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Thermodynamic study of proton transfer reactions of Re(V) *trans*-dioxocomplexes in aqueous solution

Jorge S. Gancheff,*†[a] Carlos Kremer,[a] Pablo A. Denis,[b] Claudia Giorgi[c] and Antonio Bianchi[c]

The thermodynamics of protonation of *trans*-[Re^{V}O$_2$L$_2$]$^+$ (L = aliphatic di and polyamines) complexes in aqueous solution was studied by using experimental and theoretical approaches. The complexes containing diamines undergo protonation on the oxo ligands, whereas those containing polydentate amines protonate on uncoordinated amino groups. The protonation reactions were studied experimentally by microcalorimetric techniques, in all cases exothermic with $|\Delta H^\circ|$ ranging from 7 to 50 kJ/mol. For complexes containing diamines, the exothermicity was in concordance with the basicities in some cases, while in others no systematic behaviour was found. For complexes with polydentate amines, the enthalpy dominates with a modest influence on the entropy. Theoretically, Density Functional Theory (DFT) methods were employed in the gas phase, and bulk solvent effects were treated by means of the Polarizable Continuum Model. Direct solute–solvent effects were considered adding explicit water molecules. The enthalpy change calculated in the gas phase was in marked disagreement with the experimental results due to the relevancy of solvation/desolvation processes. The explicit inclusion of water molecules led to a good improvement. A discrete-continuum model was also employed, for which ΔG° was overestimated in all cases. Further investigations, both experimental and theoretical are necessary to get a more complete picture of the proton transfer reactions of these complexes. The experimental values herein determined constitute the first step to construct a set of data to which it is possible to benchmark new theoretical approaches to compute the thermodynamics of proton transfer reactions of metal complexes in aqueous solution.

Introduction

The main focus of the contemporary interest in the chemistry of technetium and rhenium (the group 7 congeners, hereafter referred to as M) reflects the application of certain nuclides to radiopharmaceutical development.[1] ^{99m}Tc has been the prevalent radionuclide in nuclear medicine during the last 30 years due to its ideal nuclear properties, while $^{186/188}$Re have nuclear properties suitable for therapeutic applications.

The chemistry of these elements is unusual in the sense that all formal oxidation states between −1 and +7 are found in stable compounds.[2] This fact leads to a broad palette of coordination compounds. In spite of the large diversity of complexes, those containing the metal centre in a formal oxidation state +5 are the most important. The formation of chemically robust core structures, such as [M^{V}O$_2$]$^+$ or [M^{V}O]$^{3+}$, has been the key for the preparation and characterization of many M(V) complexes by several research groups.[3,4] In a recent review,[5] the past and the future of ^{99m}Tc inert metal cores as platforms for the development of radiopharmaceuticals have been discussed.

All the applications of M(V) complexes in radiopharmacy are based on the robust character of the species. The octahedral *trans*-M^V dioxo complexes (in which the four equatorial positions are usually filled by two bidentate soft ligands) are quite difficult to reduce/oxidize,[6] and substitution reactions are kinetically unfavorable.[7] The complexes containing the [M^{V}O]$^{3+}$ core, with coordination numbers 5 or 6, are more reactive than the dioxo complexes, but they can be regarded as having a low reactivity under mild reaction conditions.[8] However, despite their low reactivity, the MO$_2$$^+$ and MO^{3+} cores have been used for different purposes. Indeed, the synthesis of Re(III) and Re(II) complexes can be afforded from ReO^{3+} starting compounds,[9] and Tc(V) oxo cores have proved to be particularly effective as a template in the cyclization of substituted propylene amine oxime (known as PnAO) ligands.[10] The pH-dependent reversible isomerization of Re(V) complexes can also be observed.[11] [Re^{V}O(HEt$_2$tcb)$_2$]Cl can be converted to [Re^{V}OCl(HEt$_2$tcb)$_2$] (H$_2$Et$_2$tcb = *N*-[(*N′*,*N′*-dialkylamino)(thiocarbonyl)]benzamidine) upon acidification of the solution.

More recently, interest in the coordination chemistry of rhenium complexes has increased, especially due to their use in catalysis of organic reactions. High valence transition metal oxo complexes are ubiquitous in catalytic oxidation and oxygen transfer reactions. In this context, protonation of the oxo groups of Re(V) complexes is a key step in their catalytic activity.[12] [ReOCl$_3$(SMe$_2$)(Ph$_3$PO)] has successfully been assayed as a catalyst to generate 2-deoxy-α-glycosides from glycals,[12a] and the formation of intermediates containing Re···O···H motifs is very important in the hydrosilylation of carbonyl groups catalyzed by Re(V) dioxo complexes.[12b]

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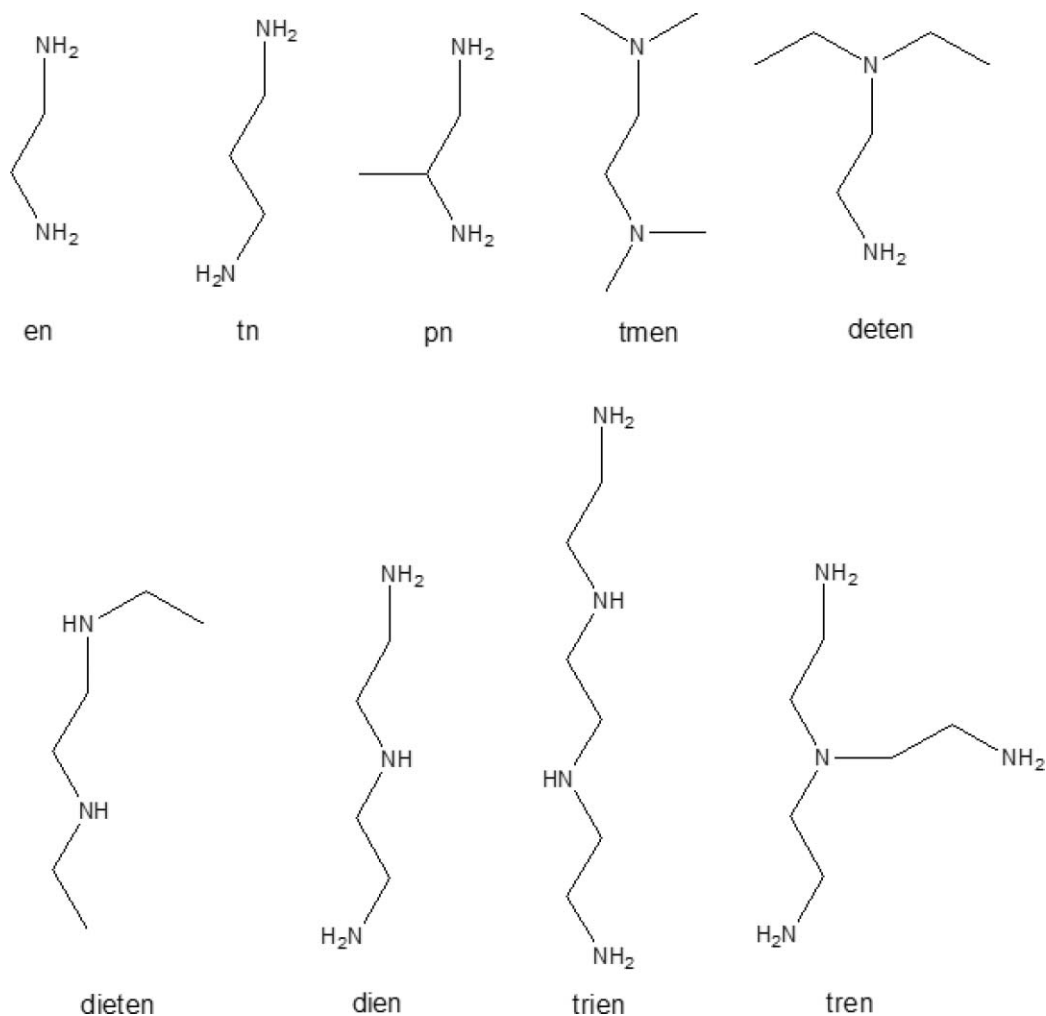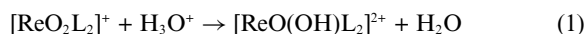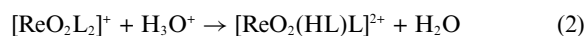
Fig. 1 Structure of the ligands used in this work.

Furthermore, the catalyzed hydrogenation of alkynes to alkenes by [Re^{V}IO$_2$(PPh$_3$)$_2$] seems to be mediated by hydrogen activation through H–H addition to the Re=O bond.[12c]

With this in mind we performed a physicochemical study on the protonation reactions involving *trans*-[ReO$_2$L$_2$]$^+$ complexes (L = ethylenediamine (en), 1,2-diaminopropane (pn), 1,3-diamino-propane (tn), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmen), *N*,*N*′-diethylethyl-enediamine (dieten), *N*,*N*-diethylethylenediamine (deten), diethylenetriamine (dien), trimethylenetetramine (trien) and *N*-tris(2-aminoethyl)amine (tren)) (Fig. 1). Protonation of these complexes proceeds through two ways, which are protonation on the oxo group:

$$[ReO_2L_2]^+ + H_3O^+ \rightarrow [ReO(OH)L_2]^{2+} + H_2O \quad (1)$$

or protonation on the amine ligand, if L has an additional free (not coordinated) basic group:

$$[ReO_2L_2]^+ + H_3O^+ \rightarrow [ReO_2(HL)L]^{2+} + H_2O \quad (2)$$

The reaction described by eqn (1) has been reported for L = en, pn, tn, tmen, dieten and deten, while those described by eqn (2) were observed for dien, trien and tren.[4a,b,g]

In the present work we have determined the reaction enthalpies by microcalorimetric measurements and density functional calculations. These results, together with the previously reported equilibrium constants for the same reactions,[4a,b,g] provide useful information for further understanding of proton transfer reactions in these systems.

Experimental

Materials

All chemicals were of reagent grade and used as received. [ReO$_2$(en)$_2$]I, [ReO$_2$(deten)$_2$]Cl·3H$_2$O, [ReO$_2$(tmen)$_2$]Cl, [ReO$_2$(pn)$_2$]I, [ReO$_2$(tn)$_2$]I, [ReO$_2$(dieten)$_2$]I·2H$_2$O, [ReO$_2$(dien)$_2$]I, [ReO$_2$(trien)$_2$]I and [ReO$_2$(tren)$_2$]I were synthesized according to previously reported procedures.[4b,13–15] The purity of compounds was checked by elemental analysis (Carlo Erba 1108 elemental analyzer).

Microcalorimetric measurements

The enthalpy changes for protonation of Re(V) dioxocomplexes were determined in 0.1 mol dm^{-3} Me$_4$NCl solution by using an automated system composed of a Thermometric AB thermal
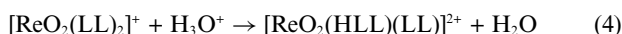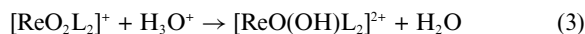
activity monitor (model 2277) equipped with a perfusion–titration device and a Hamilton Pump (model Microlabo M) coupled with a 0.250 cm³ gas tight Hamilton syringe (model 1750 LT). The microcalorimeter was calibrated by determining the enthalpy of reaction of a strong base (Me₄NOH) with a strong acid (HCl). The obtained value, −56.69(21) kJ mol⁻¹, was in good agreement with the literature value.[16] The heats of protonation were determined by titrating an acidic solution of the Re(V) dioxocomplex (5×10^{-3} mol dm⁻³, 2.0 cm³) with a standard Me₄NOH solution. Corrections for heats of dilution were applied. The corresponding enthalpies of reactions were determined from the calorimetric data by least-squares fitting using the AAAL program.[17] At least three titrations (at least 30 data points each) were performed for each system.

Theoretical calculations

All calculations were performed at the density functional level of theory, using the hybrid method B3LYP. This represents the Becke's 1988 exchange functional[18] coupled with exact (*i.e.* Hartree–Fock) exchange as in Becke's paper,[19] and the Lee–Yang–Parr correlation potential.[20] Core electrons for rhenium were treated through the pseudopotential approximations (ECP), as included in the LANL2DZ[21] basis set. This basis set takes relativistic effects into account, which is especially important when dealing with systems containing heavy atoms.[22] We have previously studied structures and vibrational behaviour of some Re(V) dioxocomplexes in the gas phase by means of the B3LYP/LANL2DZ methodology, obtaining a reasonable agreement with experimental data.[23] To analyze the thermodynamic behaviour of complex protonation, we enlarged the LANL2DZ basis set by adding a *d* function (with exponent $\alpha = 0.0437552$) for rhenium and the Pople's 6-311G(d) basis set for all non-metallic atoms. Hereafter, this enlarged basis set will be referred to as LD6311.

Proton transfer reactions were studied in the gas phase and in the presence of the solvent. It has been recognized that the solvent medium can greatly influence the energetics of proton transfer, because stabilization of charged species is favoured in polar solvents. The gas phase energetics may vary significantly if solvent effects are taken into account.[24] These effects are even more important in aqueous solution compared to organic solvents, since water can act not only as a solvent but also as an acid source supplying protons *via* hydrogen bond networks.[25]

Solvent effects were studied by applying continuum, discrete, and discrete-continuum models,[26] this hybrid explicit/implicit solvation model being also called the supermolecule-reaction field,[27] and the cluster-continuum model.[28] Calculation of the standard thermodynamic parameters was carried out at 298 K using the reactions described by:

$$[ReO_2L_2]^+ + H_3O^+ \rightarrow [ReO(OH)L_2]^{2+} + H_2O \qquad (3)$$

$$[ReO_2(LL)_2]^+ + H_3O^+ \rightarrow [ReO_2(HLL)(LL)]^{2+} + H_2O \qquad (4)$$

where L = en, pn, tn, tmen, dieten, deten, and LL = dien, trien, tren. The enthalpy change will be denoted as ΔH°. Although eqn (4) does not represent an isodesmic reaction, we proved that the error brought about by using it does not affect significantly the accuracy of the calculated thermodynamic parameters. The following procedure was adopted:

(a) $-\Delta H^\circ$ was calculated for the non isodesmic protonation reaction (4)

(b) $-\Delta H^\circ$ was calculated for the isodesmic protonation reaction (5) in which NH₃ replaces H₂O in eqn (4)

$$[ReO_2(LL)_2]^+ + NH_4^+ \rightarrow [ReO_2(HLL)(LL)]^{2+} + NH_3 \qquad (5)$$
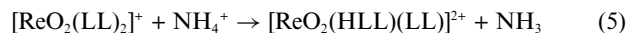
(c) from the value obtained in (a) and the experimental proton affinity (PA) of H₂O,[29] the PA value for the complex was calculated

(d) from the value obtained in (b) and the experimental PA of NH₃,[29] the PA value for the complex was calculated

(e) the PA values obtained in (c) and (d) were then compared.

The application of discrete and discrete-continuum models (see above for details) was limited to two representative complexes, [ReO₂(en)₂]⁺ (Re-en) taken as a model for complexes bearing protonation on the oxo ligands, and [ReO₂(dien)₂]⁺ (Re-dien) taken as a model for complexes bearing protonation on the amino groups.

As already mentioned, Re-dien undergoes protonation on the free amino group. This fact allows studying the influence of the intramolecular H-bond on the evaluation of thermodynamic parameters. The high flexibility of the ethyleneamino substituents and the different dispositions with respect to the complex core give rise to a very complicated system if all possible isomers and conformers are taken into account. Therefore, only two representative complex structures for the isomer *trans-trans* were analyzed (Fig. 2): one with an "open" ligand conformation,

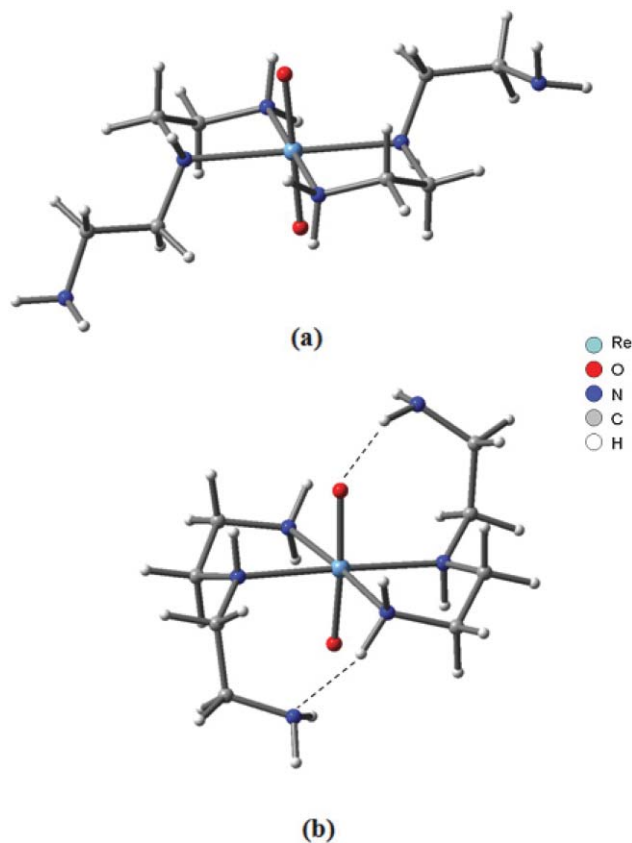**Fig. 2** Ligand conformations of *trans-trans* isomers of [ReO₂(dien)₂]⁺ studied in this work: (a) Re-dien with an "open" conformation (Re–dien_o); (b) Re-dien with a "closed" conformation (Re-dien_c) (calculated intramolecular H-bonds are shown).
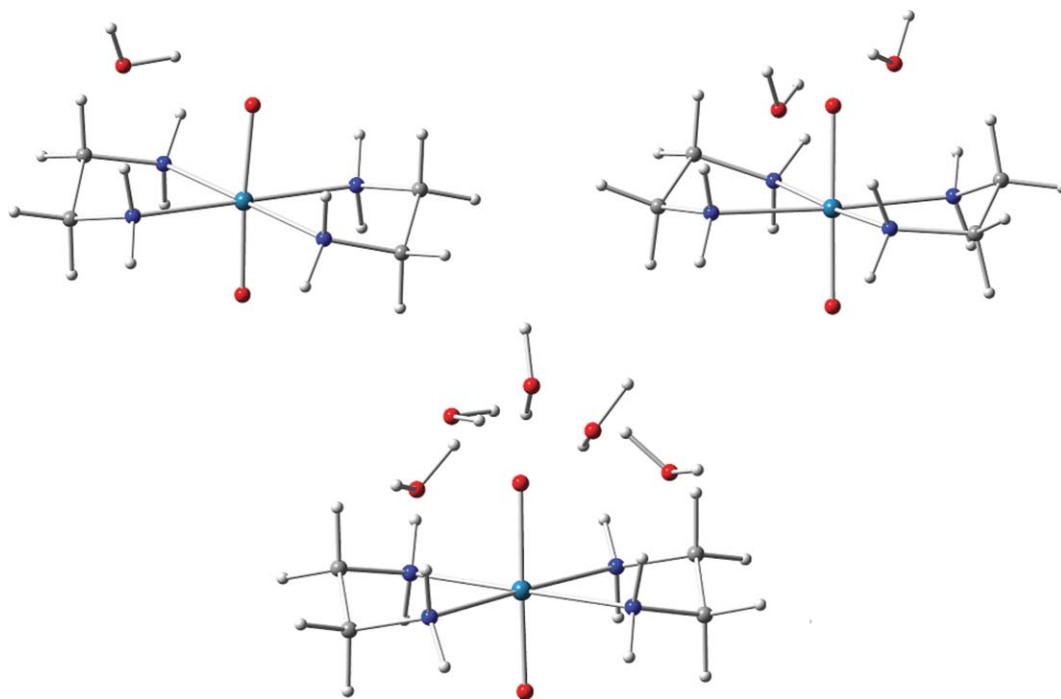
Fig. 3 Molecular assemblies considered in the discrete methodology for Re-en, representative model for a complex bearing protonation on the oxo ligand (atom assignment as in Fig. 2).

denoted as Re-dien_o, and the other with a "closed" ligand conformation, denoted as Re-dien_c, the latter including intramolecular H-bonds. The geometrical features of this isomer allow studying H-bond interactions of uncoordinated and coordinated amino groups with the oxo ligands above and below the complex equatorial plane. This property is important when the solvent molecules are treated explicitly.

Evaluation of solvent effects with the continuum model was performed by using the Polarizable Continuum Model (PCM) by Tomasi et al.[30] The systems were recalculated at the same gas phase geometry using a dielectric constant of 78.4 and the B3LYP/LD6311 methodology. This model, one of the most popular approaches, has been extensively applied to study the thermodynamics of acid/base equilibria in aqueous solution.[31-35]

In the case of systems in which solute–solvent interactions are of importance, it was proposed that the inclusion of the first hydration sphere should be taken into account.[36] Quantum mechanical calculations at different levels of calculation were performed on hexaaqua complexes of simple ions such as Sc^{3+},[37] Ti^{3+},[37] V^{3+},[37] Mn^{2+},[38,39] Mn^{3+},[37,38] Fe^{2+},[37,38,40-42] Fe^{3+},[37,38,40-42] Co^{2+},[43,44] Ni^{2+},[43-45] Cu^{2+},[43] and Zn^{2+}.[44-49] For some of them, even a second hydration shell with twelve water molecules[50] was considered. However, in cases of ions derived from coordination compounds, the inclusion of a complete first hydration shell by employing good quality theoretical HF or DFT methods would be computationally prohibited. In effect, Kovács et al.[25] employed up to five explicit water molecules to study mechanistic aspects of proton exchange in hydride rhodium(I) complexes. In this case B3LYP in combination with the so called SDDP basis set was used (for further details, see ref. 25).

In our case, the geometrical features of the representative complexes make the explicit treatment of a complete hydration environment an enormous computational task. Therefore, we decided to apply a discrete model to Re-en by including only one, two and five water molecules, as can be seen in Fig. 3. These solvent molecules are enough to build a reasonable solvation environment around the oxo ligand being protonated. For Re-dien, the explicit solvation model was applied to the "closed" ligand conformation. As aforementioned, it allows studying H-bonds involving the oxo groups, the coordinated/uncoordinated amino groups and solvent molecules. In this regard, taking the accuracy of the thermodynamic values obtained in the gas phase into account (see *"Calculated thermodynamic parameters"* for further details), only two water molecules were treated explicitly, for which a *cis* and *trans* disposition were considered (Fig. 4).

All geometry optimizations were performed without any symmetry constraints. The second derivatives were evaluated analytically in order to check the nature of the stationary point. The absence of negative values ensures that the stationary point corresponds to a minimum in energy. All calculations were carried out by using the Gaussian 03, Rev. B4 program package.[51]

Results and discussion

The complexes studied can be classified into three different groups, depending on the characteristics of the amine ligands, namely,

Group 1: Re-en, Re-pn, and Re-tn. Complexes of diamine ligands with primary nitrogen atom. They form 5-membered (Re-en and Re-pn), or 6-membered (Re-tn) chelate rings. These complexes can only undergo protonation on the oxo group.

Group 2: Re-tmen, Re-deten, and Re-dieten. Complexes of diamine ligands with at least one secondary or tertiary nitrogen atoms. The ligands bear different N-substituents: one ethyl group on each N atom of dieten, two methyl groups on each N atom
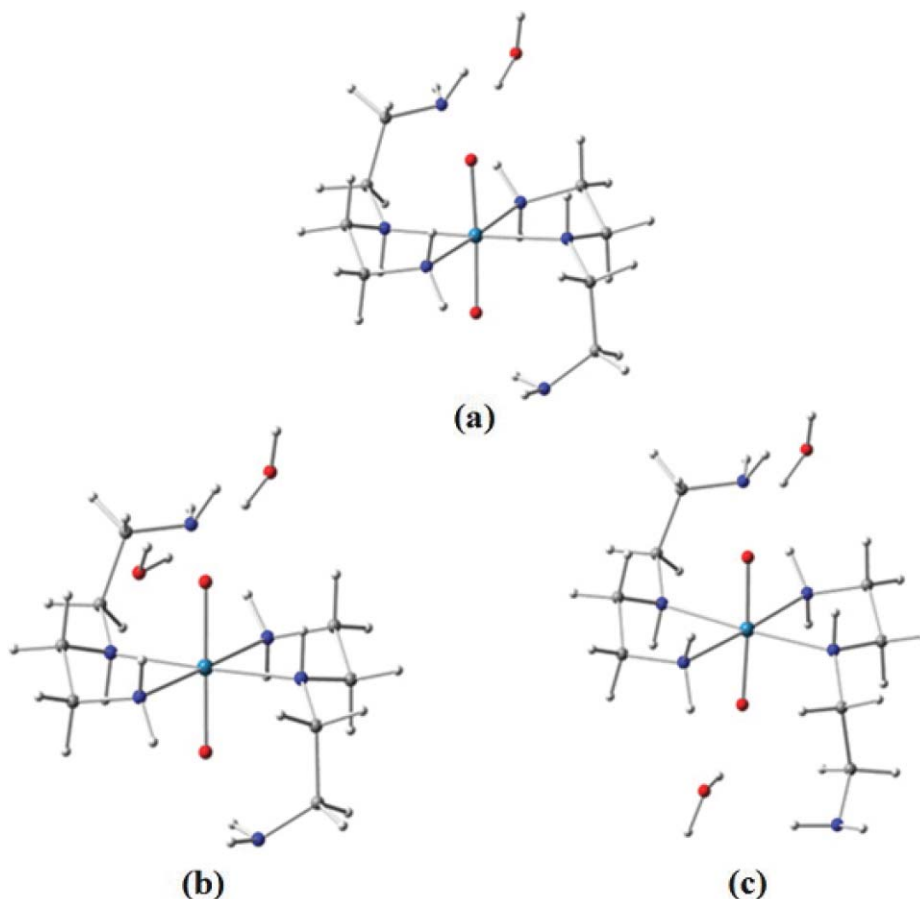
Fig. 4 Molecular assemblies included in the discrete methodology for Re-dien, representative model for complex bearing protonation on uncoordinated amino groups. (a) [Re-dien_c ⋯ (H$_2$O)]$^+$; (b) [Re-dien_c ⋯ cis-(H$_2$O)$_2$]$^+$; (c) [Re-dien_c ⋯ $trans$-(H$_2$O)$_2$]$^+$ (atom assignment as in Fig. 2).

of tmen, and two ethyl groups on the same N atom of deten. They form 5-membered chelate rings. These complexes can only undergo protonation on the oxo group.

Group 3: Re-dien, Re-trien, and Re-tren. Complexes with tri- or tetra-amine (linear and branched) ligands. They form 5-membered chelate rings. These complexes undergo protonation on the free amino groups, as these are the most basic functions of the molecule.

In the nine complexes the polyamine molecules behave as bidentate ligands.[4d] Hence, dien, trien, and tren form Re(V) dioxocomplexes in which one or two nitrogen donor atoms are not involved in the coordination to the metal centre.

Microcalorimetric results

The enthalpy changes for the proton transfer reactions, determined in aqueous solution by means of direct microcalorimetric measurements, are reported in Table 1 along with the relevant log K ($\Delta G°$) values, previously reported,[4a,b,g] and the calculated entropic contributions. All protonation reactions are exothermic, the enthalpic contribution being largely more favourable for group 3 complexes than for the other ones. The enthalpy changes for Re-en and Re-pn are in line with previously reported values, the only values available for comparison.[52]

As far as the entropic contribution is considered, different behaviors are observed for group 1 and group 2 complexes with

respect to group 3 complexes. In fact, while for complexes of the first two groups protonation takes place with favorable entropic contributions ($T\Delta S° > 0$) except for Re-tmen, unfavorable entropy changes ($T\Delta S° < 0$) were found for group 3.

The [Re^{V}O$_2$]$^+$ core is formally constituted by Re(V) and two dinegative oxo ligands. Protonation of the oxo ligands provokes local charge neutralization, while the overall positive charge of the complex increases. The two phenomena have opposite effects on complex hydration. Charge neutralization is accompanied by desolvation while the increase of charge favours solvation.

Table 1 Thermodynamic parameters (kJ mol^{-1}) for the protonation of Re(V) dioxocomplexes ($I = 0.1$ mol dm^{-3} Me$_4$NCl, $T = 298.1$ K)

Complex	log $K_1{}^a$	$-\Delta H^{°b,c}$	$T\Delta S^{°b}$	$-\Delta G^{°a}$
Re-tn	3.38 ± 0.02	7.1 ± 0.4	12.2 ± 0.4	19.3 ± 0.1
Re-en	3.41 ± 0.01	12.7 ± 1.2	6.7 ± 1.2	19.5 ± 0.1
Re-pn	3.59 ± 0.02	12.9 ± 0.6	7.6 ± 2.1	20.5 ± 0.1
Re-tmen	1.80 ± 0.08	20.1 ± 0.4	−9.6 ± 0.8	10.3 ± 0.5
Re-deten	2.42 ± 0.08	10.0 ± 0.4	3.8 ± 0.8	13.8 ± 0.5
Re-dieten	2.80 ± 0.01	7.1 ± 0.4	8.9 ± 0.3	16.0 ± 0.1
Re-dien	4.36 ± 0.12	34.8 ± 1.7	−10.0 ± 5.4	24.9 ± 0.7
Re-trien	6.04 ± 0.06	39.3 ± 1.2	−8.4 ± 1.2	34.5 ± 0.3
Re-tren	7.52 ± 0.03	49.5 ± 0.8	−6.6 ± 2.5	42.9 ± 0.2

^{a} Taken from references 4a,b,g. ^{b} This work. ^{c} Microcalorimetrically determined.

However, the increase of charge occurring upon protonation of the oxo ligand is mostly centred on the Re(V) metal center, which is buried into the complex and shielded by the external ligands. Accordingly, the global solvation is expected to be less important than the local desolvation occurring when the oxo ligand is converted into a hydroxo group, and then the overall effect is expected to be a desolvation. Such considerations justify the general behaviour observed for protonation of group 1 and group 2 complexes, showing less favourable enthalpic changes and favourable entropic contributions (Table 1), since desolvation phenomena are endothermic and are accompanied by an increase of translational entropy.

Protonation of group 3 complexes, taking place on free amino groups, gives rise to a net local charge increase which leads to greater complex solvation. Accordingly, protonation of group 3 is accompanied by a largely more favourable enthalpic contribution with respect to the previous complexes, while the entropic one is unfavourable (Table 1).

Re-tmen represents an exception within groups 1 and 2 of complexes. Protonation of this complex shows a larger favourable enthalpic contribution and a negative (unfavourable) entropic one. Again, a justification of this behaviour can be found in solvation phenomena. The ligand tmen has two tertiary nitrogen atoms. Upon coordination to the $[Re^V O_2]^+$ *core*, the two tmen molecules form a hydrophobic cover external to the complex, which consequently has a poor ability to interact with water solvent molecules. Complex protonation is then accompanied by a poor desolvation effect which makes the protonation reaction more exothermic, but deprives it of the favourable entropic contribution. Furthermore, the steric hindrance introduced by the substituent of the ligands is to be taken into account as an additional property affecting the accessibility of the oxo group for the proton. It deserves to be noted that, at least in the case of Re-pn, the presence of methyl substituents on the aliphatic chain of the ligand has no evident effect on the thermodynamics of complex protonation.

Computational studies

The previous analysis of thermodynamic data clearly shows that solvent effects play a fundamental role in determining the features of proton transfer reactions involving the studied complexes. In particular, solvation/desolvation processes involving the protonation sites seems to be of utmost importance. Owing to the lack of antecedent experimental data for proton transfer reactions involving rhenium complexes, there are no benchmark tests of the assessment of theoretical models to deal with their thermodynamic aspects. In order to get further insight into this aspect, we performed a computational study on proton transfer processes, both in the gas phase and in the presence of solvent. In our case, the presence of the solvent in the form of a structureless continuum medium was considered to describe the overall complex solvation, while, for local solvation at the protonation sites, discrete water molecules were taken into account.

Optimized structures

Although the attention of this work is focused on thermodynamic properties, we report here some relevant features of the optimized complex geometries.

Table 2 Selected structural parameters calculated for unprotonated *trans* Re(V) dioxocomplexes with aliphatic amines at the B3LYP/LD6311 level of calculation (298 K). Crystallographic values are reported in parentheses

Complex	Re–O[a]	Re–N[a,b]	N–Re–N[c,d]	O–Re–O[c]
Re-en	1.773 (1.769)[27j]	2.206 (2.152; 2.171)[27j]	78.0 (79.3; 80.0)[27j]	180.0 (179.3)[27j]
Re-tn	1.774 (1.749; 1.786)[4g]	2.213 (2.156; 2.173)[4g]	85.9 (89.5; 92.1)[4g]	179.9 (177.0)[4g]
Re-pn	1.773	2.213	77.8	179.5
Re-tmen	1.771	2.302	79.6	179.9
Re-deten	1.772 (1.769)[14]	2.252 (2.172; 2.242)[14]	79.8 (80.2)[14]	177.4
Re-dieten	1.774 (1.766)[4a]	2.242 (2.187; 2.193)[4a]	78.9 (79.9)[4a]	179.5 (180.0)[4a]
Re-dien_o	1.772	2.222	79.0	179.1
Re-dien_c	1.771	2.198	79.1	174.4
Re-trien	1.770	2.217	78.6	175.6
Re-tren	1.772	2.250	79.8	178.7

[a] Bond distances (Å). [b] Average values. [c] Bond angles (°). [d] Angle involving N atoms of the same ligand

According to the experimental and theoretical information available,[4a,6e,15,23,53] all calculations were carried out assuming an octahedral geometry with two oxo ligands in the axial positions and the amine ligands in the equatorial positions, in a closed shell d^2 configuration (singlet).

The calculated geometries (unprotonated compounds) showed Re–O and Re–N bond distances which are in reasonable agreement with the experimental values reported (Table 2). The linearity of the $[ReO_2]^+$ core is maintained in all cases. In general, the results correspond to highly symmetric complexes, even if protonated and when highly flexible substituents are present. Only a slight deviation (6°) from linearity of the $[ReO]^+$ *core* was found in Re-dien_c. The optimized structure of Re-dien_c is the only one which presents intramolecular H-bonds (Fig. 2b), one of them between a free amino group and an oxo ligand (N–H··· O distance 2.023 Å) and the other one between free amino groups belonging to different dien molecules (N··· H–N distance 1.975 Å).

The explicit addition of water molecules in Re-en and Re-dien produces a supramolecular structure assembled by H-bonds, while the geometry of the core complexes remains almost unchanged (Fig. 3 and 4). In the case of Re-en interacting with five water molecules, several H bonds are detected. Three water molecules interact with the complex *via* the N–H··· $O(w_1)$, N–H··· $O(w_2)$ and (w_3)H··· O–Re bonds (distances of 1.777, 1.764 and 1.638 Å respectively). Three H-bonds are observed on the opposite side of the complex at 2.062 (N–H··· O), 1.928 (O··· H–O) and 1.906 (H··· O–Re) Å. Upon protonation the first group remains almost unchanged (H-bond distances are of 1.757, 1.770 and 1.649 Å, respectively). The other two water molecules migrate (Fig. 5c) giving stronger H-bonds between H_2O molecules. H-bond distances are 1.694 $[(w_3)H··· O–H]$, 1.811 $[(w_3)H··· O–H]$ and 1.654 Å (O–H··· O).

The assembly of Re-dien_c with two water molecules was studied with *cis* or *trans* disposition of solvent molecules (Fig. 2 and 6). Upon protonation no significant changes are observed in the solvation environment. In the case of the *cis* configuration (Fig. 6a), both molecules remain H-bonded to the complex with distances N–H··· $O(w_1)$, (w_1)H··· O–Re, Re–O··· $H(w_2)$,
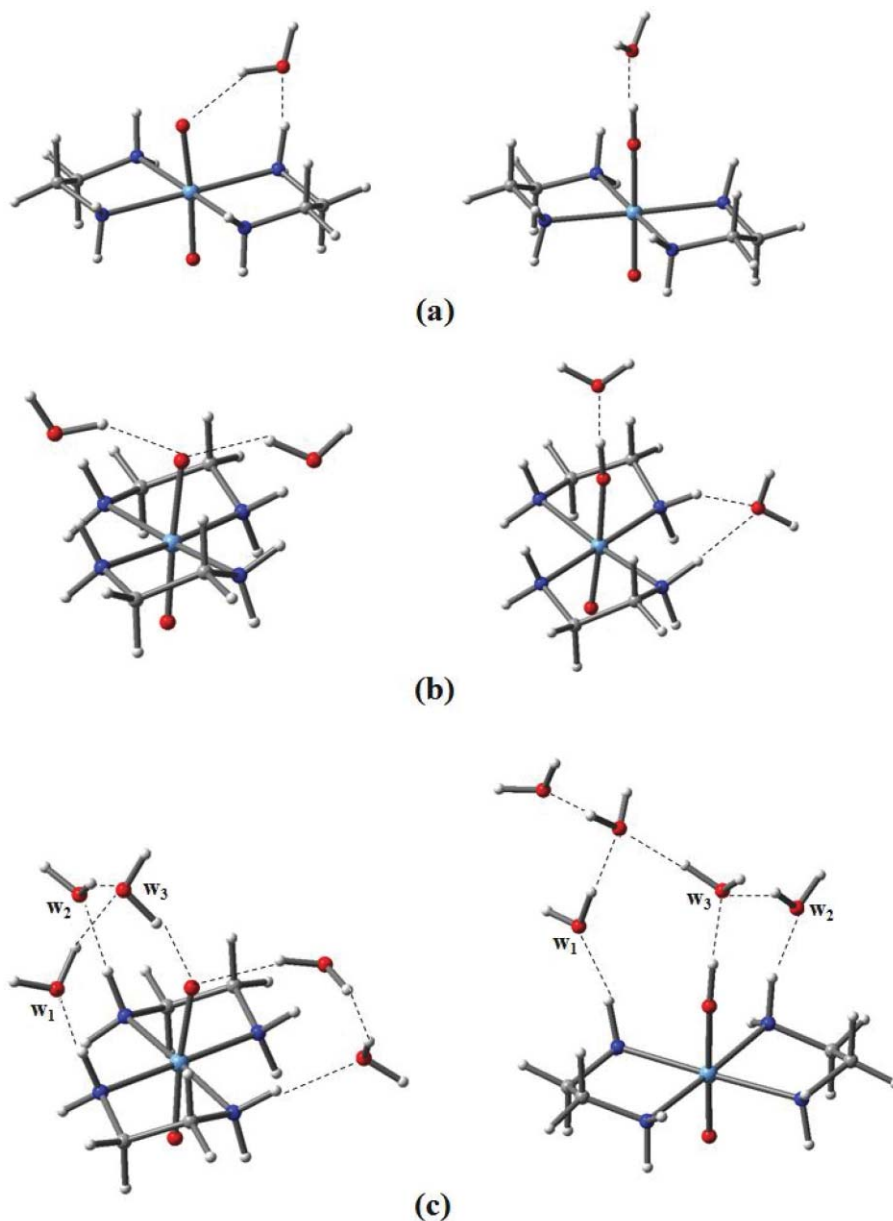
Fig. 5 Molecular assemblies for Re-en before and after protonation. Changes in the calculated H-bonds are shown. (a) $[\text{Re-en} \cdots (\text{H}_2\text{O})]^+$; (b) $[\text{Re-en} \cdots (\text{H}_2\text{O})_2]^+$; (c) $[\text{Re-en} \cdots (\text{H}_2\text{O})_5]^+$ (atom assignment as in Fig. 2).

$(\text{w}_2)\text{O} \cdots \text{H–N}$ of 1.826, 1.850, 1.794 and 2.010 Å, respectively. After protonation, one molecule (w_2) interacts with the protonated amino group forming stronger H-bonds $[\text{Re–O} \cdots \text{H}(\text{w}_2)$, 1.641 Å; $(\text{w}_1)\text{O} \cdots \text{H–N}$, 1.651 Å]. This process leads to the aforementioned slight deviation from linearity of the $[\text{ReO}_2]^+$ core.

For the *trans* configuration (Fig. 6b), complex protonation is accompanied by the formation of stronger H-bonds with one of the two water molecules. Indeed, the $(\text{w}_1)\text{H} \cdots \text{O–Re}$ distance of 1.887 Å in the unprotonated complex, becomes 1.645 Å upon protonation, while the interaction between this solvent molecule and the coordinated amino group is replaced by stronger H-bond with the uncoordinated amino group $(\text{w}_1)\text{O} \cdots \text{H–N}$, 1.645 Å. The other water molecule in the *trans* position does not show marked changes.

Calculated thermodynamic parameters

Calculations performed to determine the thermodynamic parameters for protonation of Re(V) dioxocomplexes with dien, trien, and tren were based on the non isodesmic reaction (2). To demonstrate that such a procedure does not introduce a significant error, we performed a comparative evaluation of enthalpy changes for complex protonation in the gas phase, using both H_3O^+ and NH_4^+ as the acidic source of protons (see eqn (4) and (5) in "*Experimental*"). We then used these $\Delta H°$ values to calculate the complex proton affinity (PA) for the two different reactions (Table 3). The calculated PA values should be coincident, since they are independent of the source of protons, unless a significant error has been introduced in the calculation of $\Delta H°$ values by
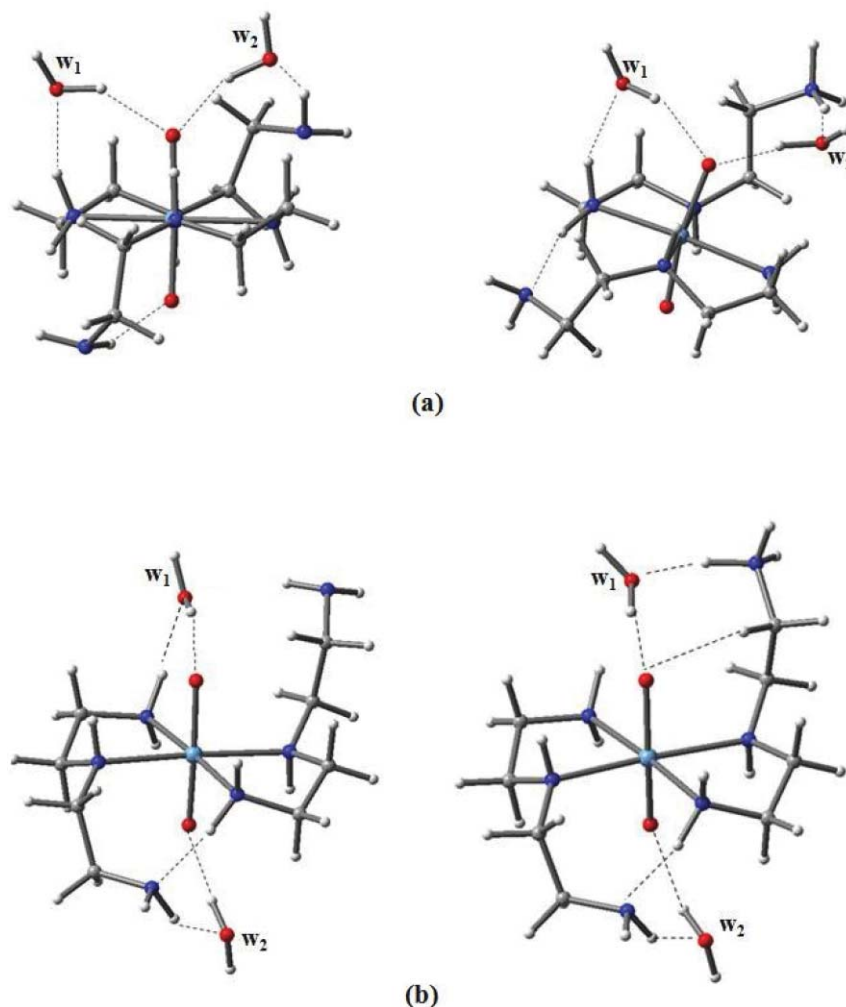
Fig. 6 Molecular assemblies with two water molecules for Re-dien before and after protonation, for which changes in calculated H-bonds are shown. (a) [Re-dien_c · · · cis-(H$_2$O)$_2$]$^+$; (b) [Re-dien_c · · · $trans$-(H$_2$O)$_2$]$^+$ (atom assignment as in Fig. 2).

Table 3 $-\Delta H^\circ_{calc.}$ and PA values (kJ mol^{-1}) in the gas phase (B3LYP/LD6311, $T = 298$ K) for the proton transfer reaction from H$_3$O$^+$ and NH$_4^+$ to dioxocomplexes of Re(V) able to be protonated on free amino groups

Complex	$-\Delta H^\circ_{calc.}$ (H$_2$O)	$-\Delta H^\circ_{calc.}$ (NH$_3$)	PA
Re-dien_o	−26.26		664.7
		−185.48	668.1
Re-dien_c	45.56		736.6
		−112.68	740.9
Re-trien	89.96		772.0
		−78.26	775.3
Re-tren	3.02		694.0
		156.20	697.4

using the non isodesmic reaction (4) with respect to the isodesmic reaction (5). Despite the large difference between the enthalpy changes obtained for complex protonation with H$_3$O$^+$ and NH$_4^+$, the discrepancy between the calculated PA values is less than 4 kJ mol^{-1} (Table 3), which represents a very small difference of *about* 0.6%. Accordingly, the non isodesmic reaction (4) can confidently be adopted in our calculations of thermodynamic parameters.

Table 4 collects the calculated thermodynamic parameters for proton transfer reactions. As far as the results obtained in the gas phase (absence of solvent) are considered, two different behaviours are observed. In the case of groups 1 and 2 complexes, bearing protonation on oxo groups, proton transfer from H$_3$O$^+$ is invariably an unfavourable process ($-\Delta G^\circ < 0$) due to a largely unfavourable enthalpy change ($-\Delta H^\circ < 0$) and a negligible entropic contribution. This means a higher basicity of water with respect to the oxo ligands in the complexes. It should be noted that a proton transfer between two such species in the absence of solvent is expected to have a small effect on the entropy change. Conversely, for group 3 complexes, bearing protonation on uncoordinated amine groups, which are more basic than water, the proton transfer reaction becomes favourable, in most cases, due to a dominant enthalpic contribution, the entropic one remaining almost negligible. The protonation processes of Re-dien in the "closed" ligand conformation, Re-trien and Re-tren (optimized structures depicted in Fig. 7) in the gas phase show different behaviours with favourable and variable enthalpic contributions and small entropic contributions.

By employing the continuum model, the free energy changes for proton transfer processes involving all complexes of groups 1–3

Table 4 Thermodynamic calculated parameters (kJ mol^{-1}) for protonation of dioxocomplexes of Re(V), in the gas phase and in the presence of solvent (B3LYP/LD6311, $T = 298$ K). All values have been calculated including ZPE corrections

Model	Complex	$-\Delta H^\circ_{calc.}$	$T\Delta S^\circ_{calc.}$	$-\Delta G^\circ_{calc.}$
gas phase	Re-en	−63.20	−3.35	−66.55
	Re-pn	−51.55	−1.91	−53.46
	Re-tn	−47.79	−3.17	−50.96
	Re-tmen	−27.92	0.81	−27.11
	Re-dieten	−23.84	−0.24	−24.08
	Re-deten	−23.80	3.24	−20.56
	Re-dien_o^a	−26.26	−1.48	−27.74
	Re-dien_c^a	45.56	−4.40	41.16
	Re-trien	89.96	−5.39	75.57
	Re-tren	3.02	−4.26	−1.24
continuum	Re-en			138.95
	Re-pn			136.14
	Re-tn			142.26
	Re-tmen			101.10
	Re-deten			128.04
	Re-dieten			132.90
	Re-dien_c^a			125.30
	Re-dien_o^a			168.25
	Re-trien			205.34
	Re-tren			178.63
discrete	$[Re\text{-}en\cdots H_2O]^+$	−32.90	4.39	−28.51
	$[Re\text{-}en\cdots(H_2O)_2]^+$	−24.86	13.32	−11.54
	$[Re\text{-}en\cdots(H_2O)_5]^+$	38.63	9.19	47.82
	$[Re\text{-}dien\_c\cdots(H_2O)]^{+b}$	53.93	−12.06	41.87
	$[Re\text{-}dien\_c\cdots trans\text{-}(H_2O)_2]^{+b}$	46.82	−7.46	39.33
	$[Re\text{-}dien\_c\cdots cis\text{-}(H_2O)_2]^{+b}$	67.84	0.86	68.70
discrete-continuum	$[Re\text{-}en\cdots(H_2O)]^+$			99.62
	$[Re\text{-}en\cdots(H_2O)_2]^+$			104.70
	$[Re\text{-}en\cdots(H_2O)_5]^+$			547.83
	$[Re\text{-}dien\_c\cdots(H_2O)]^{+b}$			175.00
	$[Re\text{-}dien\_c\cdots trans\text{-}(H_2O)_2]^{+b}$			197.37
	$[Re\text{-}dien\_c\cdots cis\text{-}(H_2O)_2]^{+b}$			212.31

^{a} See notation in Fig. 2. ^{b} See notation in Fig. 5.

become congruent with the solution data, although they show a large overestimation ($-\Delta G^\circ_{calc.}$ from 101 kJ mol^{-1} to 205 kJ mol^{-1}) of the process spontaneity (Table 4) with respect to the measured values (Table 1). In spite of this, the set of results is more consistent (compared to the results in the gas phase) with the experimental results. Protonation of group 1 complexes is quite similar and group 2 follows the same trend, the protonation being more favourable for Re-dieten. Direct comparison of parameters for group 3, with the experimental microcalorimetric results is not straightforward. More than one conformational species are expected to be present in solution and the experimental values for $-\Delta G^\circ$ should be an average.

For systems in which specific solute–solvent interactions in the first solvation sphere become important, the continuum model can be less accurate when a protic solvent such as water is used.[36,54,55] Deviation of thermodynamic parameters can be quite large when the short-range solvent effects are neglected.[56] Moreover, for ions with charge localized on oxygen and nitrogen atoms, the PCM model faired poorly when describing their

solvation, leading to obvious consequences on the thermodynamic results.[36]

In all our cases, the continuum model shows an improvement when compared to gas phase calculations, and succeeds in accounting for the overall solvation effects. However, this model is unable to describe the local effects of protonation. Therefore, we performed further calculations including discrete water molecules to describe the local solvation at the protonation sites. In this regard two representative cases were chosen: Re-en as a model for complexes bearing protonation on oxo ligands, and Re-dien as model for complexes bearing protonation on free amino groups. For Re-dien, the closed conformation (Re-dien_c) containing intramolecular H-bonds was considered.

A considerable improvement of the calculated value is obtained with the explicit inclusion of water molecules. For Re-en·5H$_2$O an exothermic reaction is obtained with $-\Delta H^\circ_{calc.}$ of 38.63 kJ mol^{-1}, and a favourable entropic parameter ($T\Delta S^\circ_{calc.} = 9.19$ kJ mol^{-1}), in reasonable agreement with the experimental values. The optimized structures of the solvated complexes afford a clear picture of the
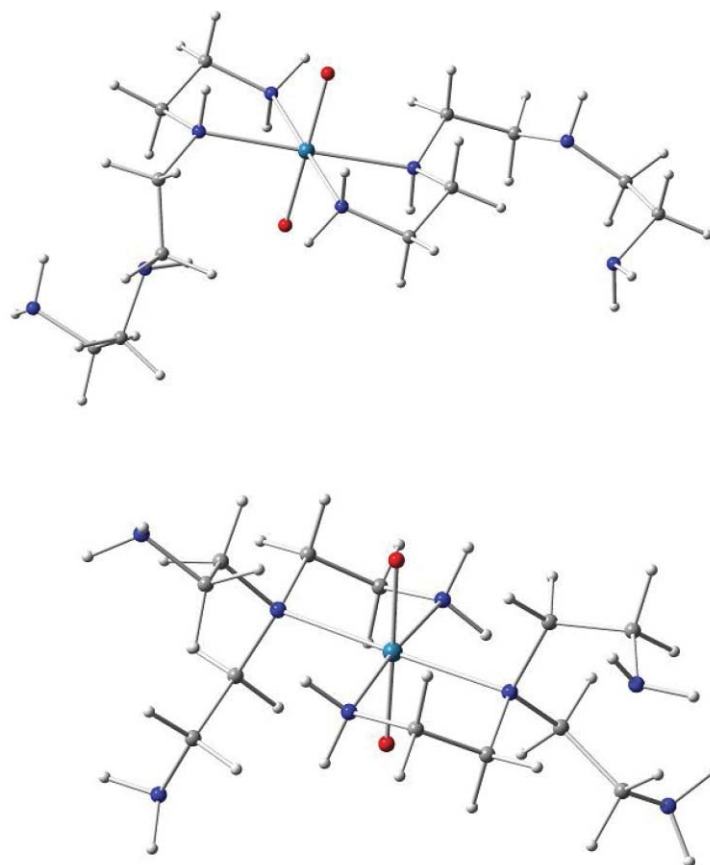
Fig. 7 Optimized geometries (B3LYP/LD6311) for Re-trien (top) and Re-tren (bottom) (for atom assignment see Fig. 2).

mobilization of solvent molecules (desolvation effect) brought about by protonation of Re-en, discussed before as the main contribution to the spontaneity of proton transfer processes involving complexes bearing protonation on oxo groups. Indeed, as shown in Fig. 5c, the five water molecules in the Re-en·5H$_2$O assembly interact with the complex, through the protonation site, in the first solvation sphere, two of which are involved in hydrogen bonds with an oxo group. On the other hand, only three of them belong to the first solvation sphere of the protonated complex, one interacting with the oxo group, while the remaining two water molecules are located in the second and in the third solvation spheres, respectively.

In the case of Re-dien_c, bearing protonation on a free amine group, the introduction of water molecules in calculations is even more effective. The presence of a single discrete water molecule in the protonation site affords a largely better estimation of free energy change (Table 4) than the continuum model, the calculated enthalpic and entropic contributions (Table 4) being congruent with the measured values (Table 1). When two water molecules are interacting with the complex, two principal conformations are possible, one containing the two molecules on the same side of the equatorial plane of the complex (Re-dien_c $\cdots$ cis-(H$_2$O)$_2$) and the other having the two molecules on opposite sides (Re-dien_c $\cdots$ trans-(H$_2$O)$_2$). A further improvement of *all* calculated thermodynamic parameters is obtained for Re-dien_c $\cdots$ trans-(H$_2$O)$_2$ while the opposite results were obtained for the *cis* analogue, which appears to be a worse model

for this complex. As discussed before, protonation of a free amino group in the dien complex is expected to favour solvation by the protonation site. As a matter of fact, a comparison of calculated structures for Re-dien_c-trans-(H$_2$O)$_2$ before and after protonation (Fig. 6) evidences the involvement of the protonated amine group in strengthening the hydrogen bond network, as discussed previously in *Optimized Structures*.

The fact that the discrete models outperform the pure continuum model can also be attributed to the introduction of strong and specific solute–solvent interaction on the solvation sites.

When the assemblies are placed into the continuum medium, favourable protonation reactions are obtained in all cases with values that overestimate the experimental ones. The assembly with five water molecules is the extreme case for which the free energy change is tremendously overestimated. It is clear that the failure of the discrete-continuum model in all cases can be traced to the continuum part of the calculation.

Concluding remarks

A thermodynamic study of proton transfer reactions of dioxo-complexes of Re(V) with polyamines in aqueous solution was performed experimentally by means of microcalorimetric techniques. All protonation reactions are exothermic with $|\Delta H°|$ values ranging from 7 and 50 kJ mol^{-1}, the enthalpic contribution being larger for complexes of group 3 than for the others. Results obtained for Re-en and Re-pn are in concordance with previously reported values. The justification of the general behaviour

observed for protonation of almost all complexes of groups 1 and 2 was founded on a balance of two phenomena with opposite effects on complex hydration: local charge neutralization *vs.* increase of positive overall charge. In all cases favourable enthalpic and entropic contributions were observed, Re-tmen being an exception with favourable enthalpic and unfavourable entropic parameters. The last ligand bears two methyl substituents which form a hydrophobic cover around the protonation site of the complex, diminishing its ability to interact with solvent. Protonation in this case takes place with a poor desolvation, the effect making the reaction more exothermic and preventing the favourable entropic contribution. In the case of group 3 complexes, protonation on free amino groups leads to a local charge increase and, concomitantly, to a greater complex solvation. This fact determines a more favourable enthalpic contribution compared to the other complexes, the entropic contribution being unfavourable in all cases.

Thermodynamic studies using density functional calculations were performed in the gas phase and in the presence of the solvent by applying continuum, discrete and discrete-continuum methods.

The results obtained in the gas phase were not able to correctly reproduce the exothermicity experimentally observed for protonation of groups 1 and 2 complexes, while for almost all group 3 complexes the opposite is true. In effect, for Re-dien in the "closed" ligand conformation the best agreement between calculated ($-\Delta H^\circ_{calc.} = 45.56$ kJ mol^{-1}) and experimental ($-\Delta H^\circ = 34.8$ kJ mol^{-1}) enthalpy changes was observed. It is worth noting that ligand conformation is an important variable sharply affecting the accuracy of calculations. Treatment of solvent effects through the PCM method led to favourable protonation reactions in all cases, regardless of the protonation sites, although we observed a significant overestimation of ΔG° values.

When the solvent was treated explicitly, a good improvement of $-\Delta H^\circ_{calc.}$ with respect to the gas phase value was obtained for Re-en, leading to an adequate description of the exothermic behaviour of the complex protonation with only five water molecules. The calculated enthalpic parameter ($-\Delta H^\circ_{calc.} = 38.63$ kJ mol^{-1}) was in reasonable concordance with the experimental one ($-\Delta H^\circ = 12.7$ kJ mol^{-1}). Contrary to Re-en, the explicit inclusion of water molecules for Re-dien did not lead to an improvement of the calculated enthalpic value with respect to the gas phase one. While the best $-\Delta H^\circ_{calc.}$ value obtained with the former methods was 46.82 kJ mol^{-1}, the value in the gas phase was 45.56 kJ mol^{-1} (experimental $-\Delta H^\circ = 34.8$ kJ mol^{-1}).

In general the explicit inclusion of only a few water molecules seems to be very important to obtain a reasonable agreement between thermodynamic parameters, while the placement of assemblies into a continuum structureless medium leads to a sensible overestimation of ΔG°. The experimental values herein determined constitute the first step to construct a set of data for which it is possible to benchmark the theoretical approaches proposed to compute the thermodynamics of proton transfer reactions of these metal complexes in aqueous solution. Further investigations, both experimental and theoretical, will be necessary, however, to get a more complete picture of such proton transfer reactions. In particular, a study of the mechanistic aspects of proton transfer would give additional important information about the influence of the solvation/desolvation processes.

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