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Ru(II) and Ru(III) complexes with cyclam and related species

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Contents

Abstract

The properties of cyclam, cyclen, and 1-(3-propylammonium) complexes of ruthenium(II/III), [Ru(macrocycle)LL′]$^{n+}$, and related species are reviewed. L and L′ are ligands such as chloro, aqua, hydroxo, nitriles, amides, imides, pyridines, and nitric oxide. These complexes display similarities and differences with related complexes such as Ru(III/II) ammines, with which they are compared and discussed. The factors responsible for the reactivity of the macrocyclic complexes include the macrocycle ring size, the metal oxidation state, and the properties of L and L′. Such factors are illustrated with relevant data and recent results concerning the synthesis, structure, electrochemistry, complex reactivity, coordinated ligand reactivity, photochemistry, and electronic, infrared, and NMR spectral data for [Ru(macrocycle)LL′]$^{n+}$.

Keywords: Cyclam; Cyclen; N-substituted cyclam; Nitric oxide; Ruthenium nitrosyl

1. Introduction

Macrocyclic ligands have long been used for the stability they impart to the complexes they form, due to

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the well-known substitution inertness of most macrocyclic ligands [1]. One early reason that drove us to study tetraazamacrocyclic ligand complexes such as cyclam (1,4,8,11-tetraazacyclotetradecane) was curiosity regarding the contribution such ligands would make to the models of photochemical reactivity of ruthenium ammines [2–4]. Since the spectrochemical strength of cyclam is similar to that of four ammonias, it was expected that its ruthenium complexes would be similar to the corresponding ruthenium tetraammines, but with the reactivity restricted to the other two ligands, given the inertness of the macrocycle towards substitution reactions. This proved to be only partly true. The Ru(II) cyclam complexes showed some differences from and some similarities with the analogous Ru(II) ammines, especially the pentaammines, with regard to properties such as UV–vis spectra and reactivity [2–6]. For instance, the energies and reduction potentials of the metal to ligand charge transfer (MLCT) bands of $[Ru(NH_3)_5(L)]^{2+}$ and *trans*-$[RuCl(cyclam)(L)]^{+}$ (L = pyridine derivative) are similar, but the spectra of the cyclam complexes display an additional absorption band between the MLCT and the UV bands, which is not reported for the pentaammines [2,4,7]. Chloride is more rapidly lost from $[RuCl(NH_3)_5]^{+}$ ($k = 5\ s^{-1}$) than from *trans*-$[RuCl_2(cyclam)]$ ($k = 2.1 \times 10^{-2}\ s^{-1}$), and loss of the second chloride occurs even more slowly [8]. More recently our interest in tetraazamacrocyclic complexes evolved to the chemistry, photochemistry, and potential biological applications of ruthenium complexes with nitrogen oxides and the function of those complexes as nitric oxide (NO) donors and scavengers [9–20].

The discovery of the roles NO plays in several physiological processes launched a spectacular increase in investigations on the subject, and stimulated interests involving prospective transition metal complexes that could act either as NO donors or NO scavengers for medical applications [21–28]. In this context, ruthenium nitrosyl complexes were attractive. For instance, the reactivity of the coordinated NO, such as redox properties, rate of release, and nucleophilicity, can be modulated by the choice of the axial ligand L in *trans*-$Ru(L)(NO)(A_4)]^{n+}$ (A_4 = tetracoordinated equatorial ligands), as has been shown for the tetraammines [15,29–32]. Again, although macrocyclic complexes bear similarities with tetraammines, the different features of the macrocyclic complexes and the observation that in *trans*-$[RuCl(L)(cyclam)]^{+}$ only one (L) coordination site is available for substitution reactions [2,5] prompted us to study these complexes with NO and related species. In addition, the nitrosyl tetraamine and tetraazamacrocyclic ruthenium complexes are, in general, quite stable and water soluble, two important features for clinical purposes. Moreover, the release of nitric oxide from such nitrosyl complexes can be chemically, electrochemically or photochemically induced [9,10,14,15,20,29–32]. In fact, the rate of release of NO, after the reduction of *trans*-$[RuCl(NO)(cyclam)]^{2+}$, was lower than all the other tetraammine nitrosyls, offering the possibility for this complex to serve as a possible controlled-release NO donor [10,15]. The results that have already been obtained with *trans*-$[RuCl(NO)(cyclam)]^{2+}$, including biological studies, showed a rich potential for this class of compounds [10,15,16].

To the best of our knowledge, studies of the reactivities of co-ligands of tetraazamacrocyclic complexes has been limited to Cr and Co complexes of ethylenediamine, acetate, nitrosyl and related ligands [33–37]. The only other co-ligands that had their reactivities with tetraazamacrocyclic complexes studied are 4-cyanopyridine (4-NCpy) and its protonated form, in *trans*-$[RuCl(cyclam)(4\text{-}NCpy)]^{n+}$, as well as their amides [38]. In the latter case, the coordinated amide displays an N–O amide linkage isomerization opposite to that observed in the pentaammines and much smaller aquation rates.

Although extensive investigations into the chemistry and physical-chemistry of Co, Ni, Cr, Fe, Os, and Cu complexes with N-functionalized, and more recently with C-functionalized, macrocycles have been carried out [36,39–48], there are few reports on ruthenium complexes with these kinds of ligands [21,49–51]. This non-exhaustive review reports the studies we have been carrying out with ruthenium(II) and ruthenium(III) complexes with tetraazamacrocyclic ligands such as cyclam, cyclen, and substituted cyclam.

2. Synthesis

Ru(III/II) tetraazamacrocyclic complexes are usually synthesized as *trans*-$[RuLL'(mac)]^{n+}$ or *cis*-$[RuLL'mac)]^{n+}$, where L and L′ can be, for instance, Cl^-, Br^-, I^-, oxalato, SCN^-, trifluoromethanesulfonato (tfms), pyridine ligands (py-X), 4-cyanopyridine (4-NCpy), 4-cyanopyridinium ($4\text{-}NCpyH^+$), 2,2′-bypiridine (bpy), 1,10-phenanthroline (phen), NO, OH^- or H_2O, and mac is a tetraazamacrocycle such as 1,4,7,10-tetraazacyclododecane (cyclen = $12aneN_4$), 1,4,7,10-tetraazacyclododecene (imcyclen), 1,4,8,11-tetraazacyclotetradecane (cyclam = $14aneN_4$); 2,3-dimethylcyclam (2,3-dmc), 1,4,8,11-tetramethylcyclam (14-tmc), 1,4,8,12-tetraazacyclopentadecane ($15aneN_4$), 1,5,9,13-tetraazacyclohexadecane ($16aneN_4$), 1-(3-aminopropyl)cyclam (3-amprcy) (Fig. 1) and its protonated form 1-(3-propylammonium)cyclam (1-pramcy). Such complexes can be obtained by several different routes, but their syntheses most usually start from $[RuCl_2(mac)]Cl$, followed by reduction of the metal center [2,6,8,38,51–62].

2.1. The trans complexes

The general procedure to prepare *trans*-$[Ru(NH_3)_4L_2]^{2+}$ involves reduction of *trans*-$[RuCl_2(NH_3)_4]^{+}$ to *trans*-$[RuCl_2(NH_3)_4]$, which rapidly releases both chlorides, to form *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ [63–66]. In the presence of an unsaturated ligand L, the latter species forms *trans*-

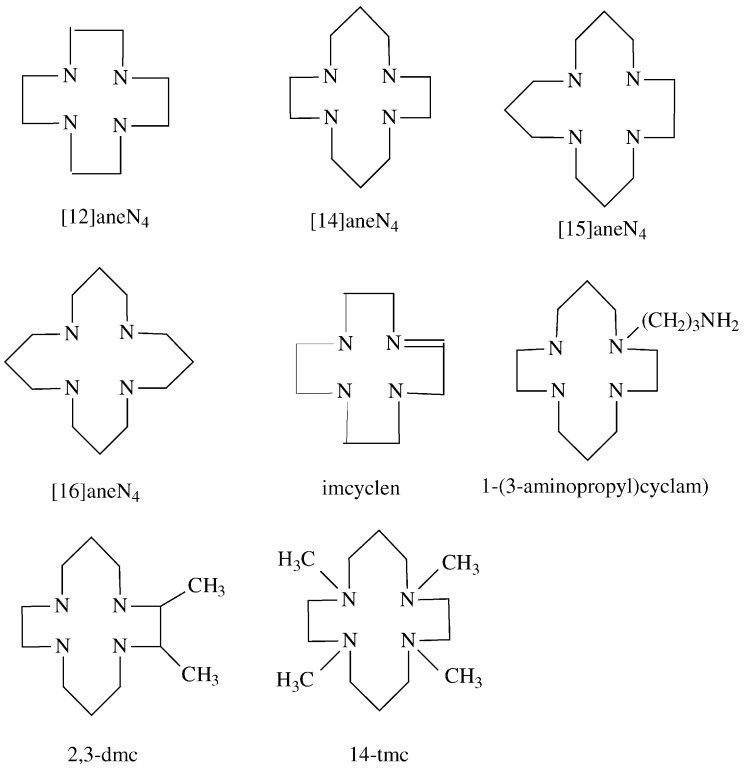


Fig. 1. Tetraazamacrocyclic ligands.

$[Ru(NH_3)_4L_2]^{2+}$ (Eqs. (1)–(5)).

$$trans\text{-}[RuCl_2(NH_3)_4]^+ \xrightarrow{+e^-} trans\text{-}[RuCl_2(NH_3)_4] \quad (1)$$

$$trans\text{-}[RuCl_2(NH_3)_4] + H_2O \xrightarrow{\text{fast}} trans\text{-}[RuCl(NH_3)_4(OH_2)]^+ + Cl^- \quad (2)$$

$$trans\text{-}[RuCl(NH_3)_4(OH_2)]^+ + H_2O \xrightarrow{\text{fast}} trans\text{-}[Ru(NH_3)_4(OH_2)_2]^{2+} + Cl^- \quad (3)$$

$$trans\text{-}[Ru(NH_3)_4(OH_2)_2]^{2+} + L \xrightarrow{k_1} trans\text{-}[Ru(NH_3)_4(OH_2)(L)]^{2+} + H_2O \quad (4)$$

$$trans\text{-}[Ru(NH_3)_4(OH_2)(L)]^{2+} + L \xrightarrow{k_2} trans\text{-}[Ru(NH_3)_4(L)_2]^{2+} + H_2O \quad (5)$$

However, the use of *trans*-[RuC1$_2$(cyclam)]Cl to form *trans*-[RuL$_2$(cyclam)]$^{n+}$ is not as straightforward [2,6,38]. The two chloro ligands are relatively inert to substitution and dissociate with discernible rates after reduction of the metal center (Eqs. (6)–(8)).

$$trans\text{-}[RuCl_2(mac)]^+ \xrightarrow{+e^-} trans\text{-}[RuCl_2(mac)] \quad (6)$$

$$trans\text{-}[RuCl_2(mac)] + H_2O \xrightarrow{k_1} trans\text{-}[RuCl(OH_2)(mac)]^+ + Cl^- \quad (7)$$

$$trans\text{-}[RuCl(OH_2)(mac)]^+ + H_2O \xrightarrow{k_2} trans\text{-}[Ru(OH_2)_2(mac)]^{2+} + Cl^- \quad (8)$$

This inertness has been assigned in part to the interactions of cyclam nitrogen hydrogen atoms with the chloro ligands [2,8]. In this case, substitution of the nitrogen hydrogens would lead to more labile chlorides. Indeed, substitution of one or four nitrogen hydrogens of cyclam by methyl groups results in facile loss of chloride from *trans*-[Ru^{II}Cl$_2$(1-pramcy)]$^+$ [51] and *trans*-[Ru^{II}Cl$_2$(14-tmc)] [56,61]. The difference in the rates of loss of the chlorides in the cyclam complex is enough to allow the synthesis of *trans*-[RuCl(L)(cyclam)]$^{n+}$ (Eq. (9)) [2,6,38].

$$trans\text{-}[RuCl(OH_2)(mac)]^+ + L \xrightarrow{k_3} trans\text{-}[RuCl(mac)(L)]^+ + H_2O \quad (9)$$

As a matter of fact, in order to dissociate the second chloride, the first syntheses required repeated digestions, using Ag^+ and heating [6]. Later, the synthesis of *trans*-[Ru^{III}Cl(tfms)(cyclam)](tfms) and *trans*-[Ru^{III}(tfms)$_2$(cyclam)](tfms) was reported [62], allowing an alternative to the synthesis of mono- and di-substututed *trans*-cyclam complexes, because of the higher lability of tfms.

Basically, the nitrosyl complexes can be obtained by three methods. One involves reaction of $K_2[Ru(NO)Cl_5]$ with the macrocycle, such as cyclam [10] to pro-

duce *trans*-[RuCl(NO)(cyclam)]$^{2+}$. Another involves the passage of NO through solutions of Ru(III) dichloro [20], Ru(III) chloro(trifluoromethanesulphonato) [10], or Ru(III) chloroaqua macrocyclic complexes [14]. The third uses the reaction between the reduced species and nitrite, in acidic medium [20]. All the reported complexes with cyanopyridines and cyanopyridinium are nitrile-bonded, despite the fact that pyridine-bonded complexes would be expected to be more thermodynamically favored [6,38]. In these cases, presumably, as occurs for ruthenium ammines [67–70], the formation reactions are kinetically controlled.

2.2. The cis complexes

The [Ru(L)(L′)(mac)] complexes can exist in two isomeric forms, *cis* and *trans*. The *cis* configuration is formed with the 12aneN$_4$ macrocycle [52], while 15aneN$_4$ and 16aneN$_4$ complexes have *trans* geometry [8]. The 14aneN$_4$ macrocycle [8,51,55,58,60,71] forms complexes with both configurations as observed by IR and NMR spectroscopies [5,14] and X-ray molecular structure [5,8,55]. To the best of our knowledge, there are no reports of ruthenium 13aneN$_4$ complexes. Unlike *trans*-[RuCl$_2$(cyclam)]$^{n+}$, only di-substitution is reported for the *cis* species, because of the higher rates of chloride loss [55,71]. When reduced in aqueous solution, the *cis*-[Ru^{III}Cl$_2$(mac)]$^+$ (mac = cyclam or cyclen) complexes release two chlorides and form *cis*-[Ru^{II}(OH$_2$)$_2$(mac)]$^{2+}$, which in the presence of L form *cis*-[Ru^{II}(L)$_2$(mac)]$^{2+}$ (Eqs. (10)–(13)) [55,71,72].

$$cis\text{-}[RuCl_2(mac)]^+ \xrightarrow{+e^-} cis\text{-}[RuCl_2(mac)] \quad (10)$$

$$cis\text{-}[RuCl_2(mac)] + H_2O \xrightarrow{k_1} cis\text{-}[RuCl(OH_2)(mac)]^+ + Cl^- \quad (11)$$

$$cis\text{-}[RuCl(OH_2)(mac)]^+ + H_2O \xrightarrow{k_2} cis\text{-}[Ru(OH_2)_2(mac)]^{2+} + Cl^- \quad (12)$$

$$cis\text{-}[Ru(mac)(OH_2)_2]^{2+} + nL \xrightarrow{k_n} cis\text{-}[Ru(mac)(L)_n]^{2+} + 2H_2O \quad (13)$$

All Ru(III) and Ru(II) cyclam and cyclen complexes are stable in aprotic solvents, or in acidic medium. At high pH, the macrocycle may undergo an oxidative dehydrogenation [14,59], and Ru(III) complexes may disproportionate to Ru(II) and oxo Ru(IV) complexes [50]. Most importantly, attempts to synthesize *cis*-[Ru^{II}(NO$^+$)(H$_2$O)(cyclen)]$^+$ resulted in an analogous unsaturated cyclen (imcyclen) complex, *cis*-[Ru^{II}(NO$^+$)(H$_2$O)(imcyclen)]$^+$ [14]. Furthermore, the synthesis resulted in two conformational isomers, which were separated in aqueous solution by HPLC and characterized by NMR spectroscopy [14]. Two conformational isomers were also observed for *cis*-[Ru^{II}(cyclen)(L)]$^{2+}$ (L = bpy, phen), *cis*-[Ru^{II}(cyclen)(4-NCpyH)$_2$]$^{4+}$, whose cyclen forms imcyclen at pH > 2 [73], and *cis*-[Ru^{II}(NO$^+$)(L)(imcyclen)]$^{n+}$ (L = Cl$^-$, OH$^-$) [14,74]. Attempts to synthesize other cyclen and imcyclen complexes are currently being carried out in our laboratories.

3. Infrared spectra

Infrared spectra can be used to differentiate between *cis* and *trans* geometries, by comparison with analogous cobalt, iron, and chromium complexes. The 900–750 cm^{-1} region, which displays bands relative to the macrocycle C–H and secondary amines N–H vibrations, is used for this purpose [57]. The spectral profile in this region is independent of other ligands as well as the metal center and its oxidation state, and depends only on the complex configuration. The *trans* complexes display two groups of bands, one with two peaks near ∼900 cm^{-1} and the other one around 800 cm^{-1}. The less symmetrical *cis* complexes show two bands in the ∼790–830 cm^{-1} region, which are due to the C–H vibrations and three bands in the ∼900–840 cm^{-1} region, due to the amine vibrations [57]. The IR spectra are very helpful not only in this respect, but also for monitoring reactivity and serving as an analytical tool in other regions.

The macrocycle can undergo oxidative dehydrogenation to the corresponding imine, which can be detected through the C=N vibration in the 1650–1500 cm^{-1} region. This is the case with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ruthenium(II) [59], ($\nu_{C=N}$ = 1622 cm^{-1}) and both conformational isomers of *cis*-[Ru(NO)Cl(imcyclen)]$^{2+}$ ($\nu_{C=N}$ = 1612 cm^{-1}) [14], which is consistent with the formation of imine in these cases, and in agreement with NMR results.

Coordinated nitriles can be easily detected near 2200 cm^{-1}, and when they are hydrolysed, the ν_{CN} stretching frequency disappears and bands in the amide region appear.

The IR spectra of the nitrosyl complexes show NO stretching frequencies between 1800 and 2000 cm^{-1}, compatible with a nitrosonium character (NO$^+$) for the NO ligand [10,14,15,20]. These frequencies were correlated to the properties of the coordinated NO in ruthenium ammines, *trans*-[Ru(NH$_3$)$_4$(L)(NO)]$^{2+}$ [15]. A linear correlation between this frequency and the reduction potential of the coordinated NO oxide in these complexes was established [15]. Frequently, in spectra recorded from Nujol mulls or KBr pellets, the NO stretching absorption appears as two or more peaks or with one peak with one or two shoulders. This feature has been assigned to solid-state effects [29]. As a matter of fact, at least for the several complexes that we have examined, recent results of IR spectra of solutions of the nitrosyl complexes show only one peak in the 1850–1950 cm^{-1} region, with small changes in the frequency if compared to the solid state. The ν_{NO} absorption of the cyclam complex, *trans*-[RuCl(NO)(cyclam)]$^{2+}$, appears at 1889 cm^{-1} in acetonitrile (Fig. 2), but is shifted to 1899 cm^{-1} in aqueous solution, indicating a solvent dependence for the ν_{NO}

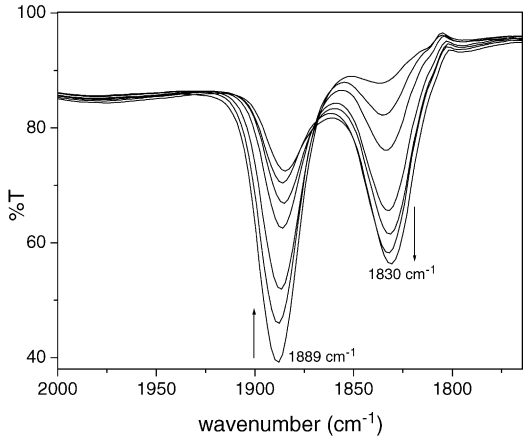


Fig. 2. Infrared spectral changes following the controlled potential electrolysis of 2.1×10^{-2} mol L^{-1} *trans*-[RuCl(NO)(cyclam)]$^{2+}$ in acetonitrile/TBA(PF_6), at −0.5 V vs. Ag, $T = 25\,^{\circ}C$.

stretching frequency. Thus, an even better correlation of the ν_{NO} stretching frequencies with reduction potentials could possibly be established with IR data obtained in the same medium as the potential. The substituted cyclam displays the ν_{NO} absorption band at 1864 cm^{-1} in aqueous solution [75], while *trans*-[RuCl(NO)(15aneN$_4$)]$^{2+}$ is reported to have an ν_{NO} at 1860 cm^{-1} in KBr pellet [20].

The coordinated NO^+ nitrosonium of *trans*-[Ru(L)(NO)(A$_4$)]$^{n+}$ can be reduced to coordinated NO followed by reactions that eventually result in release of NO with rate constants that depend on the other ligands [15]. Reduction of *trans*-[RuCl(NO)(cyclam)]$^{2+}$ in aqueous solution is first followed by fast chloride loss, to form the easily oxidized aqua species, *trans*-[Ru(OH$_2$)(cyclam)(NO)]$^{2+}$, from which NO is released at a much lower rate (Eqs. (14)–(16)) [10]. The rate of NO release is slow enough to allow the identification of the coordinated NO by EPR [17]. Upon reduction with Eu^{2+}, ν_{NO} shifts from 1885 to 1855 cm^{-1} in KBr pellet [10]. In many other systems, the NO^+ to NO shifts is reported to be on the order of 300 cm^{-1} [28,76–78]. Thus, the IR data are consistent with the formation of *trans*-[Ru(OH)(NO)(cyclam)]$^{2+}$ (Eqs. (17) and (18)). However, the EPR results with the same reducing agent are consistent with a coordinated NO^0. In fact, smaller NO^+ to NO shifts have been assigned recently to the coordinated NO [79,80].

$$\textit{trans}\text{-}[Ru^{II}Cl(NO^+)(cyclam)]^{2+} \xrightarrow{+e} \textit{trans}\text{-}[Ru^{II}Cl(cyclam)(NO^0)]^{+} \quad (14)$$

$$\textit{trans}\text{-}[Ru^{II}Cl(cyclam)(NO^0)]^{+} + H_2O \xrightarrow{k_1} \textit{trans}\text{-}[Ru^{II}(OH_2)(cyclam)(NO^0)]^{2+} + Cl^- \quad (15)$$

$$\textit{trans}\text{-}[Ru^{II}(OH_2)(cyclam)(NO^0)]^{2+} + H_2O \xrightarrow{k_2} \textit{trans}\text{-}[Ru^{II}(OH_2)_2(cyclam)]^{2+} + NO^0 \quad (16)$$

$$\textit{trans}\text{-}[Ru^{II}(OH_2)(cyclam)(NO^0)]^{2+} \xrightarrow{-e} \textit{trans}\text{-}[Ru^{II}(OH_2)(NO^+)(cyclam)]^{3+} \quad (17)$$

$$\textit{trans}\text{-}[Ru^{II}(OH_2)(NO^+)(cyclam)]^{3+} \rightleftharpoons \textit{trans}\text{-}[Ru^{II}(OH)(NO^+)(cyclam)]^{2+} + H^+ \quad (18)$$

The IR spectra of the reduced cyclam species in acetonitrile also display a small shift in the ν_{NO}. According to electrochemical data, chloride loss is not observed in acetonitrile on the time scale of the experiments, and, thus only reduction of *trans*-[RuCl(NO)(cyclam)]$^{2+}$ is observed [10]. However, IR monitoring of the non-exhaustive controlled potential electrolysis of the nitrosyl cyclam complex, to reduce the NO^+ to NO, shows the disappearance of the peak at 1889 cm^{-1} and appearance of a peak at 1830 cm^{-1}, which in acetonitrile and under a reductive potential should denote coordinated NO in *trans*-[RuCl(cyclam)(NO)]$^+$ (Fig. 2). Recent similar experiments from our laboratories showed shifts of the nitrosyl frequency on the order of 55 cm^{-1}, for *trans*-[Ru^{II}(NO^0)Cl(1-(3-propylammonium)cyclam)]$^{3+}$ and *trans*-[Ru^{II}(NO^0)(NH$_3$)$_4$(L)]$^{2+}$ (L = 4-phenylpyridine, 4-acetylpyridine, and pyridine). This small shift is similar to those recently reported and also assigned to the coordinated NO [79,80]. Considering that for many other systems the coordinated NO is reported to fall as far as 1600 cm^{-1}, we are investigating the origin of this apparent discrepancy.

Remarkably, the imcyclen complexes show two conformational isomers, with different ν_{NO} stretching frequencies at 1898 cm^{-1} for the *cis–syn–syn* complex and at 1857 cm^{-1} for the *cis–syn–anti* in aqueous solution [14]. One of the possible reasons for this difference is that one of the isomers, *cis–syn–syn*, has one of the hydrogens pointed directly to the NO group.

4. Electronic spectra and photochemistry

4.1. Electronic spectra of Ru(III) complexes

The UV–vis spectral data for some *trans*-Ru(III) complexes with cyclam and related species are shown in Table 1, while those of the *cis* complexes are in Table 2.

The UV–vis spectra of the Ru(III) complexes, [Ru(L)(L′)(mac)]$^{n+}$, are similar to those of [RuCl$_2$(en)$_2$]$^+$ and [RuCl$_2$(NH$_3$)$_4$]$^+$ and show bands below 400 nm. Most of these bands are assigned as ligand to metal charge transfer (LMCT), and their origin is dependent on the nature of the L ligands, such as Cl^-, OH^-, OH_2, *N*-amide, *N*-imide, *N*-amido, and *O*-amide, or *O*-amido [38,87–89]. The complexes with pyridine rings also display intra-ligand (IL) (π–π^*) bands below 300 nm.

The *trans*-dichloro complexes show two LMCT bands, while the *cis* complexes display three. The number of bands and their energies have been assigned earlier to arise from

Table 1
UV–vis spectral data for some *trans* Ru(III) cyclam and related species[a]

Complex	λ_{max} (nm) (log ε)	Ref.
trans-[$RuCl_2$(cyclam)]$^+$	358 (3.41), 315 (3.10)	[8]
trans-[$RuCl_2$(14-tmc)]$^+$[b]	370, 320	[61]
trans-[$RuCl_2$(1-pramcy)]$^{2+}$	358 (3.59), 330 sh (3.32)	[51]
trans-[$RuCl_2(NH_3)_4$]$^+$	331 (3.70), 295 sh (2.84)	[81]
trans-[$RuCl_2(en)_2$]$^+$	343 (3.58), 292 sh (2.90)	[82]
trans-[$RuCl(OH_2)$(cyclam)]$^{2+}$[c]	358 (3.07), 338 sh (2.60), 270 sh (2.88)	[51]
trans-[$Ru(OH_2)_2$(cyclam)]$^{3+}$[d]	320 (0.38), 240 sh	[6]
trans-[Ru(OH)(OH_2)(cyclam)]$^{2+}$[e]	305 (2.6), 255 (1.1)	[6]
trans-[RuCl(OH)(cyclam)]$^+$[b,f]	358, 328 sh, 265 sh	[51]
trans-[$RuCl(OH_2)$(1-pramcy)]$^{3+}$[c]	356 (3.47), 320 sh (3.15), 266 sh (2.95)	[51]
trans-[RuCl(OH)(1-pramcy)]$^{2+}$[b,f]	356, 315 sh, 256 sh	[51]
trans-[RuCl(cyclam)(NHCO-4pyH)]$^{2+}$	376 (3.56), 320 (3.37), 260 (3.71), 212 (3.66)	[38]
trans-[RuCl(cyclam)(NHCO-4py)]$^+$[b,f]	391 (3.42), 306 (3.44), 266	[38]
trans-[RuCl(cyclam)($OCNH_2$-4py)]$^{2+}$[b,g]	345sh (3.52), 299 (3.49), 260	[38]
[$Ru(NH_3)_5$(NHCO-4py)]$^{2+}$[c]	384 (3.57), 262 (3.71), 228 (3.61)	[83]
[$Ru(NH_3)_5$(NHCO-4pyH)]$^{3+}$	358 (3.67)	[84]

sh: shoulder.
[a] In 0.1 M HCl solution, except where noted.
[b] Data obtained from the reaction solution.
[c] In CF_3SO_3H at pH = 1.
[d] In CF_3SO_3H at pH = 0.
[e] At pH = 7.4.
[f] 0.1 M acetic acid/acetate buffer, pH = 4.65.
[g] At pH 8.7 with NaOH.

distortions resulting from hydrogen to chloro interactions, ring size effects, and symmetry lowering [8,55]. However, the *trans* chloroaqua and chlorohydroxo complexes display three bands. The lower energy one is assigned as LMCT, while the origins of the other two are still unclear, although one of them should be due to LMCT. At pH 0, the *trans*-diaqua cyclam complex shows one absorption band at 320 nm with a shoulder at 240 nm. Such bands are shifted to 305 and 255 nm in the hydroxoaqua complex at pH 7.4. Analogous Rh(III) complexes, [$RhCl_2$(cyclam)]$^+$, [$RhCl(H_2O)$(cyclam)]$^{2+}$, and [$Rh(H_2O)_2$(cyclam)]$^{3+}$ show LF bands in the ~400–250 nm region [90], with the *cis* complexes with higher energies than the corresponding *trans* isomers. There is a shift to higher energies when one goes from *trans*-dichloro to diaqua, hydroxoaqua, and dihydroxo Rh(III) cyclam complexes. This behavior is also observed in the Ru(III) complexes. Thus, considering that only the lower energy band in the *trans*-Ru(III) complexes is not being shifted, it is reasonable to assume that the lower energy band is LMCT and that ligand field (LF) transitions may be contributing to the others. For the *cis* complexes, however, three LMCT bands are reported, except for *cis*-[RuCl(OH)(cyclen)]$^+$, which displays a broad band at 360 nm with a shoulder at 300 nm. Presumably, as in the case of the *trans* isomers, LF transitions could be contributing to the absorptions of higher energy, considering the blue shift of the LF bands in going from *trans* to *cis* in the analogous Rh(III) complexes.

Table 2
UV–vis data for some *cis*-Ru(III) cyclam complexes and related species[a]

Complex	λ_{max} (nm) (log ε)	Ref.
cis-[$RuCl_2$(cyclam)]$^+$	380 (3.03), 336 (3.17), 276 (2.98)	[57]
cis-[$RuCl_2$(cyclen)]$^+$[b]	380 (2.89), 345 (3.45), 290 (3.50)	[52]
cis-[RuCl(OH)(cyclen)]$^+$[c]	360 (3.65), 300 sh	[52]
cis-[$RuCl_2(NH_3)_4$]$^+$	352 (3.21), 310 (3.14), 262 (2.80)	[85]
cis-[$RuCl_2$(en)]$^+$	354 (3.24), 314 (3.15), 269 (2.95)	[86]

sh: shoulder.
[a] In 0.1 M HCl solution, except where noted.
[b] In 6 M HCl solution.
[c] In 0.1 M acetic acid/acetate buffer, pH = 4.65.

4.2. Electronic spectra of Ru(II) complexes

The UV–vis spectral data of some *trans*-Ru(II) complexes with cyclam and related species are shown in Table 3.

The ruthenium(II) complexes, *trans*-[Ru(L)(L′)(mac)]$^{n+}$ (L = py-X, 4-NCpy, 4-NCpyH$^+$ or benzonitrile (bzn), and L′ = 4-NCpy, 4-NCpyH$^+$, bzn, Cl^-, or H_2O), have UV–vis spectra similar to analogous ammines [2,4,6,38,63,64,67,91,96,97], especially the pentaammines, but with an additional band. Excluding the NO complexes, the strong absorption bands of the ruthenium(II) complexes with pyridines, 4-NCpy, 4-NCpyH$^+$, and bzn in the UV region are similar in intensity and position to bands observed in the spectra of the free ligands and were assigned as IL, π–π^* in character. The electronic spectra of these complexes are dominated in the visible region by one intense absorption band, assigned as MLCT, in analogy to spectral assignments of similar absorptions in analogous ruthenium ammine complexes [4,63,67]. For the pyridine derivatives, this transition is highly sensitive to the substituents on the aromatic ring with a decrease in band energy with an increase of the electron withdrawing nature of the substituent [4,63,67]. As

Table 3
UV–vis spectral data for some *trans* Ru(II) cyclam and related species[a]

Complex	λ_{max} (nm) (log ε)	Ref.
trans-[RuCl(cyclam)(py)]$^{+}$	405 (3.61), 326 (2.65), 245(3.54)	[2]
[Ru(NH$_3$)$_5$(py)]$^{2+}$	407 (3.89), 244 (3.66)	[91]
trans-[RuCl(cyclam)(4-pic)]$^{+}$	390 (3.60), 340 (2.54), 244 (3.52)	[2]
[Ru(NH$_3$)$_5$(4-pic)]$^{2+}$	397 (3.89), 244 (3.66)	[92]
trans-[RuCl(cyclam)(isn)]$^{+}$	480 (3.83), 345 (2.78), 255 (3.70)	[2]
[Ru(NH$_3$)$_5$(isn)]$^{2+}$	479 (4.06), 260 (3.66)	[91]
trans-[RuCl(cyclam)(4-acpy)]$^{+}$	520 (3.72), 350 (2.78), 270 (3.32)	[2]
[Ru(NH$_3$)$_5$(4-acpy)]$^{2+}$	523 (3.97), 271 (3.53), 223 (3.76)	[92]
trans-[Ru(NH$_3$)$_4$(4-acpy)$_2$]$^{2+}$	532 (4.32), 383 (3.27), 270 (3.80), 21 (4.18)	[63]
trans-[Ru(NH$_3$)$_4$(py)(4-acpy)]$^{2+}$	508 (4.21), 366 (3.48), 271 (3.56), 247 (3.78), 21 (3.91)	[64]
trans-[RuCl(cyclam)(4-NCpy)]$^{+}$	440 (4.04), ∼360 sh, 262 (4.18), 218 (4.04)	[38]
[Ru(NH$_3$)$_5$(4-NCpy)]$^{2+}$	425 (3.73), 253 (3.95)	[93]
trans-[Ru(4-NCpyH)Cl(cyclam)]$^{2+}$[b]	548 (4.20), ∼360 sh, 270 (4.22), 212 (4.09)	[38]
[Ru(NH$_3$)$_5$(4-NCpyH)]$^{3+}$	532 (3.91), 260 (3.93)	[93]
trans-[RuCl(cyclam)(NH$_2$CO-4pyH)]$^{2+}$[b,c]	550, 357, 256	[38]
trans-[RuCl(cyclam)(OCNH$_2$-4pyH)]$^{2+}$[b,c]	∼495 sh, 357, 312, 260, 228	[38]
Ru(NH$_3$)$_5$(NHCO-4py)]$^{2+}$[d]	475	[94]
trans-[Ru(NO^{+})Cl(cyclam)]$^{2+}$	435 (1.73), 352 (2.28), 262 (3.40)	[10]
trans-[Ru(H$_2$O)(cyclam)(NO)]$^{+}$[e]	330	[10]
trans-[Ru^{II}(NO^{+})Cl(1-pramcy)]$^{3+}$	455 (1.95), 360 (2.60), 272 (3.49)	[95]
trans-[Ru(NO^{+})Cl(15aneN$_4$)]$^{2+}$[f]	352 (3.38), 268 (3.64)	[20]

sh: shoulder.
[a] In aqueous solution, except where noted.
[b] In 0.1 M HCl, pH = 1.
[c] Data obtained from the reaction solution.
[d] In phosphate buffer, pH = 11, μ = 0.1 M CF_3SO_3.
[e] In CF_3CO_2H at pH = 1, reduction with Eu^{2+}.
[f] In 2 M HCl.

for the nitrile bonded ammine complexes [Ru(NH$_3$)$_5$(NC-py)]$^{2+}$ (NC-py = 2-, 3-, or 4-cyanopyridine), protonation of the coordinated pyridine nitrogen in the nitrile bonded cyanopyridine complex, *trans*-[RuCl(4-NCpyH)(cyclam)]$^{2+}$ (pK_a = 3.5) [6] forms the corresponding 4-cyanopyridinium complex with a shift of the MLCT band to lower energy, from 440 to 548 nm [6,38]. The energy of this band is solvent dependent in the case of py-X, as is expected for a MLCT transition, and as for the Ru(II) ammines, the higher the solvent donor number, the lower the energy of the band [2,5]. Interestingly, complexes with unsaturated ligands, such as pyridines and cyanopyridines, display a third band in the 326–350 nm region. The energy of such band is rather solvent insensitive, and it has been assigned to a LF transition, although its molar absorptivity is relatively large for such a transition [2,5,6,38]. The high-energy bands of complexes such as *trans*-[RuCl(L)(cyclam)]$^{+}$ (L = py and 4-picoline (4-pic)) bury this LF band, whose energy was calculated by deconvolution of the spectra [2]. Interestingly, the UV–vis spectra of some *trans*-[Ru^{II}(NH$_3$)$_4$(L)(L′)]$^{n+}$ complexes display a similar pattern, which consists of a relatively intense low energy band, along with a much less intense higher energy band [4,63,64]. The higher energy band is much weaker when L = L′, and was assigned as a forbidden MLCT, consistent with simple MO model calculations [63,64,98]. The fact that macrocyclic ligands display rather solvent insensitive bands in the 320–360 nm region is more consistent with the LF assignment [2]. However, giving the relatively large molar absorptivity of this band, theoretical calculations and more experimental investigations should be performed to confirm the assignment. Although similar to the pentaammines, the [RuCl(L)(cyclam)]$^{+}$ complexes are *trans* complexes, and, at least conceivably, there may be a contribution from MLCT transitions, as in the *trans* ammines, and which may also involve other sources as spin-orbit coupling effects [99]. The *O*- and *N*-amide coordinated complexes of *trans*-[RuCl(NH$_2$COpyH)(cyclam)]$^{2+}$ display a MLCT band at 495 and 550 nm, respectively, just like [Ru(NH$_3$)$_5$(NHCOpy)]$^{+}$, which displays a MLCT band at 475 nm [88]. Although these energy shifts are small if compared with the pentaammine, they are consistent with protonation of the ligand.

The spectra of the NO macrocyclic complexes have been assigned by analogy to those of similar ruthenium tetraammine nitrosyls [15,100], which in contrast to analogous ruthenium(II) ammines with unsaturated ligands, do not display intense MLCT bands in the visible range. In the *trans*-nitrosyl complexes there is a relatively intense band in the 260–280 nm region, whose assignment requires clarification by theoretical calculations.

The bands at 350–360 nm are assigned to two transitions, a LF transition and a $d_{xz,yz}$ Ru → π^*NO MLCT transition. The bands at 455 and 435 nm are assigned to a dx^2-y^2 Ru → π^*NO MLCT transition. This latter band should be much weaker for 15aneN$_4$, since it was not observed at concentrations lower than 1×10^{-3} mol L^{-1}. The calculated

TD-DFT spectra of some ruthenium ammine nitrosyl complexes indicate the existence of 7–10 transitions, depending on the ligand L *trans* to NO [100]. However, only three absorptions are observed in the spectra. So, more transitions could be contributing to the reported absorptions.

The reduction of *trans*-[RuCl(NO)(cyclam)]$^{2+}$ with Eu^{2+}, in aqueous solution, was monitored by UV–vis spectroscopy. An initial disappearance of the 352 nm band was observed, followed by the appearance of an absorption at 330 nm, which should be of *trans*-[Ru(H_2O)(cyclam)(NO)]$^{2+}$ (Eqs. (14) and (15)) [10].

The UV–vis spectral data for *cis*-Ru(II) complexes with cyclam and related complexes are shown in Table 4.

The Ru(II) complexes *cis*-[$Ru^{II}(NH_3)_4(L)(L')]^{n+}$ (L or L′ = pyridine, 4-picoline, isn, 4-acpy, p_z, p_zH^+) invariably display two MLCT bands in the visible region of their electronic spectra. This is not exactly the case with the *cis*-[Ru^{II}(mac)(L)]$^{n+}$ (mac = cyclam, cyclen; L = bpy, py, 4NCpy) complexes, which exhibit one or two MLCT bands in the 300–600 nm region [55,72]. The *cis*-[Ru^{II}(cyclen)(4-NCpyH)$_2$]$^{4+}$ complex displays only one band [72]. However, this large band may in fact consist of two overlapping bands that are close in energy. As for the *trans* macrocyclic complexes, bands in the <290 nm region are due to internal ligand $\pi \rightarrow \pi^*$ transitions, which are commonly observed for Ru complexes containing N heterocycles LF bands appear in the 300–400 nm region or are probably contributing to higher energy MLCT bands.

The spectra of the *cis* NO complexes were assigned similarly to those of the *trans* complexes. The bands at ~360 nm are assigned to two transitions, one LF, and one $d_{xz,yz}$ Ru $\rightarrow \pi^*$NO MLCT. The bands at ~460 nm are assigned to a LF and a $d_{x^2-y^2}$Ru $\rightarrow \pi$*NO MLCT transition [14]. In these complexes, there is a relatively intense band at wavelengths <300 nm that was not assigned [14], and may possibly belong to more than one transition; a theoretical calculation should be done in order to make this assignment and confirm the others.

4.3. Photochemistry of Ru(II) complexes

The Ru(II) *trans*-[RuCl(L)(cyclam)]$^+$ (L = py, 4-pic, isn, or 4-acpy) complexes follow the tuning model [4,92,101,102] and show photochemical reactions similar to those of analogous ammines, which have low-lying LF and MLCT states of similar energy [3,4,92,101,102]. The tuning model predicts larger quantum yields for photosubstitution reactions in the case of the complexes that have LF states of lower energy [4,7,101–103]. The py and 4-pic cyclam complexes undergo L aquation (Eq. (19)),

$$\textit{trans}\text{-[RuClL(cyclam)]}^+ \xrightarrow[H_2O]{h\nu} \textit{trans}\text{-[RuCl(OH}_2\text{)(cyclam)]}^+ + \text{L} \quad (19)$$

while the isn and 4-acpy, with lower energy MLCT states, were classified as unreactive on the basis of their quantum yields. No chloride photoaquation was observed, and this was claimed to be due to the hydrogen bond interactions between N–H proton and the chloro ligand, which hinder dissociation [3,4]. Also, the results indicated that the d_{z^2} orbital should be lower in energy than $d_{x^2-y^2}$. In *trans*-[M(CN)$_2$(cyclam)]$^+$ (M = Rh, Cr), there is a strong orbital splitting, with a reversal in orbital order, with the d_{z^2} higher in energy with respect to $d_{x^2-y^2}$, with a consequent reversal in photochemical behavior with respect to other weak field ligands [104–106]. The Rh and Cr cyclam cyanide complexes are photochemically inert but photophysically active. Thus, it would be very interesting to examine the Ru cyclam complexes with strong field ligands such as cyanide, triethylphosphite, sulphite, where the order reversal of the orbitals of e_g parentage would be expected to occur.

The Ru complexes *trans*-[RuCl(mac)(NO)]$^{2+}$ (mac = cyclam or 15aneN$_4$) release NO when irradiated with light of 314, 334, and 355 nm [20,95,107], like other ruthenium nitrosyl complexes, especially *trans*-[Ru(NH_3)$_4$(L)(NO)]$^{3+}$ [4,9,15]. The former complexes lead to the corresponding *trans*-[RuCl(H_2O)(mac)]$^{2+}$ (Eq. (20)), without chloride aquation.

$$\textit{trans}\text{-[Ru}^{II}\text{Cl(NO)}^+\text{(cyclam)]}^{2+} \xrightarrow[H_2O]{h\nu} \textit{trans}\text{-[Ru}^{III}\text{Cl(OH}_2\text{)(cyclam)]}^{2+} + \text{NO}^0 \quad (20)$$

The quantum yields of NO release from *trans*-[Ru(NH_3)$_4$(L)(NO)]$^{3+}$ vary from 0.03 for *N*-imidazol to 0.3 for the strong *trans* labilizing triethylphosphite

Table 4
UV–vis data for some *cis* Ru(II) cyclam complexes and related species[a]

Complex	λ_{max} (nm) (log ε)	Ref.
cis-[Ru(cyclam)(py)$_2$]$^{2+}$	378 (4.10), 340 (3.70), 245 (3.99)	[55]
cis-[Ru(cyclam)(bpy)]$^{2+}$	504 (3.66), 359 (3.81), 294 (4.12), 243 (4.00)	[55]
cis-[Ru(cyclen)(bpy)]$^{2+}$[b]	516 (3.44), 380 (3.56), 344 (3.56), 292 (4.29), 243 (3.98)	[72]
cis-[Ru(cyclen)(4-NCpy)$_2$]$^{2+}$[b]	380 (3.94), 254 (4.12), 211 (4.24)	[72]
cis–syn–syn-[Ru(NO)Cl(imcyclen)]$^{2+}$[c]	463 (1.78), 361 (2.46)	[14]
cis–syn–anti-[Ru(NO)Cl(imcyclen)]$^{2+}$[c]	460 (1.72), 358 (2.43)	[14]

sh: shoulder.
[a] In aqueous solution, except where noted.
[b] In 0.1 M HCl solution, pH = 1.
[c] In 6 M HCl solution.

[4,9,15]. As for the ruthenium ammine nitrosyls, the observed photochemical reaction should come from the Ru $d_{xz,yz} \rightarrow NO\ \pi^*$ MLCT state. The quantum yield of NO release is on the order of 0.1 for the cyclam complex [95,107]. This value is close to those of *trans*-$[Ru(NH_3)_4(L)(NO)]^{3+}$ [4,9,15], (L = pyridine derivative), and also close to those in *cis*-$[Ru(bpy)_2(L)(NO)]^{3+}$ (L = py, 4-pic, 4-acpy) [12]. However, a larger quantum yield value for $15aneN_4$, on the order of 0.6, was reported [20], which is larger than that of *trans*-$[Ru(NH_3)_4(P(OEt)_3)(NO)]^{3+}$. Although the reactivity of ruthenium tetraazamacrocyclic complexes is dependent on the ring size, studies on the photochemical release of NO from other tetraazamacrocyclic systems are under investigation in our laboratories in order to explain the difference in these values and evaluate their potential application.

5. X-ray molecular structure

The X-ray molecular structure of *trans*-$[RuCl_2(cyclam)]Br$ shows significant interactions between nitrogen hydrogens and both chloro ligands. Such interactions were used to support the substitution inertness of the chloro ligands after reduction of the ruthenium(III) center. These interactions are also present in the cyclam complexes with NO and 4-acetylpyridine [5,10]. In the case of the 4-acpy complex, these interactions were also confirmed by the NMR solvatochromic behavior of *trans*-$[RuCl(4\text{-acpy})(cyclam)](BF_4)$ (4-acpy = 4-acetylpyridine) [5]. The H–Cl interatomic distances for the secondary amine hydrogens lying on the same side of the plane as the chloro ligand indicate a strong interaction. The chemical shifts of these two hydrogen atoms are solvent independent, while those of the other two hydrogens that do not interact with chloro are solvent dependent.

The Ru–N (macrocyclic nitrogen atoms) interatomic distances in the Ru(II) complexes are shorter than in other Ru(II) ammines, and are close to Ru(III)–N interatomic distances, probably because of the macrocycle constraint (Table 5). In the NO complex, the Ru–Cl interatomic distance is shorter than in the corresponding 4-acpy complex, and is even shorter than in the dichloro complex. It should be noted, however, that the electron-attracting ability of the nitrosyl ligand, in *trans*-$[Ru(NO^+)(L)(A)_4]^{3+}$, increase the acidity of the *trans* ligand for values even slightly larger than in Ru(III) complexes (consistent with Eq. (18)) [10,15,111], as predicted by Taube [112]. For instance, the pK_a of *trans*-$[Ru(NO^+)(H_2O)(cyclam)]^{3+}$ is ~3.0, one order of magnitude lower than that of $[Ru(NH_3)_5(H_2O)]^{3+}$, which is 4.1 [111]. Thus, this would explain that shorter distance. Finally, the Ru–NO interatomic distance is in the range of the distances obtained for other ruthenium nitrosyl complexes. It should also be noted that, with mpz, considered an organic equivalent of NO [113]. The Ru–N distance (1.95 Å) is longer than that of Ru–NO (1.7–1.8 Å), although it is much shorter than other Ru–N distances.

6. Electrochemical data

The $Ru^{3+/2+}$ reduction potentials for Ru cyclam complexes and related species are collected in Table 6, along with potentials referring to the $NO^{+/0}$ processes.

Examination of Table 6 shows that the reduction potential ($Ru^{3+/2+}$) of *trans*-$[RuCl_2(cyclam)]^+$ is similar to those of *trans*-$[RuCl_2(NH_3)_4]^+$ and *trans*-$[RuCl_2(en)_2]^+$. For *trans*-$[Ru^{III}Cl_2(mac)]^+$, this potential is dependent on ring size, going from −150 mV for the cyclam complex to −95 mV for $16aneN_4$, as a result of the macrocyclic effect and enlargement of the macrocyclic cavity [8]. For *trans*-$[Ru(III)LL'(mac)]^+$ this potential is also dependent on L and L′.

Substitution on the macrocycle seems to have a small or negligible effect on the reduction potentials, but there are not enough electrochemical data for Ru complexes to derive an explanation. However, on one hand tertiary amines should stabilize Ru(III) and decrease the potential, on the other hand, the H–Cl interactions are weakened (in the

Table 5
Relevant interatomic distances (Å) for some ruthenium cyclam and related complexes

Complex	Interatomic distances			
	Ru–N[a]	Ru–Cl	Ru–L	Ref.
trans-$[Ru^{II}Cl(cyclam)(4\text{-acpy})](BF_4)$	2.097	2.457	2.057	[5]
trans-$[Ru^{II}(NO^+)Cl(cyclam)](ClO_4)_2$	2.092	2.323	1.747	[10]
cis-$[Ru^{II}(cyclam)(bpy)](BF_4)\cdot H_2O$	2.083		2.080	[71]
trans-$[Ru^{III}Cl_2(cyclam)]Br$	2.083	2.342		[8]
cis-$[Ru^{III}Cl_2(cyclam)]Cl$	2.109	2.369		[55]
cis-$[Ru^{III}Cl(NH_3)_5]Cl_2$	2.103[b]	2.346		[108]
$[Ru^{II}(NH_3)_6]I_2$	2.144[b]			[109]
$[Ru^{III}(NH_3)_6](BF_4)_3$	2.104[b]			[109]
$[Ru^{II}(NH_3)_5(1\text{-mpz})]I_3$	2.153[b]		1.95	[110]

[a] Ru-macrocyclic N interatomic distance, except where noted; average value.
[b] Ru-ammine N interatomic distance, average value. 1-mpz = 1-methylpyrazinium.

Table 6
$Ru^{3+/2+}$ and $NO^{+/0}$ redox potentials for some Ru cyclam complexes and related species[a]

Complex	E (mV) (vs. NHE)[b]	Ref.
trans-$[RuCl_2(cyclam)]^+$	−150	[8]
	−152	[51]
trans-$[RuCl_2(14\text{-tmc})]^+$	−128	[61]
trans-$[RuCl_2(16aneN_4)]^+$	−95	[8]
trans-$[RuCl_2(1\text{-pramcy})]^{2+}$	−158	[51]
trans-$[RuCl_2(en)_2]^{+c}$	−188	[114]
trans-$[RuCl_2(NH_3)_4)]^+$	−160	[115]
trans-$[RuCl(OH_2)(cyclam)]^{2+d}$	12	[51]
trans-$[RuCl(OH)(cyclam)]^{+d}$	−8	[51]
trans-$[RuCl(H_2O)(1\text{-pramcy})]^{3+d}$	−18	[51]
trans-$[RuCl(OH)(1\text{-pramcy})]^{2+e}$	−78	[51]
trans-$[RuCl(cyclam)(NHC(O)\text{-}4\text{-}pyH)]^{2+}$	−68	[38]
trans-$[RuCl(cyclam)(OCNH_2\text{-}4\text{-}py)]^{2+}$	−148	[38]
trans-$[RuCl(OH_2)(NH_3)_4)]^{2+c}$	−50	[65]
trans-$[Ru(OH_2)_2(NH_3)_4)]^{3+c}$	+80	[65]
trans-$[RuCl(OH_2)(en)_2]^{2+c}$	−66	[114]
trans-$[Ru(OH_2)_2(en)_2]^{3+c}$	+92	[114]
$[Ru(NH_3)_5(NHCO\text{-}4\text{-}py)]^{2+f}$	−230	[88]
cis-$[RuCl_2(cyclam)]^+$	+32*	[52]
cis-$[RuCl_2(cyclen)]^+$	+142*	[52]
cis-$[RuCl_2(NH_3)_4]^{+c}$	−110*	[115]
cis-$[RuCl(OH_2)(NH_3)_4]^{+c}$	0	[115]
trans-$[RuCl(cyclam)(py)]^+$	+320	[2]
trans-$[RuCl(cyclam)(4\text{-}acpy)]^+$	+420	[2]
trans-$[Ru(4\text{-}NCpyH)Cl(cyclam)]^{2+g}$	+720	[38]
$[Ru(NH_3)_5(py)]^{2+h}$	+298	[116]
trans-$[Ru(NO^+)Cl(cyclam)]^{2+i}$	−78■	[10]
trans-$[Ru^{II}(NO^+)Cl(1\text{-pramcy})]^{3+g}$	−118■	[95]
cis-$[Ru(cyclam)(py)_2]^{2+j}$	+574#	[55]
cis-$[Ru(cyclam)(bpy)]^{2+j}$	+650#	[55]
cis-$[Ru(cyclam)(phen)]^{2+}$	+630#	[73]
cis-$[Ru(imcyclen)(bpy)]^{2+j}$	+905#	[73]
cis-$[Ru(NH_3)_4(bpy)]^{2+j}$	+510#	[117]
cis-$[Ru(NH_3)_4(phen)]^{2+j}$	+510 #	[117]
cis–syn–syn-$[Ru(NO^+)Cl(imcyclen)]^{2+k}$	−48■ #	[14]
cis–syn–anti-$[Ru(NO^+)Cl(imcyclen)]^{2+k}$	−68■ #	[14]

[a] In 0.1 M HCl/0.1 M KCl aqueous solution, except where noted.
[b] Reported potential values with different reference electrodes are arithmetic averages of E_{cp} and E_{ap}, except were noted and were converted to NHE for comparison purposes.
[c] In 0.01 M Htos + 0.19 Ktos.
[d] In 0.1 M CF_3SO_3H.
[e] In CH_3CO_2H/CH_3CO_2Na at pH = 4.2.
[f] In 0.5 M KCF_3SO_3.
[g] In 1 M HCl.
[h] In 0.01 M Htos/Ktos buffer.
[i] In CH_3CO_2H/CH_3CO_2Na at pH 4.
[j] In 0.1 M KCl aqueous solution.
[k] 0.1 M TBA(PF_6) acetonitrile solution.
* E_{cp}: cathodic peak potential. ■Data for $NO^{+/0}$ reduction. #E_{ap}: anodic peak potential.

N monosubstituted) or lacking (in 14-tmc), resulting in a smaller Ru–Cl interaction and an increase in potential. Apparently, these opposite effects cancel each other, resulting in reduction potentials similar to those of the unsubstituted cyclam. Current efforts in our labs have also been directed toward *cis* and N- and C- functionalized complexes, and these data may help to clarify these features. Less data are available for the *cis* tetraazamacrocyclic complexes, but they present higher redox potential values than the respective *trans* isomers (even taking into account that the values for the *cis* complexes correspond to peak potentials, not $E_{1/2}$, for the rapid chloride aquation). Interestingly, it should also be noted that the cyclam complexes do not display values similar to the tetraammines either. These higher values are probably due to the smaller constraint imposed by the *cis* over the *trans* configuration.

Upon substitution of the anionic chloride ligand by the neutral aqua ligand in the *trans* complexes, an average shift of ∼+150 mV is observed for the first chloride. The few available data indicate that substitution of OH^- for H_2O results in decrease of the potential of −20 and −60 mV for cyclam and 1-pramcy, respectively.

The amide-bonded complexes (with cyclam) show redox potential values of −68 and −148 mV, for the *N*- and *O*-bonded coordinated complexes, respectively. Such values lie in the same range as the ones of the analogous pentaammine complex [38,70,87,88], indicating a larger Ru(II) affinity for the N bonded complex.

The redox potentials of the *trans*-$[Ru^{II}Cl(L)(cyclam)]^+$ complexes are similar to those of the corresponding pentaammines [2,6,38] and, as in the case of the ammines increase in the L ligand π acceptor character results in higher potentials, stabilizing the Ru(II) oxidation state. The *cis* cyclam complexes with py, bpy and phen have reduction potentials ca. 100 mV higher than those of the corresponding tetraammines. The *cis* imcyclem complexes present even higher values, which is consistent with the unsaturation in the ring.

The reduction potentials of nitrosyl complexes refer to the reduction of NO^+ to NO^0 (or from *trans*-$[RuCl(NO)(mac)]^{2+}$ to *trans*-$[RuCl(mac)(NO)]^+$) and their values are in the range of those of nitrosyl tetraammines [15]. The cyclam nitrosyl complex has two cathodic reduction potentials. The higher potential is pH independent and has been assigned to the reduction of NO^+ to NO^0. The lower potential peak is pH dependent and has been attributed to the reduction of *trans*-$[Ru^{II}(H_2O)(NO^+)(mac)]^{3+}$, which results from the coupled chemical reaction of chloride loss following reduction (Eqs. (14)–(18)) [10]. The profile of the 1-pramcy nitrosyl complex, however, is more complicated since there is also a pH dependence of the amine pendant arm, which is being investigated. The reported potential value for the 1-pramcy nitrosyl complex refers to a 1 M HCl solution of the complex.

7. Aquation reactions of Ru(III) and Ru(II) cyclam complexes and related species

The Ru(III) complexes, $[Ru^{III}L_2(mac)]^+$, are relatively inert with regard to aquation of the L ligands, especially the second one (Eqs. (7), (8), (11), (12)). The aquation rates are dependent on the metallic center, configuration of the complexes and ligand identity. For some *trans* Ru(III) complexes, such as 14-16aneN4, the chloride inertness in aqueous solution is observed for at least 24 h, but other Ru(III) complexes

have larger aquation rate constants. That is the case of *trans*-[RuCl(tfms)(cyclam)]$^+$, which has a rate constant ($k_1 = 6.0 \times 10^{-2}\ s^{-1}$) that is four orders of magnitude larger than that of *trans*-[$RuCl_2(NH_3)_4$]$^+$ ($k_1 = 1.7 \times 10^{-6}\ s^{-1}$). The aquation reaction of *trans*-[$RuCl_2$(14-tmc)]$^+$ (Eq. (7)), *trans*-[$RuCl_2$(1-(3-propylamonium)cyclam)]$^{2+}$ and *cis*-[$RuCl_2$(cyclen)]$^+$ have pseudo-first order rate constant values of 2.7×10^{-4}, 8.2×10^{-5} and $3.6 \times 10^{-3}\ s^{-1}$, respectively.

The specific rate constant values of aquation for the first chloride (k_1) in the ruthenium complexes are smaller than in the corresponding Co(III) complexes (Table 7). In the case of Ru(III), the dichlorotetraammine complex has a rate constant of $3.1 \times 10^{-6}\ s^{-1}$, while for the dichlorocyclam complex no aquation was noticed for at least 24 h. The respective values for the Co(III) complexes are 1.8×10^{-3} and $1.1 \times 10^{-6}\ s^{-1}$, with the ring size effect resulting in a six order of magnitude increase from cyclam to 16aneN$_4$. For the Co(III) complexes, the rates of aquation are dependent on the *trans* ligand, but there is not enough data for the Ru complexes to see if this trend is followed.

The increase in the rates of the N-substituted macrocyclic complexes is consistent with the weakening of the chloro hydrogen bonds when compared to the cyclam complex. Indeed, the aquation rate of *trans*-[$Ru^{III}Cl_2$(14-tmc)]$^+$ (Eq. (7)) [61], which has four nitrogen hydrogen atoms substituted, is much larger than that of the mono substituted *trans*-[$Ru^{III}Cl_2$(1-pramcy)]$^+$ [51] (Table 7).

Table 7
Rate constant values for the aquation of Cl^- in [MLAX]$^{n+}$ complexes at 25 °C[a]

M	L	A	X	k_1 (s^{-1})	Ref.
Ru^{3+}	1-pramcy	Cl^-	Cl^-	8.2×10^{-5}	[51]
Ru^{3+}	cyclam	Cl^-	Cl^-	Very slow	[118]
Ru^{3+}	cyclam	Cl^-	Tfms	6.0×10^{-2}	[62]
Ru^{3+}	$(en)_2$	Cl^-	Cl^-	4.2×10^{-6}	[119]
Ru^{3+}	$(NH_3)_4$	Cl^-	Cl^-	1.7×10^{-6}	[56]
Ru^{3+}	tmc	Cl^-	Cl^-	2.7×10^{-4}	[61]
Ru^{3+}	cyclen	Cl^-	Cl^-	3.6×10^{-3}	[52]
Ru^{3+}	$(NH_3)_4$	NH_3	Cl^-	3.1×10^{-6}	[120]
Ru^{3+}	$(NH_3)_4$	NH_3	Tfms	9.3×10^{-2}	[121]
Co^{3+}	cyclam	Cl^-	Cl^-	1.1×10^{-6}	[122]
Co^{3+}	cyclam	Cl^-	Tfms	4.8×10^{-2}	[62]
Co^{3+}	cyclam	tfms	Tfms	3.8×10^{-2}	[62]
Co^{3+}	cyclam	NCS^-	Cl^-	3.2×10^{-8}	[122]
Co^{3+}	16aneN4	Cl^-	Cl^-	2.57	[123]
Co^{3+}	$(en)_2$	Cl^-	Cl^-	3.5×10^{-5}	[122]
Co^{3+}	$(en)_2$	NCS^-	Cl^-	4.6×10^{-8}	[122]
Co^{3+}	$(NH_3)_4$	Cl^-	Cl^-	1.8×10^{-3}	[122]
Co^{3+}	$(NH_3)_4$	NCS^-	Cl^-	3.6×10^{-6}	[122]
Ru^{2+}	cyclam	Cl^-	Cl^-	0.036	[6]
Ru^{2+}	$(NH_3)_4$	NH_3	Cl^-	5	[124]
Ru^{2+}	cyclam	NO^0	Cl^-	2.1	[10]
Ru^{2+}	cyclam	H_2O	NO^0	6.1×10^{-4}	[10]
Ru^{2+}	1-pramcy	Cl^-	Cl^-	0.29	[51]
Ru^{2+}	15aneN$_4$	Cl^-	Cl^-	0.064	[6]
Ru^{2+}	2,3-dimethylcyclam	Cl^-	Cl^-	0.032	[6]

[a] *trans* complexes, except where noted.

Reduction of [$Ru^{III}L_2$(12-16aneN$_4$)]$^+$ results in larger rates of aquation of the ligand L. However, the aforementioned chloro hydrogen bonds in the cyclam complexes are too strong to make the Ru(II) complex as labile as the chloro ammines (Table 7), and loss of the second chloride is slow enough as to make the synthesis of *trans*-[RuClL(cyclam)]$^{n+}$ complexes feasible (Eqs. (7)–(9)) [8]. The rates of dissociation for Ru(II) complexes with saturated unsubstituted tetraaza macrocycles, *trans*-[$Ru^{II}Cl_2$(mac)], provide evidence for the macrocycle strain energy effect in the aquation reaction. These rates of dissociation follow the order cyclam < 15aneN$_4$ < 16aneN$_4$, suggesting that the chloride aquation is influenced by the macrocycle ring size [6,8].

It was pointed out [8,55] that the major effect observed for the labilization of chloride is associated with nephelauxetic and solvation effects. Nephelauxetic effects should favor lability of *trans* chloro ligands. However, the nitrogen hydrogen atom–chloro interactions seem to surpass the nepheulaxetic effect, since the chloro ligands in the *trans* complexes are substitution inert, and the absence of those interactions in the *cis* complexes renders all of them, but those of nitrosyl, more labile, especially for Ru(II) (Table 7). However, it would be interesting to investigate the effect of *trans* labilizing ligands, such as phosphites and sulphite, on the chloride lability in *trans*-[Ru(Cl)X(mac)]$^{n+}$.

All the macrocyclic complexes for which aquation have been reported, exhibit retention of configuration for the macrocyclic ligand in the aquation product. This is consistent with the assumption of a dissociative mechanism.

Reduction of *trans*-[RuCl(NO)(cyclam)]$^{2+}$ is followed by chloride aquation (Eqs. (14) and (15)), with a rate constant ($k = 1.5\ s^{-1}$ at pH 4) larger than those of other Ru(II) cyclam complexes, suggesting a *trans* labilizing effect for NO^0. This aquation is followed by a slow NO release (Eq. (16)), with a specific rate constant ($6.1 \times 10^{-4}\ s^{-1}$) [10,15] four to two orders of magnitude smaller than those of the analogous *trans* nitrosyl tetraammines, which have rate constants of NO aquation going from 5.1 for the carbon bonded imidazole [26] to $0.02\ s^{-1}$ for the 4-picoline complex [15]. In addition, this rate is one order of magnitude smaller than for [Ru(NO)(Hedta)]$^{2+}$ ($k_{obs} = 7.3 \times 10^{-3}\ s^{-1}$), whose aqua complex is a known NO scavenger [15,125]. This rate constant shows that the range of rates of NO release can be expanded with the tetraazamacrocycles.

The *trans*-[RuCl(NO)(cyclam)]$^{2+}$ and *trans*-[$Ru(P(OEt_3)(NO)(NH_3)_4]^{3+}$ complexes presented a very interesting biological effect [15,16,18,19]. In addition to their low toxicity, endovenous administration of the complexes in hypertensive rats resulted in decrease of the blood pressure, as does sodium nitroprusside, a classical nitrovasodilator. These complexes showed an immediate and intense effect, similar to the NO donor sodium nitroprusside. However, while the effect of both *trans*-[$Ru(P(OEt_3)(NO)(NH_3)_4]^{3+}$ and sodium nitroprusside lasted for only a few seconds, the effect of the cyclam complex lasted for about 15 min. The difference was explained on the basis of different rate values

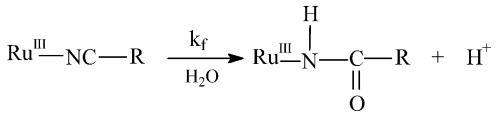
for NO release, $0.97\,s^{-1}$ for the phosphite complex, and $6.4 \times 10^{-4}\,s^{-1}$ for cyclam.

Simultaneous administration of the nitrosyl cyclam precursor *trans*-[RuCl(tfms)(cyclam)]$^{+}$ inhibited the cyclam nitrosyl effect. This fact was explained by the reaction of *trans*-[Ru(OH)(H_2O)(cyclam)]$^{2+}$, formed in the reactions involved, with the released NO, from the cyclam nitrosyl, to form *trans*-[Ru(OH)(NO)(cyclam)]$^{2+}$, which acts as a NO scavenger. The rates of the reactions between NO and Ru(III) aqua and hydroxo tetraazamacrocyclic complexes and the rates of NO dissociation from the Ru(II) complexes are being determined in our lab.

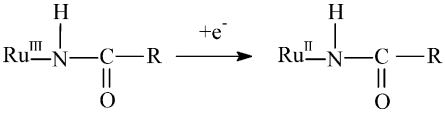
8. Nitrile hydrolysis and amides

Ruthenium(III) ammines with N-bonded amides can be easily synthesized from the corresponding nitrile complex. As with other transition metals, coordinated nitriles can undergo hydrolysis to amides when coordinated to Ru(II) or Ru(III) complexes [38,70,84,88,89,126–128]. The rate constant values of hydrolysis are larger for the more electrophilic Ru(III). In aqueous media, oxidation of the corresponding Ru(II)-nitrile to Ru(III) is followed by a pH dependent hydrolysis to the N-bonded amide (Eqs. (21)–(24)), even under acidic conditions. This Ru(III)-amide complex can then be reduced to give the corresponding Ru(II) N-bonded amide complex. In the case of the ammine complexes, they undergo fast aquation, among other possible reactions, depending on the nature of the amide [38,70,84,88,89,127–129].

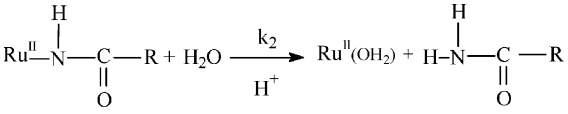
$$Ru^{II} - NC - R \xrightarrow{-e} Ru^{III} - NC - R \qquad (21)$$



(22)



(23)



(24)

Despite their similarity, different features resulted from the reactions of *trans*-[Ru^{II}Cl(cyclam)(4-NCpyH)]$^{2+}$ and *trans*-[Ru^{II}Cl(cyclam)(4-NCpy)($Ru^{II}(NH_3)_5$)]$^{3+}$ upon oxidation to Ru(III). The oxidized species undergo hydrolysis of the coordinated nitriles to form the corresponding Ru(III)-amide complexes [Ru^{III}Cl(cyclam)(L)]$^{n+}$ and [Ru^{III}Cl(cyclam)(L)$Ru(NH_3)_5$]$^{n+}$ (L = amide bonded 4-pyridinecarboxamide) [38,83,130]. Reduction to Ru(II) results in relatively long-lived amido bonded complexes that show relatively slow linkage isomerization of the *N*- and *O*-bonded coordinated amide, in contrast to the fast aquation and isomerization observed in different [$Ru(NH_3)_5$] analogues [38,70,83].

The estimated rate constant value, k_f, for the hydrolysis of the *trans*-[Ru^{III}Cl(cyclam)(4-NCpyH)]$^{2+}$ at pH 1 is $0.245\,s^{-1}$ [38], which is similar to the value of $0.193 \pm 0.001\,s^{-1}$ observed for [$Ru^{III}(NH_3)_5$(4-NCpyCH$_3$)]$^{3+}$ at the same pH [84]. There are several different modes of amide bonding (protonated and deprotonated) in the *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ and *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-py)($Ru^{III}(NH_3)_5$]$^{3+}$ complexes, including *N*- and *O*-linkage isomers, bonded through the amide N or the amide O [38,83]. The identity of the formed species is pH dependent, and the nitrogen-bonded amide prevails at acidic pH, while the oxygen-bonded amide is formed through linkage isomerization in basic solution [38,83], in contrast with the behavior of the pentaammines. The *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ complex has a pK_a of 3.9 for the coordinated amide [38], which is close to the 4.3 value of the analogous [$Ru^{III}(NH_3)_5$(NH-C(O)-4-pyH)]$^{3+}$ complex [88]. Despite the fact that the protonation site is not close to Ru, the slightly smaller pK_a value of the cyclam complex is consistent with the *trans*-[Ru^{III}Cl(cyclam)]$^{2+}$ core being more acidic. This can be inferred from the pK_a of 1.1 of *trans*-[Ru^{III}(cyclam)(H_2O)$_2$]$^{2+}$, which is smaller than that of *trans*-[$Ru(NH_3)_4(H_2O)_2$]$^{3+}$ (pK_a = 2.6) [6] and [$Ru(NH_3)_5(H_2O)$]$^{3+}$ (pK_a = 4.2) [131,132], indicating that cyclam makes Ru(III) more acidic than do ammines.

The spectral changes of *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ in the pH range 4.5-11 allowed the calculation of another pK_a (∼7.9) [38]. The *N*-bonded isomer undergoes relatively fast linkage isomerization to the *O*-bonded isomer, *trans*-[Ru^{III}Cl(cyclam)(OC(NH_2)-4-py)]$^{2+}$, at high pHs (pH > pK_a), contrasting with the behavior of other ruthenium(III) amides [87,133] which undergo isomerization to the nitrogen bonded species at high pH and are relatively inert with respect to substitution [38].

In the acidic medium, reduction of the metal center in *trans*-[Ru^{III}Cl(cyclam)(NHC(O)-4-pyH)]$^{2+}$ leads to *trans*-[Ru^{II}Cl(cyclam)(NH_2C(O)-4-pyH)]$^{2+}$ and does not result in fast aquation ($k \cong 2.4 \times 10^{-5}\,s^{-1}$), as in the case of other amides with ruthenium(II) pentaammine, but is followed by a relatively slow ($k \cong 2 \times 10^{-2}\,s^{-1}$) linkage isomerization to form the oxygen-bonded species [38]. Aquation and isomerization rates are smaller than in the pentaammines. The smaller rate of aquation has been rationalized by the amide modes of bonding, which also involve iminol and cyclam nitrogen hydrogen. The reactions of the related bimetallic complex *trans*-[Ru^{II}Cl(cyclam)(4-NCpy)($Ru^{II}(NH_3)_5$]$^{3+}$ are being investigated.

9. Concluding remarks

Despite the similarities with analogous ruthenium ammines, the tetraazamacrocyclic complexes of ruthenium show

a chemistry that is rich in several aspects, especially in terms of spectra and reactivity, such as that of nitriles and amides, which are being investigated in our labs. This rich chemistry is very interesting with regard to the rapidly developing field of NO chemistry, as the biological results with cyclam complexes have demonstrated. Based on these results, in addition to other systems being studied, we are currently exploring the immobilization and support of ruthenium nitrosyl complexes, aiming at using them in materials for controlled NO release in specific sites. For this purpose, specially designed substituted ruthenium macrocyclic complexes, such as the reported *trans*-[$RuCl_2$(1-(3-propilamonium)cyclam)]$^{2+}$, are also being investigated in our laboratories.

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