_2$ was synthesized by a similar procedure described for the *fac* complex. A mixture of $RuNOCl_3$ prepared using 0.50 g (2.05 × 10^{-3} mol) of $RuCl_3 \cdot nH_2O$ and cyclam (0.42 g, 2.1 × 10^{-3} mol) was refluxed in 150 mL of ethanol. After filtration of the reaction mixture, the filtrate was evaporated to dryness. Purification was performed in the same way as for the *fac* complex. The yellow product band eluted with 0.2 mol L^{-1} HCl solution. This fraction was rotary-evaporated to ~10 mL, and an excess of NH_4PF_6 was added. The resulting yellow precipitate was collected by vacuum filtration, washed with acetone, and stored under vacuum in the dark. Yield 27% (0.37 g, 0.56 mmol). Anal. Calcd for $C_{10}H_{24}N_5OP_2F_{12}ClRu$: C, 18.28; H, 3.68; N, 10.66. Found: C, 18.17; H, 3.94; N, 10.20.

Spectroscopy. UV–vis spectra were recorded using a Hewlett-Packard 8452A spectrophotometer. Infrared (IR) spectra were obtained in a Bomem MB 102 FTIR spectrophotometer using KBr pellets or nujol mulls in the range 4000–400 cm^{-1}. ^1H and ^{13}C were obtained in 5 mm NMR tubes on a Bruker Avance DRX400 or Avance DRX500 model spectrometers in D_2O, acetone-d_6 or acetonitrile-d_3. Electron spin resonance (ESR) spectra were recorded on a Bruker ESP 300e spectrometer using an ER 041XK microwave source operating in the X band equipped with a 941ST380 standard cavity model at 77 K.

Mass Spectrometry (MS). MS measurements were performed using a high-resolution hybrid quadrupole (Q) and orthogonal time-of-flight (Tof) mass spectrometer (Q-Tof, from Waters Micromass, U.K.) operating in positive ion electrospray ionization mode. Tandem mass spectrum (ESI-MS/MS) was acquired using the product ion scan mode to select all isotopologues of the singly charged complex and to perform its 15 eV collision induced dissociation (CID) with argon and high resolution orthogonal Tof mass analysis of the CID ionic fragments. For the analysis of the metal complexes, samples were diluted in a CH_3OH:H_2O (1:1) mixture or methanol for free ligand and injected through a 10 μL min^{-1} continuous flux syringe pump.

X-Ray Crystallography. The crystal was mounted on an Enraf-Nonius Kappa-CCD difractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program;[67] integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs.[68] Absorption corrections were carried out using the Gaussian method.[69] The structure was solved by direct methods with SHELXS-97.[70] The model was refined by full-matrix least-squares on F^2 by means of SHELXL-97.[71] All hydrogen atoms were stereochemically positioned and refined with the riding model. Figure 2 was prepared using ORTEP-3 for windows (Oak Ridge thermal ellipsoid plot).[72]

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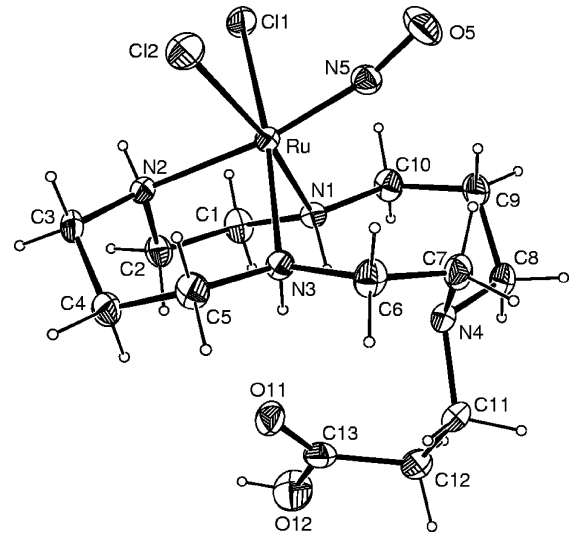

Figure 2. ORTEP structure of **I**.

Table 1. Crystallographic Data for **I**

chemical formula	$C_{13}H_{30}Cl_3N_5O_4Ru$
formula weight	527.84
wavelength	0.71073 Å
space group	$P\bar{1}$, No. 2
unit cell dimensions	a = 8.501(1) Å, α = 72.564(5)° b = 9.157(1) Å, β = 82.512(5)° c = 14.200(1) Å, γ = 80.308(5)°
volume	1035.78(18) Å^3
Z	2
T	20 °C
D_{calcd}	1.692 g/cm^3
final R indices [$I > 2\sigma(I)$]	R1 = 0.0307, wR2 = 0.0786

Table 2. Main Interatomic Distances of **I** and *trans*-[RuCl(NO)cyclam]$(ClO_4)_2$

bond	interatomic distance, Å	
	I	*trans*-[Ru(NO)Cl(cyclam)]$(ClO_4)_2$[54]
Ru−Cl(1)	2.3789(7)	2.327(1)
Ru−Cl(2)	2.3798(7)	
Ru−N(1)	2.133(2)	2.097(4)
Ru−N(2)	2.111(2)	2.088(4)
Ru−N(3)	2.146(2)	2.089(4)
Ru−N(4)	3.696(4)[a]	2.093(4)
Ru−N(5)	1.739(2)	1.747(4)
O(5)−N(5)	1.149(3)	1.128(5)

[a] Estimated value.

Results and Discussion

Molecular Structure. Figure 2 shows the molecular structure obtained by X-ray diffraction for **I**. One solvent–water molecule, as well as the chloride counterion, is omitted for clarity. Incidentally, two water molecules, symmetry related by a crystallographic inversion center, are hydrogen bonded to two similarly related chloride ions acting as electron donors and, in turn, they are also hydrogen bonded to the O12 atoms of two complexes related by the same inversion center acting as electron acceptors, giving rise to a polymeric chain (Supporting Information). Table 1 summarizes the data collection and experimental details. Tables 2 and 3 give selected interatomic distances and angles. For comparative purposes, atoms are numbered in the same order of the previously reported *trans*-[Ru(NO)Cl(cyclam)]-$(ClO_4)_2$.[56]

Table 3. Main Bond Angles For **I** and *trans*-[RuCl(NO)cyclam]$(ClO_4)_2$

bond	bond angle, degree	
	I	*trans*-[RuCl(NO)cyclam]$(ClO_4)_2$[54]
N(5)−Ru−N(2)	171.54(9)	93.1(2)
C(7)−N(4)−C(8)	110.6(2)	115.6(5)
N(3)−Ru−Cl(1)	171.95(6)	85.37(13)
C(5)−N(3)−C(6)	109.7(2)	115.3(6)
C(10)−N(1)−C(1)	110.3(2)	115.0(4)
O(5)−N(5)−Ru	167.7(2)	178.0(4)
Cl(2)−Ru−N(1)	170.91(6)	
Cl(1)−Ru−Cl(2)	89.50(3)	
N(5)−Ru−Cl(1)	87.36(8)	117.43(14)
N(5)−Ru−Cl(2)	85.61(7)	
N(2)−Ru−Cl(1)	85.95(6)	85.22(12)
N(2)−Ru−Cl(2)	89.15(6)	

As Figure 2 shows, the molecular structure of **I** differs greatly from that of the closely related macrocycle complexes *trans*-[Ru(NO)Cl(cyclam)]$(ClO_4)_2$[56] and *trans*-[Ru(NO)(OH)-(tmc)]$(ClO_4)_2$.[57] For the latter two complexes, the Ru atom is placed essentially on the plane of the macrocyclic and is coordinated to the four N atoms of the cyclic amine. For the present case (*fac*), the Ru atom is coordinated only to three N atoms, whereas the fourth N atom, which holds the carboxypropyl pendant arm, remains uncoordinated. Two chloride ions and one nitrosyl complete the six coordination sites. The coordination mode of the macrocyle shows a lowering of the denticity from the expected κ^4 to an unexpected κ^3. As a result of this N-functionalization with the carboxypropyl pendant arm, the complex adopts the *fac* configuration. It should be noted that in some cases with other transition metal ions, the N- or C-substituted cyclam adopts the *cis* configuration[24,73] and that in the chemistry of Cr(III) it has been noticed that *cis*-cyclam complexes are much more difficult to isomerize to the more stable *trans* when there are N-functional groups.[24] However, in all of these cases all four cyclam ring nitrogens are coordinated.

The origin of the denticity lowering for the substituted cyclam ligand in **I** is not yet fully understood. However, some rationales can be offered. The presence of the carboxypropyl pendant arm on the uncoordinated N suggests that this group influences the chemical properties of the N atom. It is known that N-substitution converts a secondary amine to a tertiary amine, a poor σ donor for steric reasons.[1] As a matter of fact, the protonation of the uncoordinated N atom, as verified by X-ray crystallography, elemental analysis, NMR spectra, and mass spectrometry does not occur in H^+ concentration as high as 0.5 mol L^{-1} which was the medium acidity where the crystals were grown. However, 1-(3-aminopropyl)cyclam also has a tertiary amine, and yet, its dichloro Ru complex is *trans* and κ^4 according to its properties (electrochemistry, UV–vis, and IR spectra)[29]. Therefore, substitution alone seems not to be the reason for the denticity lowering and may be influenced by the nature of the substituent on the pendant arm, amine or carboxyl, which should have different inductive effects.[1] However, Slep and co-workers[30] report a Ru nitrosyl complex with *N*-(2-methylpyridyl) mono-N-substituted cyclam with a *cis* configuration where Ru is coordinated to the four macrocyclic N atoms. More work is therefore required to achieve a better understanding of the mono-N-substitution effects on the configuration of Ru cyclam complexes.

Another possibility to the κ^4 to κ^3 denticity change would be the synthetic route. The related complex *trans*-[Ru(NO)-Cl(cyclam)]$^{2+}$ is generally prepared by the reaction of NO with *trans*-[RuCl(tfms)(cyclam)]$^{2+}$ or by addition of cyclam to $K_2[RuCl_5NO]$.[56] These synthetic routes were also investigated using the (1-carboxypropyl)cyclam ligand, but attempts to isolate products suitable for analysis were unsuccessful. A new route to the synthesis of the carboxypropyl complex adding the (1-carboxypropyl)cyclam ligand to $RuNOCl_3$ was therefore used, resulting in the *fac* complex. For comparison, this route was also used for the cyclam complex, resulting in the *trans* complex, as evidenced by elemental analysis, ^1H and ^{13}C NMR, UV–vis, and IR spectra, as well as cyclic voltammetry which agree with previous results.[56] Thus, the synthetic route is not responsible for the obtainment of the *fac* complex instead of the *trans* with the (1-carboxypropyl)cyclam ligand.

Considering that the κ^4 denticity would be the most favored for the tetraazamacrocycle because the chelate effect should be, in principle, thermodynamically favorable and in the absence of further evidence, the κ^3 denticity seems to result from a kinetically controlled reaction during synthesis. Potentially the (1-carboxypropyl)cyclam ligand could be κ^5; however, because of the protonation of the carboxyl at the pH of synthesis, this denticity is not favored.

The Ru−N interatomic distances in Ru am(m)ines and related complexes depend on the oxidation state of Ru.[12,13,31,56,57,74–78] The average Ru−N_{cyclam} interatomic distance of the coordinated nitrogens in **I** (Table 2) of 2.130(2) is closer to the average interatomic distance exhibited by Ru(II)−N_{ammine} (2.14 Å), as in $[Ru^{II}(NH_3)_6]I_2$ (2.144 Å)[74] and $[Ru^{II}(NH_3)_5(1\text{-mpz})]I_3$ (from 2.17(1) (*trans*) to 2.136(8)),[75] than to that of Ru(III) ammines (2.10 Å), as in $[Ru^{III}(NH_3)_6](BF_4)_3$ (2.104 Å),[74] $[Ru^{III}(NH_3)_5(1\text{-mpz})](tos)_4 \cdot 5H_2O$ (from 2.10(1) Å to 2.118(8) Å),[75] and $[Ru^{III}(NH_3)_5Cl]$ (from 2.096(4) Å to 2.108(4) Å).[76] The complexes *trans*-[Ru(NO)Cl(cyclam)]$(ClO_4)_2$[56] and *trans*-[RuCl-(cyclam)(4-acpy)](BF_4)[31] show an average Ru−N_{cyclam} interatomic distance 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. Ru−N_{cyclam} interatomic distances in **I**, as mentioned above, are closer to those of Ru(II) ammine and longer than those in *trans*-[Ru(NO)Cl(cyclam)]-$(ClO_4)_2$[56] and *trans*-[RuCl(cyclam)(4-acpy)](BF_4).[31] In *trans*-[RuCl(cyclam)(4-acpy)](BF_4), the shortening of 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} inter-

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atomic distance of 2.092). This constraint is absent for **I** because of its configuration in which the Ru atom is located outside the plane, bringing the average $Ru-N_{cyclam}$ interatomic distance close to those of $Ru(II)-N_{ammine}$, as observed. The presence of an additional chloride bound to Ru should also decrease the positive charge on the metal center and therefore increase the $Ru-N_{cyclam}$ distances. The nearly linear Cl(2)−Ru−N(1) and Cl(2)−Ru−N(3) bond angles (Figure 2 and Table 3) result in interatomic distances of Ru−N(1) 2.133(2) Å and Ru−N(3) 2.146(2) Å longer than that of Ru−N(2) 2.111(2), where N(2) is in *trans* position to NO.

The intramolecular distance Cl(1)···H−N(2) of 2.652 Å in **I** is smaller than the sum of van der Waals radii for H and Cl (3.0–3.3 Å) suggesting a hydrogen bond. The chloride inertness toward substitution for *trans*-[RuCl(cyclam)(4-acpy)](BF_4),[31] *trans*-[Ru(NO)Cl(cyclam)]$(ClO_4)_2$,[56] and *trans*-[$RuCl_2$(cyclam)]Br, [12] which have N···H distances of 2.70 Å, 2.43 Å, and 2.71 Å, respectively, is credited to these interactions. So, a similar behavior would be expected for **I**. Nonetheless, for the other chloride (Cl(2)), the Cl(2)···H−N(2) distance of 3.150 Å is longer than the other but it is still within the range of the van der Waals radii, thus making its effect difficult to predict.

Ruthenium nitrosyl structures generally show a nearly linear Ru−N−O bond angle.[41,56,57,77,79–83] In **I** (Table 3), the Ru−N−O bond angle of 167.7° is slightly smaller than those of some other ruthenium nitrosyl complexes, which ranges from 180 to 170.4(5).[41,83] Besides the slight bond angle O(5)−N(5)−Ru bending in **I**, the interatomic distance observed of 1.739(2) Å is in the range of those observed for other ruthenium nitrosil ammines which ranges from 1.715(5) to 1.81 Å.[41]

NMR Spectra. The structure of the cation of **I** in D_2O or acetone-d_6 was also investigated by ^1H and ^{13}C NMR. The ^1H NMR spectrum in D_2O (Supporting Information) shows 18 sets of signals over 1.5–4.0 ppm because of the CH_2 hydrogens of the cyclam ligand and the pendant arm. The sharp lines indicate a diamagnetic character that is in agreement with the silent ESR spectrum. Unfortunately, an unambiguous assignment for each proton is difficult because the methylenic hydrogens have very close chemical shifts and there is a high multiplicity from possible couplings (Supporting Information). This behavior may be related to the low symmetry of the complex and/or to a possible flexibility of the CH_2 groups in the neighborhood of the uncoordinated N atom as well as the carboxypropyl pendant arm. However, the relative intensities of the 18 sets of signals correspond to 24 hydrogens, as expected. The ^1H NMR spectrum in acetone-d_6 (Supporting Information) shows three N−H signals from 5.0 to 8.0 ppm in the intensity ratio of 1:1:1 which is in agreement with the *fac* configuration, indicating, also, that the configuration is retained in solution. These signals are not seen in D_2O because of the fast H exchange by D.[31,80,84] A broad peak with small intensity around 12 ppm may be assigned to the acidic hydrogen from the carboxylic group. The ^{13}C NMR spectrum (Supporting Information) shows 13 signals, 12 of those being in the 20–60 ppm range because of the CH_2 groups and one at 180 ppm because of the carbonyl group carbon. The presence of 13 nonequivalent NMR signals is in agreement with the molecular structure determined by X-ray diffraction. The ^1H and ^{13}C NMR spectra obtained for *trans*-[Ru(NO)Cl(cyclam)]$^{2+}$ in D_2O or CD_3CN are in agreement with the *trans* configuration and show the same patterns of those reported previously.[56]

Mass Spectrometry. The structure and fragmentation chemistry of the gaseous *fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]$^+$, that is, the cation [M − Cl]$^+$ was investigated by ESI-MS and ESI-MS/MS. These techniques have been used extensively by us[85–90] and others[91–94] to characterize Ru complexes.

When a H_2O-CH_3OH (1:1) solution of **I** was analyzed by ESI-MS, the spectrum shown in Figure 3 was collected. Note the predominant cluster of isotopologues ions of *m*/*z* ranging mainly from 468.2 to 480.2, which characterize a species containing a single Ru and two Cl atoms. The isotopic pattern is consistent therefore with the $C_{13}H_{28}O_3N_5RuCl_2$ composition. Note also in Figure 3 that the experimental distribution and relative abundance of the isotope cluster ions match perfectly that calculated for [M − Cl]$^+$. The other less abundant clusters of lower *m*/*z* correspond to fragment ions formed by the loss of HCl and/or NO as revealed by ESI-MS/MS data (Supporting Information).

The ESI-MS/MS for collision induced dissociation of some selected isotopologues of mainly *m*/*z* 474.2, 475.2, and 476.2 shows that the gaseous cationic complex fragments initially by either NO (*m*/*z* 444.6) or HCl (*m*/*z* 438.2) loss. Note that this fragmentation chemistry is coherent with the proposed

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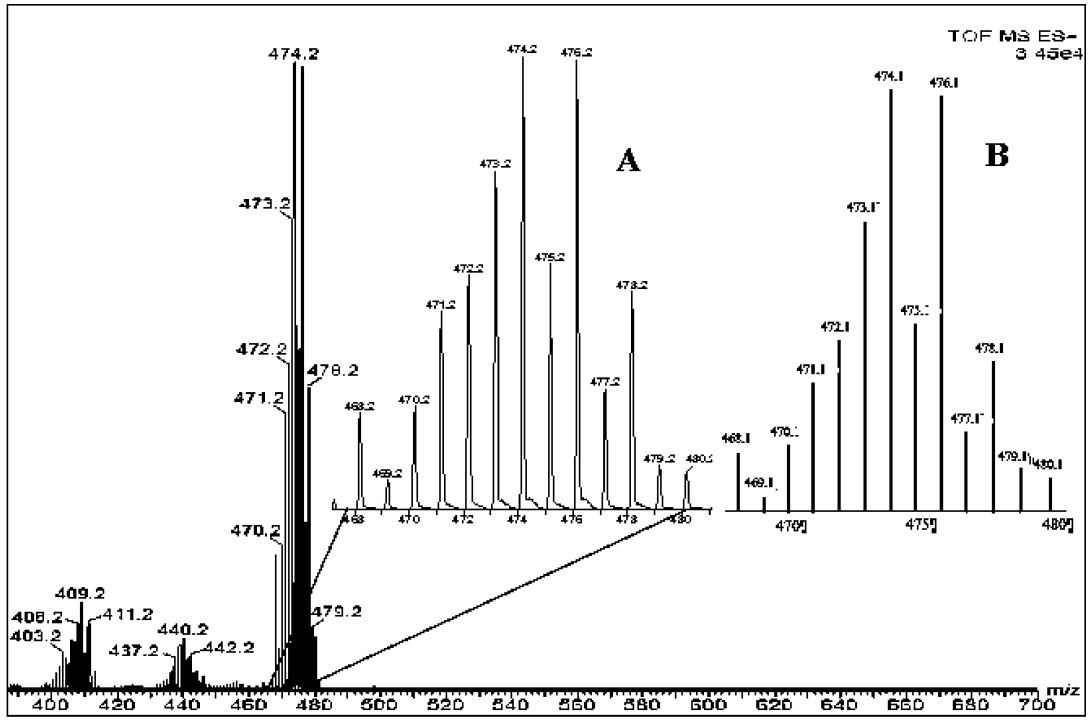
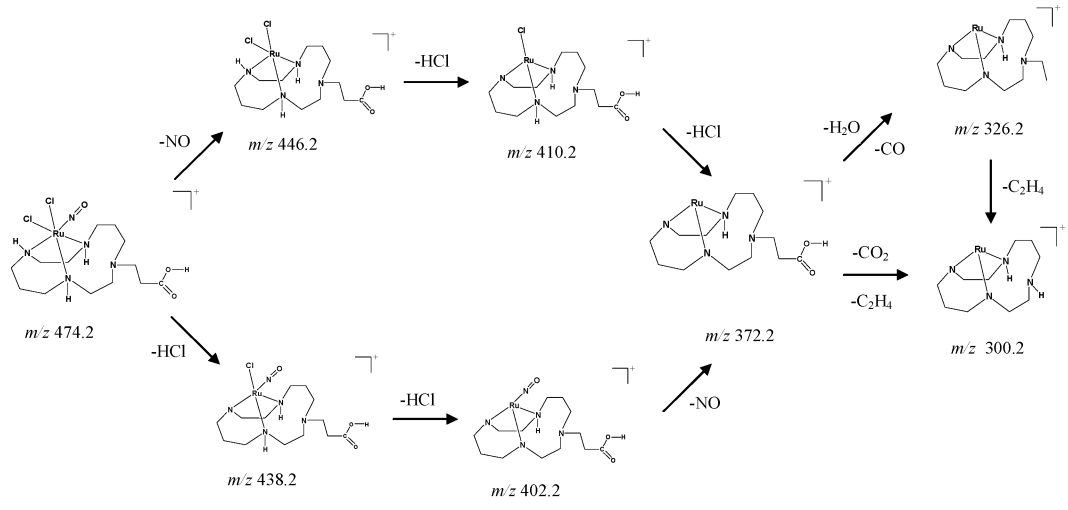


Figure 3. Positive ion ESI-MS for **I** in H_2O-CH_3OH (1:1) solution from a fresh prepared sample. (A) Experimental isotopical distribution; (B) calculated isotopical distribution.

Scheme 1. Proposed Fragmentation Mechanism for *fac*-[Ru(NO)Cl_2(κ^3N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]$^+$



structure, and initial NO versus HCl fragmentation was also observed for other ruthenium nitrosyl complexes.[91–93] As Scheme 1 summarizes, fragmentation then proceeds by a series of HCl or NO losses and [CO_2 + C_2H_4] losses. A nearly "mono-isotopic" ion of *m/z* 354.2 is also formed likely by the loss of mainly ^{102}RuOH (Supporting Information).

Vibrational and Electronic Spectra. The ν_{NO} in the infrared absorption spectrum of **I** (1881 cm^{-1}) in KBr pellets is in the range generally associated with nitrosyl metal complexes,[13,41,95] and its energy is comparable to those of *trans*-[Ru(NO)Cl(NH_3)$_4$]$^{2+}$ (1880 cm^{-1})[96] and *trans*-[Ru(NO)Cl(cyclam)]$^{2+}$ (1875 cm^{-1}).[56] The regions of ν_{NO} for bent and linear ν_{NO} overlap over a wide a range. Bent M−N−O moieties generally display ν_{NO} in the ∼1700–1400 cm^{-1} range, while linear moieties show it in the ∼2000–1450 cm^{-1}.[95] As observed in the molecular structure of I, the O(5)−N(5)−Ru bond angle is 167.7(2) while the similar angle observed for *trans*-[Ru(NO)Cl(cyclam)](ClO_4)$_2$ is 178.0(4). The results indicate that this small bending in **I** is not enough to result in a significant ν_{NO} decrease. In addition to the ν_{NO} stretching band, the IR spectra show the characteristic stretching bands of CH (1400–800 cm^{-1}) and NH (3200 cm^{-1}) and of the carbonyl (1688 cm^{-1}) because of the macrocyclic ring.

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The electronic absorption spectra of *fac*-[Ru(NO)Cl_2(κ^3-N^4,N^8,N^{11}(1-carboxypropyl)cyclam)]$^+$ in HCl 0.1 mol L^{-1} show three electronic absorption bands located at 264 nm (log ε = 3.27), 404 nm (log ε = 2.53), and 532 nm (log ε = 1.88) and are similar to those of other ruthenium nitrosyl am(m)ine compounds.[13,41,97] Regarding the spectra of the analogous *trans*-[Ru(NO)Cl(cyclam)]$^{2+}$ [13,41,56] which has bands at 262, 352, and 435 nm, the higher energy band has a similar energy for both complexes but the lower energy bands are red-shifted for the *fac*. The origin of this shift could be related to the different molecular structures of the complexes. Complexes of the type of *trans*-[Ru(NH_3)$_4$L(NO)]$^{n+}$-(L = Cl^-, H_2O, NH_3, OH^-, py e pz) show from seven to ten possible transitions according to TD-DFT calculations.[97] These results have been applied to the assignment of the UV–vis spectra of the analogous *trans*-[Ru(NO)Cl(cyclam)]$^{2+}$.[13,56] Ruthenium nitrosyl complexes with cyclic amines present electronic absorption bands in the ranges 260–280 nm, 300–350 nm, and 420–480 nm.[13] The bands at 260–280 nm have been assigned to a ligand-to-metal charge transfer (LMCT) [p_π(Cl) - e_g(Ru)] and at least one d−d $^1A_1$ - $^1T_1$ with contribution of a metal-to-ligand charge transfer (MLCT) (d_π(Ru)→NO) transition. The bands at 300–350 nm have been assigned to two transitions, one ligand field (LF) and one $d_{xy}d_{yz}$(Ru) → π^*(NO) MLCT transition. The low intensity band in 420–480 nm have been attributed to a t_{2g}(Ru)→π^*(NO) MLCT transition.[13] Although the electronic transitions mentioned above might be present in the spectra of *fac*-[Ru(NO)Cl_2($\kappa^3$$N^4$,$N^8$,$N^{11}$(1-carboxypropyl)cyclam)]$^+$, it is difficult to precisely attribute the observed bands to expected transitions despite that those type of transitions are expected to occur in the *fac* complex.

Concluding Remarks. Mono-N-substitution with a carboxypropyl pendant in the cyclam ligand reduces the denticity of the protonated pentadentate ligand from κ^4 to an unexpected κ^3 as observed by X-ray diffraction of complex **I**. The ESI-MS and ESI-MS/MS, NMR, and IR results are in agreement with the molecular structure obtained. As a result of the ligand denticity lowering, the ruthenium nitrosyl complex showed a *fac* configuration where the ruthenium center is coordinated to only three cyclam N atoms. This structure affects the properties of complex **I** such as, for example, its electronic spectrum and will probably influence its chemical properties. Also, release of one coordinated chloride may provide to **I** an additional site for coordination. Noteworthy, the presence of a carboxy group in the pendant arm also makes complex **I** prone to be attached to solid surfaces or biomolecules, such as antibodies; hence, **I** may possibly act as a selective NO donor. Its resemblance with Ru complexes with 1,4,7-triazacyclononane seems to indicate potential catalytic properties for **I**. Its labile sites can also be useful to catalytically convert nitrite, the most common of the bioavailable NOx species, into NO, as observed for some other related Ru complexes,[98–101] with the advantage of greater selectivity when attached to an antibody. This enhanced selectivity may have valuable therapeutic applications.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, IR spectrum, ESI-MS/MS spectra, and crystallographic and structure data for *fac*-[Ru(NO)Cl_2($\kappa^3$$N^4$,$N^8$,$N^{11}$(1-carboxypropyl)cyclam)]$^+$ complex, with atomic coordinates, interatomic distances, bond angles, hydrogen coordinates with isotopic displacements parameters (PDF), and additional data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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