Synthesis and Structural Studies of Rhenium(V) Complexes Stabilized by a Monoanionic Cyclen Ligand

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The novel cationic (oxo)Re^{V} complexes [ReO(cyclen-H)Cl]X [X = Cl (**3a**), BPh$_4$ (**3b**)] and [ReO(cyclen-H)I]I (**4**) have been prepared by treating cyclen (1,4,7,10-tetrazacyclododecane) with (Bu$_4$N)[ReOCl$_4$] (**1**) and *cis*-[ReO$_2$I(PPh$_3$)$_2$] (**2**), respectively. The X-ray structural analyses of **3a** and **4**, as well as ^{1}H NMR spectroscopy, showed that the macrocyclic ligand is coordinated in the unprecedented monoanionic form. ^{1}H and ^{13}C NMR spectroscopy also demonstrated that **3a**,**b** and **4** exist in solution as single isomers. To the best of our knowledge, **3a** and **4** are the first examples of structurally characterized oxo complexes of d transition elements with cyclen bound to the metal atom through one amido and three amine groups. In both complexes, the geometry around the Re^{V} center is best described as distorted octahedral. The terminal oxo and halo ligands are coordinated in relative *cis* positions, and the amido and three amino nitrogen atoms from cyclen occupy the four remaining coordination positions. The Re–N(amido) bonds [1.894(9) Å in **3a** and 1.888(12) Å in **4**] are *trans* to the halo ligands and, as expected, are considerably shorter than the Re–N(amine) bonds, which span from 2.110(6) to 2.246(8) Å and from 2.124(8) to 2.268(10) Å for cations the cations of **3a** and **4**, respectively.

Introduction

Macrocyclic polyamines, especially those based on cyclen (1,4,7,10-tetrazacyclododecane) or cyclam (1,4,8,11-tetrazacyclotetradecane) frameworks are widely used in the coordination chemistry of the d and f elements in search of applications in a wide variety of areas such as catalysis, biomimicry and medicine.[1] The coordination chemistry explored with macrocyclic polyamines for rhenium has involved only cyclam[2–4] and tacn (1,4,7-triazacyclononane)[5–11] type ligands. In the case of cyclam, part of this research work has been pursued due to the relevance of rhenium complexes in the development of diagnostic or therapeutic radiopharmaceuticals.[3,4] In fact, the β-emitters ^{186}Re and ^{188}Re are potentially useful as therapeutic radionuclides, and rhenium complexes are adequate surrogates of complexes of radioactive ^{99m}Tc, which is the most widely used radionuclide in diagnostic nuclear medicine.[12–14]

The (cyclam)rhenium chemistry so far reported is restricted almost to the cationic *trans*-[ReO$_2$(cyclam)]$^+$ species, which contains the macrocycle coordinated in a neutral, tetradentate and equatorial fashion.[2–4] The strong tendency of cyclam to form complexes with the *trans*-[ReO$_2$]$^+$ core is well illustrated by the fact that *trans*-[ReO$_2$(cyclam)]$^+$ can be prepared using rhenium starting materials as diverse as [ReOCl$_3$(PPh$_3$)$_2$], [ReNCl$_2$(PPh$_3$)$_2$], or even [ReCl$_3$(CH$_3$CN)(PPh$_3$)$_2$].[3] In contrast, for tacn type ligands a much more diverse rhenium chemistry has been developed. These neutral, facial and tridentate ligands allowed the stabilization of a plethora of rhenium complexes, with the metal atom in oxidation states spanning from I to VII.[5–11]

Until now, research on rhenium chemistry with cyclen, also a potentially tetradentate macrocycle like cyclam but displaying a smaller cavity size, has remained completely unexplored. Aiming to widen the scope of the chemistry of Re^{V} oxides with cyclic tetradentate polyamines, and taking into account that cyclen tends to form mainly *cis*-octahedral complexes,[15] we decided to evaluate the possibility of using cyclen as an anchor to stabilize complexes with [Re=O]$^{3+}$ or *cis*-[ReO$_2$]$^+$ cores. In this contribution we describe reactions of cyclen with the Re^{V} starting materials (Bu$_4$N)[ReOCl$_4$] (**1**) and *cis*-[ReO$_2$I(PPh$_3$)$_2$] (**2**), which led to the formation of [ReO(cyclen-H)Cl]Cl (**3a**) and [ReO(cyclen-H)I]I (**4**), respectively. Herein, we also discuss the mechanism involved in the formation of complex **4**, which most probably proceeds through the intermediate *cis*-[ReO$_2$(cyclen)]$^+$, as indicated by ^{1}H and ^{13}C NMR spectroscopic studies.

Results and Discussion

While there is an extensive literature[16] on mono(oxo)Re^{V} complexes, namely with chelating N-donor ligands, complexes with the *cis*-[ReO$_2$]$^+$ core are scarce. To the best of our knowledge, the latter class of compounds

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is comprised of only the five-coordinate *cis*-[$ReO_2I(PPh_3)_2$] (**2**)[17] and the six-coordinate *cis*-[ReO_2(bipy)(py)$_2$] (bipy = 2,2′-bipyridine)[18] and *cis*-[$ReO_2(OH_2)(Me_3tacn)]^+$ (Me_3-tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane)[11]. For the synthesis of mono(oxo)Re^V complexes, several methodologies are available, namely oxygen abstraction reactions of Re^{VII} compounds already containing the ancillary ligands, reduction of perrhenate in the presence of the incoming ligands or metathesis reactions of (halo)(oxo)Re^V complexes, such as (Bu_4N)[$ReOCl_4$] (**1**) or [$ReOCl_3(PPh_3)_2$].[16,19–21] In contrast, there are no well-established synthetic methods for preparing *cis*-dioxorhenium(V) complexes.

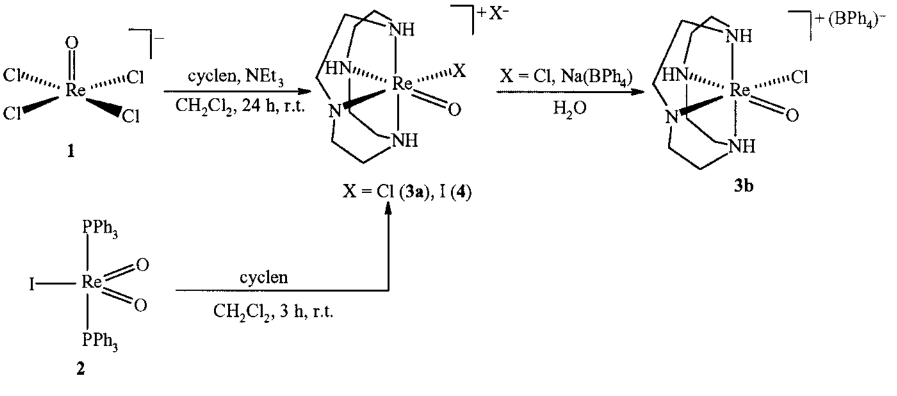
To enter into the chemistry of mono(oxo)Re^V complexes with cyclen we decided to start from (Bu_4N)[$ReOCl_4$] (**1**),[22] while for preparing cyclen complexes with the *cis*-[$ReO_2]^+$ core we selected *cis*-[$ReOI_2(PPh_3)_2$] (**2**)[17] as the more convenient starting material. As depicted in Scheme 1, compound **1** reacts smoothly with cyclen in dichloromethane giving [ReO(cyclen-H)Cl]Cl (**3a**) in moderate yield (57%). Compound **3a** slowly precipitates from the reaction mixture as a grey-green microcrystalline solid. ^1H NMR analysis of the precipitate showed the presence of **3a** contaminated with a small amount of protonated cyclen, due to release of HCl which is scavenged by the cyclen still present in solution. To suppress the formation of protonated cyclen, we have studied the reaction of **1** with cyclen in the presence of Et_3N. However, even under these conditions **3a** co-precipitates with protonated cyclen, which was removed by successive washings with methanol. An alternative for purification of [ReO(cyclen-H)Cl]$^+$ is the replacement of the counterion in **3a** by the larger anion BPh_4^- (Scheme 1). Treatment of an aqueous solution of crude **3a** with $NaBPh_4$ was accompanied by the precipitation of [ReO(cyclen-H)Cl](BPh_4) (**3b**), which was recovered analytically pure in 65% yield, after washing with water and methanol.

The reaction of *cis*-[$ReO_2I(PPh_3)_2$] (**2**) with cyclen in dichloromethane is quite fast, resulting in a brown solution from which a red solid precipitates almost immediately. During the course of the reaction, this insoluble red solid slowly vanishes and, meanwhile, a green microcrystalline solid starts to precipitate. This green material, recovered after a reaction time of 3 h, was identified as [ReO(cyclen-H)I]I (**4**), the iodo analogue of **3** (Scheme 1). Compound **4** was obtained in approximately 40% yield after purification by successive washings with warm water to remove some protonated cyclen and perrhenate, which were formed during the reaction.

Compounds [ReO(cyclen-H)Cl]X [X = Cl (**3a**), BPh_4 (**3b**)] and [ReO(cyclen-H)I]I (**4**) were unambiguously identified by the common analytical techniques which included X-ray crystallographic analysis in the case of **3a** and **4**.

The analysis of compounds **3a**, **3b** and **4** by ^1H and ^{13}C NMR spectroscopy demonstrated that the respective complex cations exist in solution as single isomers. In fact, the ^{13}C NMR spectra of these compounds in [D$_6$]DMSO showed four resonances for the methylene carbon atoms of cyclen in the range δ = 49.8−71.9 ppm, and three additional resonances for the aromatic carbon atoms of the counterion in the case of **3b**. These ^{13}C NMR spectra are consistent with the solid-state structures found for **3a** and **4**, and can be accounted for by the presence of a horizontal mirror plane which bisects the macrocycle and makes each pair of chelate rings magnetically equivalent.

The ^1H NMR spectra of **3a**,**b** and **4** should display eight resonances for the 16 diastereotopic methylene protons of the monodeprotonated cyclen, one resonance for the two equivalent apical N*H* protons and one resonance for the equatorial N*H* proton. Using [D$_6$]DMSO as the solvent, all the expected NH resonances were observed but some signals of the methylene protons of cyclen overlapped with the signal from residual water. In **3a**,**b** and **4**, the two apical N*H* resonances appear between δ = 9.64 and 9.84 ppm, and are considerably deshielded in comparison with the equatorial NH proton which resonates between δ = 4.25 and 4.52 ppm. All spectra display four poorly resolved multiplets in the range δ = 3.50−4.00 ppm, integrating for 8 CH_2 protons, and two high-field-shifted multiplets between δ = 2.4 and 2.8 ppm, integrating each for 2 CH_2 protons. For complex **3a** there is one CH_2 resonance very close to the residual water signal, appearing at δ = 3.52 ppm, and another under the water signal as demonstrated by 2D COSY and 2D HETCOR experiments. In fact, in the COSY spectrum of **3a** three correlations were found between the water signal and three of the CH_2 resonances, while in the HETCOR spectrum one correlation was observed between the water signal and the carbon atom reson-



Scheme 1

ating at $\delta = 64.1$ ppm. In the spectra of compounds **3b** and **4**, two resonances are missing for the cyclen methylene protons. By analogy with the spectrum of 3**a**, these resonances must be under the signal of residual water, which appears at $\delta \approx 3$ ppm.

X-ray quality crystals of **3a** and **4** were obtained from methanol or water solutions, respectively, in the presence of air. Compound **3a** crystallized as [ReO(cyclen-H)Cl]Cl$_{0.67}$(ReO$_4$)$_{0.33}$, most probably due to partial oxidation of **3a** during the recrystallization process. Noticeably, for compound **4** no partial oxidation or hydrolysis of the rhenium−iodo bond was observed during its recrystallization from water, as evidenced by the crystal structure being consistent with intact [ReO(cyclen-H)I]I (**4**).

The crystallographic analyses showed that the complex cations **3a** and **4** are monomeric with approximately octahedral coordination geometries. ORTEP views of the structures are shown in Figures 1 and 2, and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

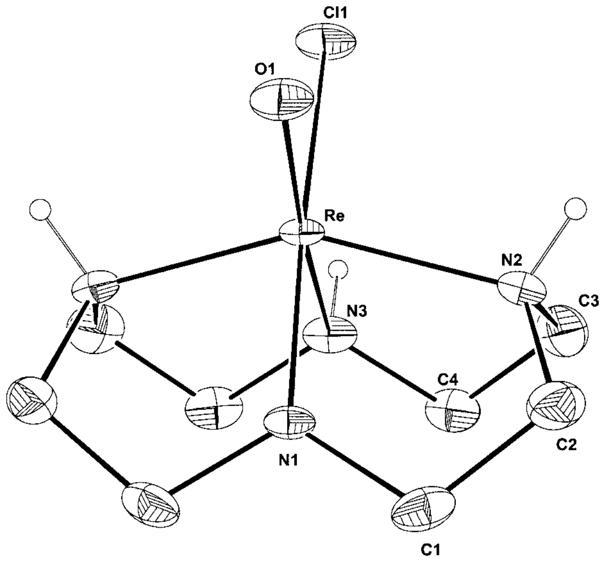


Figure 1. ORTEP view of the cationic complex **3a**; thermal ellipsoids are drawn at the 30% probability level

To the best of our knowledge, **3a** and **4** are the first reported structurally characterized examples of oxo complexes of d transition metals stabilized by a cyclen ligand. The presence of a monodeprotonated cyclen ligand is another unique feature of the structures of **3a** and **4**. In all reported structures of cyclen complexes the macrocycle is coordinated as a neutral ligand.[23−25] In both complexes, the rhenium center is coordinated by the one amido and three amine groups from cyclen, an oxo ligand and a halo ligand. The oxo and halo ligands are in *cis*-positions, as imposed by the *cis*-octahedral coordination of the tetradentate cyclen which occupies the remaining four coordination sites.

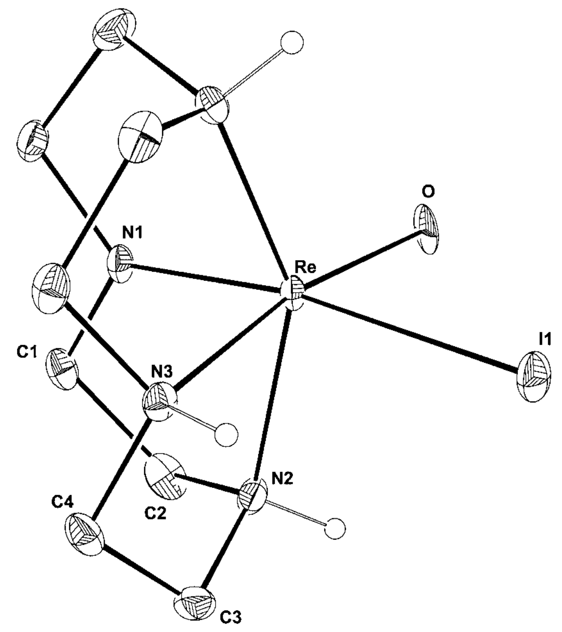


Figure 2. ORTEP view of the cationic complex **4**; thermal ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] for cation **3a**

Re−O(1)	1.704(8)	Re−N(1)	1.894(9)
Re−N(2)	2.110(6)	Re−N(3)	2.246(8)
Re−Cl(1)	2.525(3)		
O(1)−Re−N(1)	108.8(3)	O(1)−Re−N(2)	105.2(2)
O(1)−Re−N(3)	164.3(4)	O(1)−Re−Cl(1)	87.8(3)
N(1)−Re−N(2)	79.8(2)	N(1)−Re−N(3)	86.9(4)
N(1)−Re−Cl(1)	163.4(3)	N(2)−Re−N(2)*[a]	147.5(3)
N(2)−Re−N(3)	76.9(2)	N(2)−Re−Cl(1)	96.1(2)
N(3)−Re−Cl(1)	76.5(3)		

[a] Equivalent atoms generated by the symmetry operation $-x$, $-x + y$, z.

Table 2. Selected bond lengths [Å] and angles [°] for cation **4**

Re−O	1.715(9)	Re−N(1)	1.888(12)
Re−N(2)	2.124(8)	Re−N(3)	2.268(10)
Re−I(1)	2.8791(10)		
O(1)−Re−N(1)	110.1(5)	O(1)−Re−N(2)	105.2(2)
O(1)−Re−N(3)	162.7(5)	O(1)−Re−I(1)	85.0(4)
N(1)−Re−N(2)	79.5(2)	N(1)−Re−N(3)	87.2(5)
N(1)−Re−I(1)	164.9(4)	N(2)−Re−N(2)*[a]	147.4(4)
N(2)−Re−N(3)	77.2(2)	N(2)−Re−I(1)	96.9(2)
N(3)−Re−I(1)	77.7(3)		

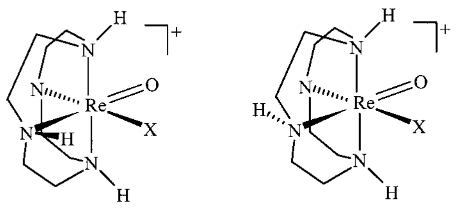
[a] Equivalent atoms generated by the symmetry operation $-x$, y, z.

The presence of the rhenium−amido bonds is confirmed by their short lengths [Re−N(1) 1.894(9) Å in **3a**; Re−N(1) 1.888(12) Å in **4**], and by the almost planar sp^2-hybridized N(1) atom. The Re−N(1) bond lengths in **3a** and **4** are similar to the Re−amido bond lengths recently reported for cationic (oxo)Re^{V} complexes with an acyclic tetradentate N-donor ligand.[16] As expected, these Re−N(1) bonds are considerably shorter than the three Re−N(amine) bonds, which span from 2.110(6) to 2.246(8) Å and from 2.124(8) to 2.268(10) Å for **3a** and **4**, respectively. Among the Re−N(amine) bonds, the longest are those corresponding to the nitrogen atom coordinated *trans* to the oxo ligand

[Re−N(3) 2.246(8) Å in **3a**; Re−N(3) 2.268(10) Å in **4**], reflecting the *trans* effect of this multiply bound ligand. The Re=O bond lengths [1.704(8) Å in **3a**; 1.715(9) Å in **4**] are within the expected range for octahedral mono(oxo)Re^{V} complexes but the Re−Cl [2.525(3) Å in **3a**] and the Re−I [2.8791(10) Å in **4**] bonds are longer than the values usually observed in (halo)(oxo)Re^{V} complexes.[16,17]. The lengthening of the Re−X (X = Cl, I) bonds can probably be accounted for by the presence of intramolecular hydrogen bonds involving the halo ligands and the equatorial N−H hydrogen atoms [Cl···N(3) 2.968 Å in **3a**; I···N(3) 3.262 Å in **4**].

In the structures of cations **3a** and **4**, the cyclen ligands adopt a folded and butterfly-like configuration, defining four chelate rings. There is a crystallographic mirror plane which contains the Re, O, N(1), N(3) and halide atoms, bisecting the coordinated macrocycle and resulting in two pairs of crystallographically equivalent five-membered chelate rings. The crystallographically equivalent chelate rings containing the deprotonated N(1) atom {[Re, N(1), C(1), C(2), N(2)] and [Re, N(1), C(1*), C(2*), N(2*)]} adopt an envelope conformation, while the other two equivalent five-membered chelate rings {[Re, N(2), C(3), C(4), N(3)] and ([Re, N(2*), C(3*), C(4*), N(3)]} assume a twisted conformation. The small cavity size of cyclen imparts a significant angular strain on the folded ring, as clearly indicated by the axial N(2)−Re−N(2*) bond angles of 147.5(3)° in **3a** and 147.4(4)° in **4**, which bend away the macrocycle from the oxo and halo ligands coordinated in the equatorial positions. This bending is more pronounced than that usually observed in *cis*-octahedral complexes containing neutral and tetradentate cyclen, where the axial angles usually lie between 160 and 170°.[23−25] The increased bending of the macrocycle in **3a** and **4** most probably reflects the presence of the Re−N(amido) bonds, which introduce additional steric constraints in the *cis*-octahedral coordination of the small sized cyclen.

For complexes **3a** and **4**, two isomeric forms could exist, depending on the *syn* or *anti* orientation of the equatorial N−H hydrogen atoms (see Figure 3), but only one isomeric form was detected, both in solid state and in solution. In the solid-state structures found for **3a** and **4**, the two apical NH hydrogen atoms and the equatorial NH hydrogen atom are directed towards the oxo and halo ligands, corresponding to the *syn*(X) (X = Cl, I) form. The establishment of the above-mentioned intramolecular hydrogen bonds X···H [X = Cl (**3a**), I (**4**)], involving the equatorial N−H hydrogen atoms, certainly contribute to the formation of the single *syn* isomers.



syn (X) ***anti (X)***

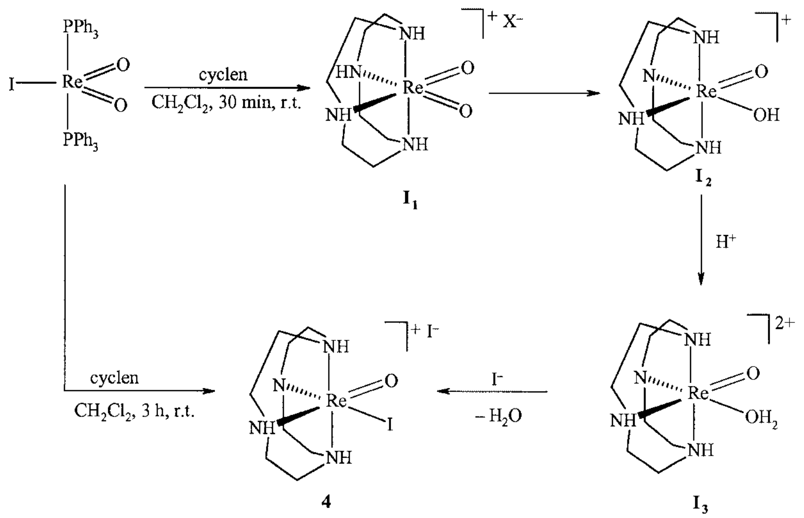
Figure 3. Schematic representation of the two possible isomers for cations [ReO(cyclen-H)X]$^{+}$ [X = Cl (**3**), I (**4**)]

Interestingly, the solid-state structures of **3a** and **4** give some support to the conjugate base catalyzed dissociative mechanism (D_{cb}), generally accepted for substitution reactions of (cyclen)Co^{III} complexes. Such mechanism involves intermediate Co^{III} complexes containing a monodeprotonated cyclen, but these intermediates were never isolated.[25]

In order to have a better insight into the nature of the intermediates involved in the formation of green [ReO(cyclen-H)I]I (**4**), we tried to identify the red solid which was formed almost immediately when *cis*-[ReO$_2$I(PPh$_3$)$_2$] (**2**) was treated with cyclen. After a short reaction time of 30 min, the red insoluble solid was separated and washed with dichloromethane. After drying under vacuum, the recovered red and microcrystalline material was analyzed by ^{1}H and ^{13}C NMR spectroscopy. As will be discussed below, the collected NMR spectroscopic data indicated that we must have isolated the cationic complex "*cis*-[ReO$_2$(cyclen)]$^{+}$" (**I$_1$**). However, complex **I$_1$** was never obtained analytically pure, being always contaminated with cyclenH^{+} and perrhenate. All attempts to purify **I$_1$** were unsuccessful because of its tendency to be transformed into [ReO(cyclen-H)I]I (**4**), even under strictly anhydrous and anaerobic conditions.

The ^{13}C NMR spectrum in [D$_6$]DMSO of the intermediate *cis*-[ReO$_2$(cyclen)]$^{+}$ (**I$_1$**) is even simpler than those of **3** and **4**, displaying only two methylene resonances at δ = 63.6 and 58.1 ppm for the coordinated cyclen. This pattern is consistent with the formulation proposed for **I$_1$**, since all the chelate rings are expected to be magnetically equivalent, due to the higher symmetry of this complex, which displays one horizontal mirror plane containing the metal atom, the oxo ligands and the equatorial nitrogen atoms, and one vertical mirror plane passing through the apical nitrogen atoms and the metal atom. Consistent with this, the ^{1}H NMR spectrum of **I$_1$** shows two broad resonances, centered at δ = 9.38 and 6.18 ppm and integrating for 2 protons each, which we have attributed to the two equivalent apical N*H* protons and to the two equivalent equatorial N*H* protons, by comparison with the ^{1}H NMR spectroscopic data of compounds **3a**,**b** and **4**, which have been unambiguously identified. Based on the formulation proposed for complex **I$_1$**, four resonances were expected for the CH$_2$ protons of cyclen with relative intensities of 4:4:4:4. In [D$_6$]DMSO, the ^{1}H NMR spectrum of **I$_1$** displays three resonances at δ = 3.01, 3.19 and 3.74 ppm, integrating each for 4 protons. The missing resonance also probably overlapped with the signal of residual water, as discussed above for complexes **3a**,**b** and **4**. Hence, the NMR spectroscopic properties of **I$_1$** seem to be in accord with its formulation as a *cis*-dioxo complex containing a tetradentate and neutral cyclen ligand.

In spite of the occurrence of parallel oxidation processes, we believe that formation of compound **4** involves **I$_1$** as an intermediate, as proposed in Scheme 2. The observed *cis*-dioxo intermediate **I$_1$** most probably rearranges into the (hydroxo)(oxo)Re^{V} derivative **I$_2$**, following an intramolecu-



Scheme 2

lar proton transfer from cyclen to one of the oxo ligands. Further protonation of the hydroxo ligand, eventually by adventitious water, gives the intermediate aqua complex **I$_3$**, which is finally transformed into the (iodo)(oxo) complex **4** upon replacement of the water molecule by the halide anion. The driving force for the transformation of **I$_1$** into **4** is certainly the basicity of the oxo ligands associated with the unstable *cis* configuration of the $[ReO_2]^+$ unit, due to the antibonding interactions between the metal d orbitals and the oxygen lone pairs.[26] In fact, the scarcity of *cis*-dioxorhenium(V) complexes has been attributed to electronic factors, the *trans* arrangement of the MO_2 unit being the most stable in octahedral dioxo transition metal complexes with a d^2 configuration.[26]

Conclusions

The novel cationic [ReO(cyclen-H)Cl]X [X = Cl (**3a**), BPh_4 (**3b**)] and [ReO(cyclen-H)I]I (**4**) were prepared in moderate yields using $(Bu_4N)[ReOCl_4]$ (**1**) or *cis*-$[ReO_2I(PPh_3)_2]$ (**2**), respectively, as the starting materials. The cations of compounds **3** and **4** are the first examples of d transition metal oxo complexes anchored to a monoanionic cyclen ligand. In the case of **3a** and **4**, the unprecedented coordination mode of the macrocycle was confirmed by X-ray crystallography, and the deprotonation of cyclen is certainly justified due to the enhanced Lewis acidity of the d^2 rhenium center. Apparently, the geometrical constraints of *cis*-octahedral cyclen could impose the *cis* geometry on the ReO_2 unit, but the resultant reactive *cis*-dioxo complex, *cis*-$[ReO_2(cyclen)]^+$, is readily converted into compound **4**. This transformation more than likely involves deprotonation of one amine group from cyclen, protonation of one of the oxo ligands from the *cis*-ReO_2 unit, and coordination of the incoming halide ion. A possible strategy for the efficient trapping of cyclen *cis*-dioxorhenium(V) derivatives could be the use of tetrasubstituted *N*-alkylated cyclen ligands, which are unable to undergo deprotonation.

Remarkably, in complexes **3** and **4** the cyclen ligand remains deprotonated even under aqueous conditions, indicating that cations **3** and **4** exhibit considerable stability in water and under aerobic conditions. These features may offer the possibility of applying such systems in the development of ^{99m}Tc or $^{186/188}$Re radiopharmaceuticals, which is nowadays one of the most relevant areas for the application of rhenium coordination compounds.

Although not yet explored, a diverse derivative chemistry can be anticipated for complexes **3** and **4**, based on oxygen transfer or metathesis reactions, allowing an interesting comparison with the chemistry reported so far for the related macrocyclic cations $[ReO(tacn)Cl_2]^+$ and $[ReO(Me_3tacn)Cl_2]^+$.[7]

Experimental Section

General: The syntheses of the complexes were carried under nitrogen, using standard Schlenk techniques and dry CH_2Cl_2, while the workup procedures were performed under air. The starting materials $[Bu_4N][ReOCl_4]$ (**1**) and *cis*-$[ReO_2I(PPh_3)_2]$ (**2**) were prepared according to literature methods.[17,22] Other chemicals were used as purchased. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Unity 300 MHz spectrometer. ^{1}H and ^{13}C chemical shifts are given in ppm and were referenced to the residual solvent resonances relative to Me_4Si. IR spectra were recorded as KBr pellets with a Perkin−Elmer 577 spectrometer. C, H and N analyses were performed with an EA 110 CE Instruments automatic analyzer.

[ReOCl(cyclen)]Cl (3a): To a solution of $[Bu_4N][ReOCl_4]$ (**1**) (200 mg, 0.34 mmol) in CH_2Cl_2 (15 mL) was added a solution of cyclen (58 mg, 0.34 mmol) and triethylamine (0.36 mmol, 50 mL) in CH_2Cl_2 (5 mL) at room temperature. The initially yellow solution became dark brown after complete addition of the ligand. The reaction mixture was stirred for 24 h and, after this time, a red supernatant and an insoluble gray-green solid were obtained. This solid, which was recovered using a centrifuge, was washed with methanol and formulated as **3a**. Yield: 86 mg (0.19 mmol, 57%). $C_8H_{19}Cl_2N_4ORe$ (444.38): calcd. C 21.61, H 4.27, N 12.60; found C 21.36, H 4.15, N 12.33. IR: $\tilde{\nu}$ = 940 [ν(Re=O)] cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 2.49 (br., 2 H, CH_2), 2.70−2.82 (m, 2 H, CH_2), 3.40−3.52 (m, 2 H, CH_2), 3.75−4.15 (m, 8 H, CH_2), 4.24 (br., 1 H, NH), 9.84 (br., 2 H, NH) ppm. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 50.5, 60.9, 64.6, 71.1 ppm.

[ReOCl(cyclen)]BPh$_4$: A solution of $NaBPh_4$ (77 mg, 0.23 mmol) in distilled water (10 mL) was added to a solution of **3a** (50 mg, 0.13 mmol) in water (10 mL), causing the immediate formation of **3b** as a yellow-green microcrystalline solid. Compound **3b** was recovered using a centrifuge, followed by successive washings with methanol. Yield: 60 mg (0.085 mmol, 65%). $C_{32}H_{39}BClN_4ORe$ (728.16): calcd. C 52.78, H 5.40, N 7.69; found C 53.18, H 5.73, N 7.72. IR : $\tilde{\nu}$ = 940 [ν(Re=O)] cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 2.49 (br., 2 H, CH_2), 2.72 (m, 2 H, CH_2), 3.72−4.15 (m, 8 H, CH_2), 4.24 (br.,1 H, NH), 6.78 (m, 4 H, Ar), 6.91(m, 8 H, Ar), 7.16 (m, 8 H, Ar), 9.84 (br., 2 H, NH) ppm. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 50.5, 60.9, 64.6, 71.1, 121.5, 125.3, 135.5 ppm.

[ReOI(cyclen)]I (4): To a solution of *cis*-[$ReO_2I(PPh_3)_2$] (130 mg, 0.15 mmol) in CH_2Cl_2 (15 mL) was added a solution of cyclen (28 mg, 0.16 mmol) in CH_2Cl_2 (5 mL). The initially purple solution became brown, and a red solid started to precipitate almost immediately. During the course of the reaction, the red solid vanished and, meanwhile, a green microcrystalline solid started to precipitate. After 3 h, the green solid, which was formulated as **4**, was recovered using a centrifuge, washed with CH_2Cl_2 and warm water, and dried under vacuum. Further purification of **4** was achieved by recrystallization from distilled water. Yield: 38 mg (0.06 mmol, 40%). $C_8H_{19}I_2N_4ORe$ (627.28): calcd. C 15.30, H 3.03, N 8.93; found C 15.65, H 2.96, N 8.79. IR: $\tilde{\nu}$ = 940 [ν(Re=O)] cm^{-1}. ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 2.49−2.60 (m, 2 H,CH_2), 2.78−2.83 (m, 2 H, CH_2), 3.83−3.98 (m, 6 H, CH_2), 4.07−4.15 (m, 2 H, CH_2), 4.52 (br.,1 H, NH), 9.64 (br., 2 H, NH) ppm. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 51.2, 61.1, 63.4, 71.9 ppm.

X-ray Crystallographic Analysis: Crystals were obtained by recrystallization from a saturated methanol solution (**3a**) or from a saturated aqueous solution (**4**) and mounted in thin-walled glass capillaries. Data were collected at room temperature with an Enraf−Nonius CAD-4 diffractometer with graphite-monochromated Mo-K_α radiation, using an ω-2θ scan mode. The crystal data are summarized in Table 3. The data were corrected[27] for Lorentz and polarization effects, and empirically for absorption by Ψ-scans. The heavy-atom positions were located by Patterson methods using SHELXS-97.[28] The remaining atoms were located in successive Fourier difference maps and refined by least-squares refinements on F^2 using SHELXL-97.[29] All non-hydrogen atoms were refined anisotropically; the contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon atoms with group U_{iso} values assigned. Atomic scattering factors and anomalous dispersion terms were as in SHELXL-97.[29] The drawings were made with ORTEP-3.[30] Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-215009 (**3a**) and -215010 (**4**). Copies of the data can be obtained free of charge on applicaton to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for cations **3a** and **4**

	3a	**4**
Empirical formula	$C_8H_{19}Cl_{1.67}N_4O_{2.33}Re_{1.23}$	$C_8H_{19}I_2N_4ORe$
Formula mass	515.96	627.27
Crystal size [mm]	0.40 × 0.12 × 0.09	0.28 × 0.20 × 0.12
Crystal system	hexagonal	orthorhombic
Space group	$P6_3cm$	*Cmc*21
a [Å]	14.156(3) Å	8.9853(10)
b [Å]	14.156(3) Å	12.9086(14)
c [Å]	11.952(3) Å	12.3257(17)
V [Å]	2074.2(8) Å^3	1429.6(3)
Z	6	4
T [K]	293(2)	293(2)
$D_{calcd.}$ [g cm^{-3}]	2.478	2.914
μ (Mo-K_α) [mm^{-1}]	12.011	12.807
F(000)	1452	1136
No. reflections Measured	3294	1359
No. unique Reflections	1761 (0.0352)[a]	1122 (0.0202)[a]
*R*1[b]	0.0314	0.0261
wR_2	0.0451	0.0628

[a] Value of *R*(int). [b] The values were calculated for data with $I > 2\sigma(I)$.

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