

# ReO<sub>2</sub><sup>+</sup> chelates with aliphatic diamines. Structural and proton transfer properties

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The structure and protonation of the complexes *trans*-[Re<sup>V</sup>O<sub>2</sub>L<sub>2</sub>]<sup>+</sup> (L = tmen (*N,N,N',N'*-tetramethylethylenediamine), deten (*N,N*-diethylethylenediamine) and dieten (*N,N'*-diethylethylenediamine)) were studied. The structure of [ReO<sub>2</sub>(dieten)<sub>2</sub>]I · 2H<sub>2</sub>O shows a *trans*-dioxo geometry (Re–O average distance 1.766(5) Å) and an equatorial plane defined by four N atoms belonging to two bidentate amines (Re–N average distance 2.190(7) Å). The Re atom lies on an inversion centre. These complexes can be protonated in aqueous solution and the protonation constants have been determined at 25 °C and *I* = 0.5 M KCl. The protonated species [ReO(OH)(deten)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was isolated and characterized by X-ray diffraction. The squashed octahedral geometry is maintained around the Re(v) atom (which also lies on an inversion centre) with larger Re–O distances (average 1.780(6) Å). By the use of *N*-alkylated diamines as equatorial ligands, complex protonation is confined to a low pH range (pH < 3) and one oxo group is preserved even in very acidic media.

## Introduction

Coordination compounds of rhenium, as well as group seven congeners Mn and Tc, are known with the metal in the oxidation states from –1 to +7. By far, the largest number of structurally characterized complexes contains the metal ion in the oxidation state +5.<sup>1</sup> These d<sup>2</sup> complexes are stabilized by the presence of multiply bonded axial donor ligands. If the axial substituent is an oxo group, five-coordinate monoxo [M<sup>V</sup>O]<sup>3+</sup>, six-coordinate *trans*-dioxo [M<sup>V</sup>O<sub>2</sub>]<sup>+</sup>, six-coordinate oxo–hydroxo [M<sup>V</sup>O(OH)]<sup>2+</sup> and six-coordinate oxo–aquo [M<sup>V</sup>O(OH<sub>2</sub>)]<sup>3+</sup> mononuclear species are typically formed.<sup>1,2</sup>

Bidentate aliphatic amines, like other neutral ligands, generally prefer the [ReO<sub>2</sub>]<sup>+</sup> center. For example, [ReO<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> (en = ethylenediamine),<sup>3</sup> [ReO<sub>2</sub>(tn)<sub>2</sub>]<sup>+</sup> (tn = trimethylenediamine),<sup>4</sup> [ReO<sub>2</sub>(eten)<sub>2</sub>]<sup>+</sup> (eten = *N*-ethylethylenediamine),<sup>5</sup> were characterized many years ago. Very recently, these complexes have attracted considerable interest since they proved useful for different applications.<sup>6–12</sup> They have been used as simple models to develop <sup>99m</sup>Tc radiopharmaceuticals,<sup>6</sup> to study the influence of the excited electronic states on the ground state properties,<sup>7,8</sup> and for the development of cata-

lysts for many organic reactions such as glycosylation,<sup>9</sup> oxygen atom transfer,<sup>10,11</sup> and etherification.<sup>12</sup>

An important process of these complexes in aqueous solution is the proton transfer equilibrium involving the oxo ligands, which affects at large extent their properties, in particular their redox stability.

During the last few years, some of us have been interested in the chemistry of Re(v) dioxo complexes with aliphatic diamines.<sup>4,13–19</sup> Cationic complexes [ReO<sub>2</sub>L<sub>2</sub>]<sup>+</sup> (L = bidentate amine) have been prepared and characterized. All of them exhibit the oxo groups in *trans* position, while the two amine ligands complete the equatorial plane.

In order to achieve a more comprehensive understanding of the characteristics of similar complexes we have extended the study to the chemistry of Re(v) dioxo complexes with the *N*-substituted ligands dieten (*N,N'*-diethylethylenediamine), deten (*N,N*-diethylethylenediamine) and tmen (*N,N,N',N'*-tetramethylethylenediamine), since these complexes offer the opportunity of getting information about the effect of *N*-substituents on their structures and on the proton transfer processes they are involved with in aqueous solution. We report here the results of this study.

## Experimental

### Materials

All chemicals were of reagent grade and used as received. [ReO<sub>2</sub>I(PPh<sub>3</sub>)<sub>2</sub>] and [ReOCl<sub>2</sub>(OEt)(PPh<sub>3</sub>)<sub>2</sub>] were obtained using the methods reported.<sup>8,20</sup>

### Physical measurements

IR spectra were recorded as KBr pellets on a Bomem MB FT-IR spectrophotometer and visible spectrum on a Spectronic

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3000 instrument. Elemental analysis was accomplished on a Carlo Erba model 1108 elemental analyzer. Fast atom bombardment spectra were obtained from a 3-nitrobenzyl alcohol matrix using a Micromass-Autospec spectrometer. HPLC chromatograms were obtained with an HPLC system by Merck, equipped with a variable wavelength monitor and a PRP-X200 (10  $\mu\text{m}$ ) cation exchange column (4  $\times$  250 mm). A 0.2 M aqueous solution of  $\text{Na}_2\text{SO}_4$  was used as mobile phase with 1.0  $\text{mL min}^{-1}$  flow. Detection was carried out at 255 nm.

### Synthesis

**[ReO<sub>2</sub>(dieten)<sub>2</sub>]I · 2H<sub>2</sub>O (1).** This complex was synthesized following the procedure reported by us,<sup>17</sup> and the purity checked by elemental analysis. Suitable crystals for X-ray diffraction studies were obtained by slow evaporation of a solution of the crude product in isopropyl alcohol at room temperature.

**[ReO<sub>2</sub>(deten)<sub>2</sub>]Cl · 3H<sub>2</sub>O (2).** This complex was prepared as previously described,<sup>21</sup> and the purity checked by elemental analysis.

**[ReO(OH)(deten)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (3).** To an aqueous solution of **2**, a mixture of  $\text{HClO}_4$  (70%)– $\text{H}_2\text{O}$  (2:1; v/v) solution was added until a dark pink solution was obtained. The solution was then filtered and pink crystals suitable for X-ray diffraction studies were obtained by slow evaporation at room temperature. Yield: 30%. Anal. Calc. for  $\text{C}_{12}\text{H}_{33}\text{N}_4\text{Cl}_2\text{O}_{10}\text{Re}$ : C, 22.2; N, 8.6; H, 5.1. Found: C, 22.3; N, 8.3; H, 5.3%.

**[ReO<sub>2</sub>(tmen)<sub>2</sub>]I (4).**  $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$  (600 mg, 0.70 mmol) was suspended in 30 mL of methanol and tmen (530  $\mu\text{L}$ , 3.50 mmol) was added. The mixture was stirred at room temperature for 60 min. The solution was then added to 10 mL of diethyl ether and a pale orange solid was obtained. This solid was washed with acetone (5  $\times$  5 mL) and diethyl ether (3  $\times$  5 mL). Yield: 50%. Anal. Calc. for  $\text{C}_{12}\text{H}_{32}\text{N}_4\text{IO}_2\text{Re}$ : C, 23.5; N, 9.1; H, 5.7. Found: C, 23.2; N, 9.1; H, 5.5%. IR ( $\text{cm}^{-1}$ ): 540.9 (s), 697.6 (m), 721.8 (m), 780.0 (s), 793.8 (s), 814.5 (s), 954.9 (m), 1002.3 (m), 1069.4 (w), 1121.3 (m), 1171.5 (m), 1190.8 (m), 1474.5 (s), 3468.5 (s). FAB mass spectrum:  $m/z$  451/449 ( $\text{M}^+$ ), 335/333 ( $\text{M}^+ - \text{tmen}$ ). HPLC retention time (min): 1.6 ( $\text{I}^-$ ), 3.1 (cation).

**[ReO<sub>2</sub>(tmen)<sub>2</sub>]Cl (5).** This complex was prepared as previously described<sup>20,22</sup> and the purity was checked by elemental analysis.

### Potentiometric measurements

Potentiometric titrations of compounds **2** and **5** were carried out in aqueous solution at 25 °C and ionic strength  $I = 0.5 \text{ M}$  in KCl. Solutions were freed of carbon dioxide by Ar bubbling. The titrant solution (0.1 M HCl in 0.5 M KCl) was prepared from Merck standard ampoules.

Equilibrium constants for complex protonation were determined through three potentiometric titrations (*ca.* 150 experimental points each) in the concentration range 1 to 4 mM, covering pH values between 1.5 and 5. In all cases, the solutions were poured into a 50 mL titration cell. After thermal equilibrium was reached, hydrogen ion concentrations

were determined in successive readings, each performed after a small incremental addition of standard 0.1 M HCl solution (carried out with the help of a Crison 2031 piston buret). Electromotive force values were recorded with the help of a Radiometer 85 pH meter, using a glass electrode and a calomel reference electrode. Pre-saturated argon (free of  $\text{CO}_2$ ) was bubbled through the solutions during titrations to eliminate the effect of atmospheric carbon dioxide and the temperature was kept at 25.0 ( $\pm 0.1$ ) °C. The cell constants  $E^\circ$  and the liquid junction potentials were determined according to the methods of Biedermann and Sillén<sup>23</sup> and Liberti and Light (ref. 24). Data were analyzed using the HYPERQUAD program,<sup>25</sup> and species distribution diagrams were produced using the HySS program.<sup>26</sup> The fit of the values predicted by the model to the experimental data was estimated on the basis of the parameter  $\sigma$ , corresponding to the scaled sum of square differences between predicted and experimental values.

### Crystallographic data collection and structure determination

Pale yellow crystals of **1** suitable for X-ray diffraction were obtained. Data collection was performed at room temperature (298(2) K) on a Rigaku AFC-7S diffractometer using monochromated (graphite) Mo-K $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) in the  $\omega$ – $2\theta$  scan mode. During the data collection, the intensity of three standard reflections was monitored every 150 reflections to correct for intensity decay. Lorentz, polarization and absorption corrections were applied.<sup>27</sup> This structure was solved by direct methods using the SHELXS-97 program.<sup>28</sup> It was completed by successive difference Fourier maps. Refinement was anisotropic for all non-hydrogen atoms (SHELXL-97).<sup>29</sup> Hydrogen atoms were located at calculated positions and were refined according to the linked atoms.

Analysis of pink single crystals of **3** has been carried out by an OXFORD XCALIBUR 3 ( $\lambda(\text{Mo-K}\alpha) = 0.71068 \text{ \AA}$ ). The intensities of some reflections were monitored during data collection to check the stability of the crystal: no loss of intensity was observed during data collection. The integrated intensities were corrected for Lorentz–polarization effects and for absorption (SADABS).<sup>30</sup> The structure was solved by direct methods (SIR-97).<sup>31</sup> Refinement was performed by means of full-matrix least-squares using the SHELXL-97<sup>29</sup> program. All non-hydrogen atoms were anisotropically refined while the hydrogen atoms were introduced in calculated position and their coordinates were refined according to the linked atoms. No residual electron density was found at the end of refinements.

A summary of the crystallographic data for both compounds is reported in Table 1.

CCDC reference numbers 616325 and 616326.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606797b

## Results and discussion

### Synthesis

The preparation of  $[\text{ReO}_2\text{L}_2]^+$  type complexes starting from  $[\text{ReO}_2\text{I}(\text{PPh}_3)_2]$ , has proved to be a very useful synthetic route. In a previous paper,<sup>17</sup> we described the preparation of the

**Table 1** Crystallographic data for compounds **1** and **3**

	<b>1</b>	<b>3</b>
Empirical formula	C <sub>12</sub> H <sub>36</sub> N <sub>4</sub> IO <sub>4</sub> Re	C <sub>12</sub> H <sub>33</sub> N <sub>4</sub> Cl <sub>2</sub> O <sub>10</sub> Re
<i>M<sub>r</sub></i>	613.56	650.6
Crystal system	Monoclinic	Orthorhombic
Space group	C2/c	<i>Pbca</i>
<i>a</i> /Å	13.8941(17)	8.513(5)
<i>b</i> /Å	19.078(4)	15.322(5)
<i>c</i> /Å	10.2235(14)	16.926(5)
$\beta$ /°	128.293(5)	90
<i>V</i> /Å <sup>3</sup>	2126.9(6)	2207.8(2)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.915	1.957
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	7.184	5.801
<i>F</i> (000)	1184	1296
Crystal dimensions/mm	0.23 × 0.23 × 0.07	
$\theta$ Range for data collection/°	2.13–27.49	4.31–25.85
Limiting indices, <i>hkl</i>	–1 to 18, –1 to 24, –13 to 10	–9 to 9, –16 to 16, –20 to 17
Reflections: collected/unique/ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> ) ( <i>R</i> <sub>int</sub> )	2915/2451/1909 (8.36%)	8468/1789/1192 (3.38%)
Completeness to $\theta$ /°	27.49	25.85
<i>R</i> <sub>1</sub> , <sup>a</sup> <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )] (%)	4.30, 12.60	4.22, 8.34
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.102	1.044
Largest diff. peak/hole	4.161/–2.359	0.657/–0.717

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_c|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

dioxo complexes with dien (diethylenetriamine), trien (trimethylenetetramine), tren (*N*-tris(2-aminoethyl)amine), pn (1,2-diaminopropane) and deten. In this work, we have extended this synthesis to tmen ligand. Elemental analysis and FABMS data support the formula [ReO<sub>2</sub>(tmen)<sub>2</sub>]I. According to previous work on similar compounds,<sup>3–5,21</sup> **4** belongs to the series of Re(v) *trans* dioxo complexes, as confirmed by the presence of the [ReO<sub>2</sub>]<sup>+</sup> asymmetric stretching vibration (a doublet at 794 and 814 cm<sup>-1</sup>) in its absorption spectrum.

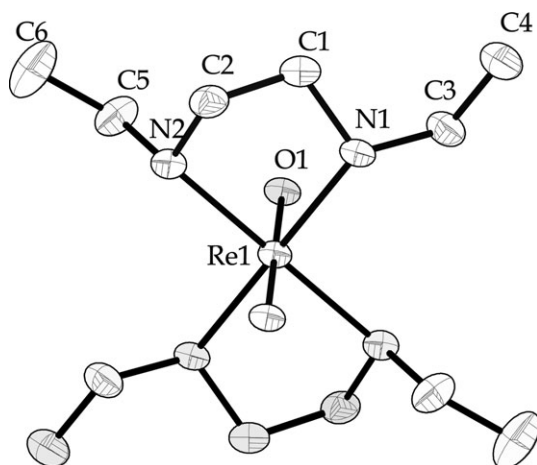
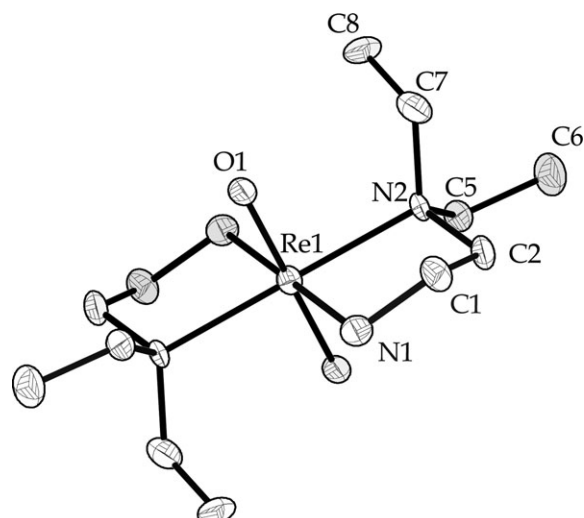
### Description of the structures

The structures of [ReO<sub>2</sub>(dieten)<sub>2</sub>]I · 2H<sub>2</sub>O (**1**) and [ReO(OH)(deten)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (**3**) were determined. ORTEP drawings of the complex cations are shown in Fig. 1 and 2, while selected distances and angles are listed in Table 2. Cations [ReO<sub>2</sub>(dieten)<sub>2</sub>]<sup>+</sup> and [ReO(OH)(deten)<sub>2</sub>]<sup>2+</sup> consist of squashed octahedrons around the Re(v) atom. The equatorial planes are

defined by the four N atoms belonging to two diamine ligands. Oxygen atoms, in *trans* position, occupy the apical sites.

Re–O bond length in **1** is 1.766(5) Å, which is in agreement with the average for Re=O bonds reported as 1.761 Å,<sup>32</sup> reflecting the expected double bond character. The X-ray structural analyses of **3** shows that the rhenium atom sits on an inversion centre (this is also the case of **1**) with the oxo and hydroxo oxygens disordered, resulting in the observation of longer average Re–O bond lengths of 1.780(6) Å.

The average Re–N distance is 2.190(7) Å for both compounds. In **1** the distances are almost the same, while in **3**, a significant difference is observed. One of the nitrogen atoms, N(2), which is bound to two ethyl groups exhibits a longer distance (2.228(6) Å). The presence of the ethyl groups seems to introduce steric crowding which rules out a closer position of the nitrogen atom. Further evidence in this respect is given

**Fig. 1** ORTEP view of the cation [ReO<sub>2</sub>(dieten)<sub>2</sub>]<sup>+</sup>; 30% probability ellipsoids; H atoms are omitted for clarity.**Fig. 2** ORTEP view of the cation [ReO(OH)(deten)<sub>2</sub>]<sup>2+</sup>; 30% probability ellipsoids; H atoms are omitted for clarity.

**Table 2** Selected bond lengths (Å) and angles (°) for **1** and **3**<sup>a</sup>

	<b>1</b>	<b>3</b>
Re(1)–N(1)	2.193(7)	2.152(7)
Re(1)–N(2)	2.187(6)	2.228(6)
Re(1)–O(1)	1.766(5)	1.780(6)
N(1)–C(1)	1.491(10)	1.481(11)
N(2)–C(2)	1.479(10)	1.502(10)
C(1)–C(2)	1.507(13)	1.488(12)
O(1)–Re(1)–N(1)	90.3(3)	90.3(3)
O(1)–Re(1)–N(2)	90.0(2)	88.8(2)
N(1)–Re(1)–N(2)	79.9(2)	80.5(3)
N(1)–Re(1)–N(1')	180.0	180.0
N(2)–Re(1)–N(2')	180.0	180.0
Re(1)–N(1)–C(1)	107.6(5)	110.0(5)
Re(1)–N(2)–C(2)	108.5(5)	105.3(5)

<sup>a</sup> The atoms labeled (') are related by the symmetry operation  $1.5 - x, 1.5 - y, 1 - z$  (in **1**) and  $-x, -y, -z$  (in **3**).

by the average Re–N distances in  $[\text{ReO}_2(\text{en})_2]^+$  (2.162 Å)<sup>3</sup> and  $[\text{ReO}_2(\text{eten})_2]^+$  (2.162 Å, for unfunctionalized N and 2.191 Å for ethyl-substituted N).<sup>5</sup>

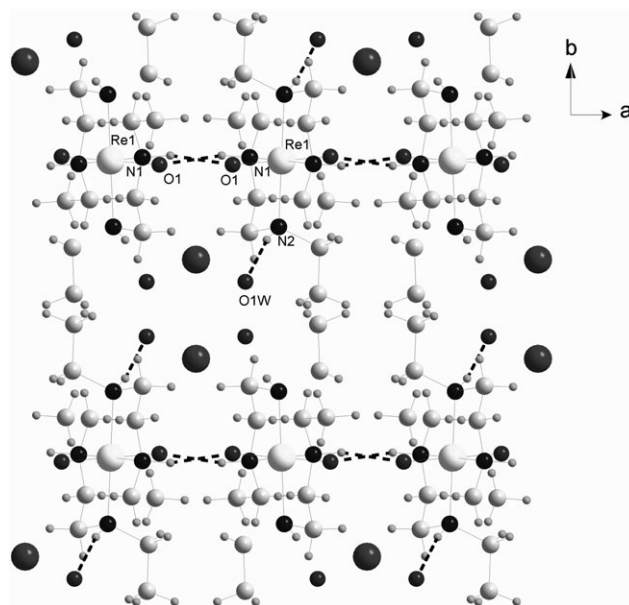
For an unstrained bidentate en, the ideal bite size (N–N distance in the ring) is 2.8 Å.<sup>33</sup> Complexes **1** and **3** fit the ideal bite size (N–N distance of 2.83(1) and 2.81(1) Å, respectively). Accordingly, the N–C–C angles are close to the theoretical value of 109.5° (111.2(7) and 108.1(7) Å for **1** and 109.2(7) and 108.0(7) Å for **3**). The five-membered rings formed between Re, N and C atoms offer the possibility of having molecules in different conformations. In both cations, a  $\lambda\delta$  conformation is adopted. As previously studied by molecular mechanics and semi-empirical calculations,<sup>15</sup> there is not great energetic difference between the conformers. However, in the solid state, **1**, **3** and  $[\text{ReO}_2(\text{en})_2]^+$  exhibit the same  $\lambda\delta$  conformation.

The rhenium atoms in **3**, order following a face centered orthorhombic arrangement. The minimum Re–Re distance is 8.515 Å, the *a*-axis parameter. In compound **1**, the minimum Re–Re distance is 5.700(1) Å.

The packing of **1** is mainly dictated by hydrogen bonds parallel to the *a* direction (Fig. 3). The bonds are established between the O atom of the  $[\text{ReO}_2]^+$  core and the H atoms of the amine (N1) belonging to a neighbour cation. Additional H bonds are detected between the lattice water and the other nitrogen atom (N2). On the other hand, the packing of **3** is dominated by the presence of perchlorate anions which forms many H bonds with the protonated oxo groups and the amine coordinated ligands.

### Proton transfer processes

The equilibrium constants determined in this work for the proton transfer processes involving complexes  $[\text{ReO}_2(\text{deten})_2]^+$  and  $[\text{ReO}_2(\text{tmen})_2]^+$  are shown in Table 3 along with analogous data for other Re(v) complexes of the same type. Proton binding by the simplest  $[\text{ReO}_2(\text{amine})_2]^+$  compounds (amine = en, pn, tn) takes place in successive steps on the oxo groups leading to the formation of the monoprotonated ( $[\text{ReO}(\text{OH})(\text{amine})_2]^{2+}$ ) and the diprotonated ( $[\text{Re}(\text{OH})_2(\text{amine})_2]^{3+}$  or  $[\text{ReO}(\text{OH})_2(\text{amine})_2]^{3+}$ ) species as pH becomes more acidic.<sup>4</sup> The involvement of oxo groups in



**Fig. 3** The crystal structure of **1** as viewed in the *a* direction. The H bonds are indicated by dashed lines.

complex protonation was clearly proved by solid-state studies<sup>34,35</sup> and rationalized by molecular mechanics and semi-empirical calculations.<sup>15</sup>

A second group of complexes contain tri- and tetradentate amines (dien, trien, tren) which only use two nitrogen donor atoms in the coordination to the  $[\text{ReO}_2]^+$  unit.<sup>17</sup> In such cases complex protonation takes place at higher pH values (Table 3) on the nitrogen atoms not involved in coordination. Species such as  $[\text{ReO}_2(\text{amine})_2]^+$ ,  $[\text{ReO}_2(\text{Hamine})(\text{amine})]^{2+}$  and  $[\text{ReO}_2(\text{Hamine})_2]^{3+}$  can be found in solution in different pH regions.

Complexes  $[\text{ReO}_2(\text{dieten})_2]^+$ ,  $[\text{ReO}_2(\text{deten})_2]^+$  and  $[\text{ReO}_2(\text{tmen})_2]^+$ , containing N-alkylated diamines derived from en, show a different behaviour, being involved in a single proton transfer process taking place in very acidic solutions (Table 3). As shown by the crystal structure of **3**, protonation occurs at the oxo groups, as previously observed for the analogous complexes with en, tn and pn.<sup>4,16</sup> In the present cases, however, the complexes show a lower affinity (smaller equilibrium constants) for the proton than their analogue with unsubstituted en. Alkyl groups have  $\sigma$ -donating properties but prevent the formation of hydrogen bonds between the amine groups

**Table 3** Protonation constants of  $[\text{ReO}_2(\text{amine})_2]^+$  complexes (25 °C, *I* = 0.5 M in KCl)

Complex	log $K_1$	log $K_2$	Ref.
$[\text{ReO}_2(\text{en})_2]^+$	3.41 ± 0.01	1.72 ± 0.02	4
$[\text{ReO}_2(\text{tn})_2]^+$	3.38 ± 0.02	1.79 ± 0.03	4
$[\text{ReO}_2(\text{pn})_2]^+$	3.59 ± 0.02	1.65 ± 0.04	17
$[\text{ReO}_2(\text{dien})_2]^+$	4.36 ± 0.12	1.13 ± 0.14	17
$[\text{ReO}_2(\text{trien})_2]^+$	6.04 ± 0.06	2.75 ± 0.06	17
$[\text{ReO}_2(\text{tren})_2]^+$	7.52 ± 0.03	1.72 ± 0.04	17
$[\text{ReO}_2(\text{dieten})_2]^+$	2.80 ± 0.01	—	17
$[\text{ReO}_2(\text{deten})_2]^+$	2.42 ± 0.08	—	This work
$[\text{ReO}_2(\text{tmen})_2]^+$	1.80 ± 0.08	—	This work

and the water solvent molecules which contribute, *via* H<sub>2</sub>O ···HN interactions, to the σ-donating properties of nitrogen atoms.<sup>36</sup> In general the second effect prevails and complexes with N-alkylated donors form less stable complexes than their unsubstituted analogues in aqueous solution.<sup>37</sup> Hence, although structural data (see above and also ref. 5) show that Re–O distance in the complexes is independent of the basicity of the equatorial ligands suggesting similar electron densities on the oxo groups in the solid state, in aqueous solution we expect that the N-alkylated en derivatives give rise to weaker interaction with the metal centre lowering the basicity of the oxo groups. As a matter of fact, as shown by the crystal structure herewith reported, N-alkylation leads to some lengthening of the N–Re bond distances, probably due to the steric crowding introduced by the substituents. This effect should be more evident in solution, where the substituents have higher mobility, in agreement with reduced basicity of the oxo groups in the complexes with N-alkylated ligands. Indeed, the [ReO<sub>2</sub>(tmen)<sub>2</sub>]<sup>+</sup> complex with tetramethylated en shows the lowest protonation constant (Table 2). Furthermore, dioxo complexes with tri- and tetradentate polyamines which use only two nitrogens in the coordination to Re and consequently contains bulky, uncoordinated residues, do not bear protonation on the oxo groups even in very acidic solution.<sup>17</sup>

### Concluding remarks

We have expanded the investigation on Re(v) dioxo-complexes, by studying the effect brought about by N-alkylation on their structural and proton transfer properties. The structure of the cationic complexes is quite similar to those found for [ReO<sub>2</sub>(en)<sub>2</sub>]<sup>+</sup> and [ReO<sub>2</sub>(tn)<sub>2</sub>]<sup>+</sup>. The presence of alkyl substituents only introduces slight distortions in the equatorial plane of the octahedron and some lengthening in one of the N–Re bond distances.

On the other hand, the proton transfer properties of the complexes are remarkably affected by the alkyl substituents. [ReO<sub>2</sub>(amine)<sub>2</sub>]<sup>+</sup> species (amine = deten, dieten and tmen) show a lower tendency to protonate (compared to complexes with en, pn, tn) and the formation of diprotonated [Re(OH)<sub>2</sub>(amine)<sub>2</sub>]<sup>3+</sup> species was not detected under our experimental conditions. The different behaviour can be ascribed to different solvation of N-alkylated amines and to the steric crowding introduced by the bulky substituents. Hence, by appropriately selecting the equatorial ligands it is possible to perform a rather fine tuning of the complex proton transfer properties. In particular, by using N-alkylated diamines as equatorial ligands, protonation is confined to a lower pH range (pH < 3) and one oxo group is preserved even in very acidic media. Therefore, the use of similar equatorial ligands may afford Re(v) dioxo catalysts for applications in a wider range of conditions.

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