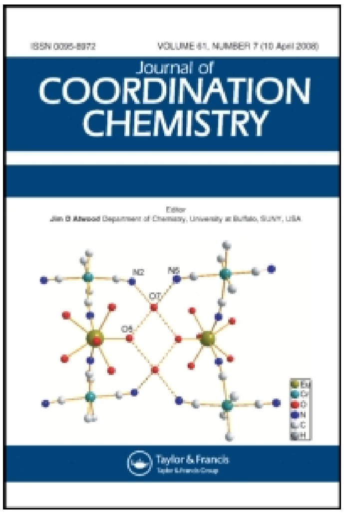

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SYNTHESIS, CHARACTERIZATION AND SOLUTION CHEMISTRY OF NEW Re(V) DIOXO COMPLEXES

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In this work, we report the synthesis, characterization and potentiometric studies of new Re(V) complexes of general formula $[ReO_2(amine)_2]^+$ (amine = 1,2-diaminopropane, 1,4-diaminobutane, N,N'-diethylethylenediamine, diethylenetriamine, triethylenetetramine and N-tris(2-aminoethyl)amine). Compounds were prepared starting from $[ReO_2I(PPh_3)_2]$ and characterized by several techniques. The presence of different substituent groups in the diamines (including alkyl and amine groups) allows the presence of pendant arms. When these groups are free amino groups, they can react with acids such as H^+ and M^{2+} cations and studied by potentiometry. The formation of very stable binuclear species was demonstrated.

Keywords: Rhenium(V); Dioxo complexes; Amine complexes; Solution chemistry

INTRODUCTION

The synthesis and characterization of several rhenium (V) and technetium (V) dioxo complexes have been previously reported [1–6]. It is well known that a way to stabilize hard Tc(V) and Re(V) centers is by forming a *trans*-$[MO_2]^+$ (M = Tc, Re) core. The four equatorial positions are usually filled

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*Corresponding author. e-mail: ckremer@bilbo.edu.uy by polyamine or polyphosphine ligands (L), resulting in six-coordinate complexes with general formula $[MO_2L_n]^+$ (n = 1, 2, 4). The development of new Re(V) and Tc(V) compounds is a very important goal since most diagnostic and therapeutic radiopharmaceuticals based on these metals are complexes of this kind [7]. On the other hand, since *in vivo* behavior of the complexes is determined by both the structure and the reactivity in aqueous solution, it is very important to understand the chemical changes they can undergo in saline solutions.

With this in mind, the objective of this work was to prepare new Re(V) dioxo complexes with polyamines, especially those which can be used to study the influence of L on the structure and reactivity of the complexes. Hence, Re(V) complexes with diethylenetriamine (dien), triethylenetetramine (trien) and N-tris(2-aminoethyl)amine (tren), 1,2-diaminopropane (pn), 1,4-diaminobutane (bn) and N,N′-diethylethylenediamine (deen) were prepared and characterized by several techniques. The behavior of the complexes in solution was studied by potentiometry. In the case of dien, trien and tren, the formation of $[MO_2L_2]^+$ species provided a pendant arm with a free amino group, that would be able to interact with M^{2+} cations, forming interesting binuclear complexes. The other amines were selected to introduce alkyl groups in the complexes. The comparison with the simplest complexes of this series, $[ReO_2(en)_2]^+$ (en = ethylenediamine) and $[ReO_2(tn)_2]^+$ (tn = 1,3-diaminopropane) provided useful information about the influence of changing chelate rings and substituents on the ring on the physical and chemical properties of the complexes.

EXPERIMENTAL

Materials

All chemicals were of reagent grade and used as received. HPLC grade methanol and all other solvents (reagent grade) were used without further purification. Violet microcrystals of $[ReO_2I(PPh_3)_2]$ were obtained using the reported method [8] except for $NH_4[ReO_4]$, which was used in place of $H[ReO_4]$. $[ReOCl_3(PPh_3)_2]$ was prepared according to literature [9].

Apparatus

IR spectra were recorded as KBr pellets on a Bomen MB FT-IR spectrophotometer and UV-vis spectra on a Spectronic 3000 instrument. Solutions of I^- of the same concentration as those for the complexes were used as reference. Elemental analysis was accomplished on a Carlo Erba model 1108 elemental analyzer. Rhenium was determined spectrophotometrically by reaction with α-furildioxime [10]. Fast Atom Bombardment spectra were obtained from a 3-nitrobenzylalcohol 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 μm) cation exchange column (4 × 250 mm). A 0.2 M aqueous solution of Na_2SO_4 was used as mobile phase with 1.5 mL min^{-1} flow. Detection was accomplished at 255 nm.

Synthesis of the Complexes

[ReO$_2$(dien)$_2$]I (1)

[$ReO_2I(PPh_3)_2$] (1.20 g, 1.40 mmol) and dien (0.8 mL, 7.4 mmol) were stirred in acetone (16 mL) for 15 minutes at room temperature. A pale brown solid was obtained which was separated by centrifugation. The solid was washed with acetone (3 × 5 mL) and diethylether (2 × 5 mL). Yield 80–90%. The complex is hygroscopic and should be stored under P_2O_5. IR: 800 (ν_{as}(O=Re=O)) and 910 (ν_s(O=Re=O)) cm^{-1}. Electronic spectrum (water; λ, nm (ε, M^{-1}cm^{-1})): 244 (1748), 284 (sh), 343(484), 445(sh). HPLC retention time (nm): 3.0 (main peak) and 4.3. Anal. Calcd. for $C_8H_{26}IO_2N_6Re$ (%): C, 17.4; H, 4.8; N, 15.2; Re, 33.8. Found: C, 17.7; H, 4.6; N, 15.1; Re, 33.3.

[ReO$_2$(trien)$_2$]I (2)

This pale brown complex was obtained as (**1**), using 1.6 mL (10.5 mmol) of trien. Yield 70–80%. The complex is hygroscopic and should be stored under P_2O_5. IR: 799 (ν_{as}(O=Re=O)) and 910 (ν_s(O=Re=O)) cm^{-1}. Electronic spectrum (water; λ, nm (ε, M^{-1}cm^{-1})): 246 (2461), 286 (sh), 345(606), 445(sh). HPLC retention time (min): 4.6 (main peak) and 7.4. Anal. Calcd. for $C_{12}H_{36}IO_2N_8Re$ (%): C, 22.6; H, 5.7; N, 17.6; Re, 29.2. Found: C, 21.9; H, 5.9; N, 17.8; Re, 30.0.

[ReO$_2$(tren)$_2$]I (3)

[$ReO_2I(PPh_3)_2$] (300 mg, 0.35 mmol) and tren (105 μL, 0.70 mmol) were stirred in acetonitrile (10 mL) for 10 minutes at room temperature. A pale brown solid was obtained which was separated by centrifugation. The solid was washed with dichloromethane (4 x 5 mL), acetone (2 x 5 mL) and diethylether (2 x 5 mL). Yield 20–30%. The complex is hygroscopic and should be stored under P_2O_5. IR: 796 (ν_{as}(O=Re=O)) and 911 (ν_s(O=Re=O)) cm^{-1}. HPLC retention time (min): 4.8. Anal. Calcd. for $C_{12}H_{36}IO_2N_8Re$ (%): C, 22.6; H, 5.7; N, 17.6. Found: C, 22.8; H, 5.3; N, 14.2. Alternatively, [ReO_2(tren)$_2$]Cl could be prepared by stirring a mixture of [$ReOCl_3(PPh_3)_2$] (200 mg, 0.24 mmol), tren (72 μL, 0.48 mmol) and 10 mL of dichloromethane. The solid was treated as in the case of **(3)**. Yield: 30–40%.IR: 796 (ν_{as}(O=Re=O)) and 912 (ν_s(O=Re=O)) cm^{-1}. Electronic spectrum (water; λ, nm (ε, M^{-1}cm^{-1})): 267 (548), 276 (sh), 440 (21). Anal. Calcd. for $C_{12}H_{36}ClO_2N_8Re$ (%): C, 26.4; H, 6.6; N, 20.5. Found: C, 26.2; H, 7.1; N, 17.1.

[ReO$_2$(pn)$_2$]I (4)

[$ReO_2I(PPh_3)_2$] (1.20 g, 1.40 mmol) and pn (4 mL, 46.9 mmol) were stirred in methanol:diethylether (1:1, v:v) (120 mL) for 30 minutes at room temperature. A pale brown solid was obtained which was filtered off. The solid was washed with ethanol (3 x 3 mL) and diethylether (2 x 3 mL). Yield 40–50%. The complex could be recrystallized in a mixture of ethanol : water (2:1, v:v). IR: 815 (ν_{as}(O=Re=O)) and 912 (ν_s(O=Re=O)) cm^{-1}. Electronic spectrum (water; λ, nm (ε, M^{-1}cm^{-1})): 257 (999), 282 (sh), 443(21). HPLC retention time (min): 3.5. Anal. Calcd. for $C_6H_{20}IO_2N_4Re$ (%): C, 14.6; H, 4.1; N, 11.4. Found: C, 14.2; H, 4.4; N, 11.9.

[ReO$_2$(deen)$_2$]I (5)

500 mg (0.57 mmol) of [$ReO_2I(PPh_3)_2$] were suspended in 10 mL of a mixture of methanol : diethylether (1 : 1, v : v). Then, 1 mL of deen (7.0 mmol) was added under vigorous stirring. The mixture was allowed to react for 30 minutes at room temperature. A clear brown solution was obtained. This solution was added over 100 mL of diethylether. A pale brown solid was obtained and centrifuged. The solid was dissolved in 5 mL of dichloromethane and precipitated by adding 50 mL of diethylether. The mixture was centrifuged and the solid washed with ether (2 x 5 mL). Yield: 60–70%. The complex was recrystallized in 2-propanol. IR: 784 (ν_{as}(O=Re=O)) and 912 (ν_{as}(O=Re=O)) cm^{-1}. Electronic spectrum (water; λ, nm (ε, M^{-1}cm^{-1})): 254 (856), 280 (sh), 429(21). HPLC retention time (min): 2.8, 3.5 (main peak) and 12.5. Anal. Calcd. for $C_{12}H_{32}IO_2N_4Re$ (%): C, 25.0; H, 3.4; N, 5.5. Found: C, 24.6; H, 3.4; N, 5.3.

$[ReO_2(bn)_2]I$ (6)

300 mg (0.35 mmol) of $[ReO_2I(PPh_3)_2]$ was suspended in 23 mL of a mixture of methanol : diethylether (1 : 2, v : v). Then, 1 mL of bn (11.2 mmol) was added under vigorous stirring. The mixture was allowed to react for 30 minutes at room temperature. A brown solid was separated and washed by decantation with ethanol (5 x 3 mL) and ether (3 x 3 mL). Yield: 50–60%. The complex is extremely hygroscopic and should be stored under P_2O_5. IR: 789 (ν_{as}(O=Re=O)) and 908 (ν_s(O=Re=O)) cm^{-1}. Due to decomposition of **(6)** in the usual solvents, the electronic spectra were performed by measurements through a filter paper impregnated with a Nujol suspension of the material: 450 nm. Anal. Calcd. for $C_8H_{24}IO_2N_4Re$ (%): C, 18.4; H, 4.6; N, 10.7. Found: C, 18.0; H, 4.3; N, 9.7.

Potentiometry Measurements

The potentiometric titrations were carried out in aqueous solution at 25°C and ionic strength I = 0.5 M in KCl. The experimental procedure can be found elsewhere [6]. Further details can be seen in Table I. For the systems Re-tren/Ni(II) and Re-tren/Cu(II), solutions of $CuCl_2 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$ were prepared by dissolving the respective salts in aqueous HCl (4.8 mM for Cu(II) and 3.3 mM for Ni(II)) and standarized against Na_2H_2EDTA (murexide as indicator). In the reaction vessel, a mixture of complex **(3)** and Cu(II) or Ni(II) solutions was titrated with 0.1 M HCl. Measurements were taken in 2 and 4 mM solutions of $[ReO_2(tren)_2]Cl$ and molar ratios (Re-tren/M(II)) 1 : 1 and 2 : 1 were used. The experimental potentiometric data were analyzed by means of the SUPERQUAD program [11].

TABLE I Protonation constants of $[ReO_2(amine)_2]^+$ complexes (25°C, I = 0.5 M in KCl). Data for $[ReO_2(en)_2]^+$ and $[ReO_2(tn)_2]^+$ are presented for comparison and were taken from Ref. [4]

Complex	*Complex concentration (mM)*	*Titrations*	*pH range*	*Exp. points*	σ	*Log K_1*	*Log K_2*
(1)	0.8–1.7	3	1.5–6.0	116	1.9	4.36 ± 0.12	1.13 ± 0.14
(2)	0.8–1.7	3	1.7–8.1	126	0.6	6.04 ± 0.06	2.75 ± 0.06
(3)	1.8–3.2	2	1.6–8.4	127	1.2	7.52 ± 0.03	1.72 ± 0.04
(4)	1.0–2.5	3	1.9–6.7	96	0.6	3.59 ± 0.02	1.65 ± 0.04
(5)	1.3–4.3	3	1.4–3.3	225	1.1	2.80 ± 0.01	–
Re-en	0.8–1.3	2	1.8–5.0	57	1.2	3.41 ± 0.01	1.72 ± 0.02
Re-tn	0.8–1.3	2	1.9–4.4	69	1.8	3.38 ± 0.02	1.79 ± 0.03

RESULTS

Based on the synthetic route previously reported [3], the complexes with general formula $[ReO_2(amine)_2]I$ could be easily prepared from the neutral precursor $[ReO_2I(PPh_3)_2]$. Elemental analysis agreed with the proposed formula. In addition, the FAB mass spectra confirmed this composition for compounds **(4)** and **(5)**, showing evidence for the molecular ion peaks (m/z = 367/365 for **(4)** and 451/449 for **(5)**) and a prominent daughter ion (m/z = 349/347 for **(4)** and 433/431 for **(5)**) from loss of water ($M^+ - 18$). This is in line with the spectra of other Re(V) dioxo complexes [4]. For the other compounds, the spectra show a complicated pattern that only includes small fragments due to much decomposition.

Complexes are soluble in water, only slightly soluble in methanol and insoluble in other organic solvents. Moreover, compounds **(1)**, **(2)**, **(3)** and **(6)** are very hygroscopic. Compound **(6)** is only soluble in water, but decomposes very quickly to a black powder. For this reason it could not be purified. The IR spectrum of the black solid shows a strong absorption at 913 cm^{-1}, as expected for the very stable ReO_2.

The IR spectra of complexes **(1)**–**(6)** show a characteristic very strong doublet absorption, one around 800 cm^{-1} and the other around 910 cm^{-1}. The first is the typical asymmetric stretching vibration of the $[ReO_2]^+$ core. The second absorption can be assigned to the symmetric stretching vibration of the core. It seems to be the result of the low symmetry of the complexes.

Electronic spectra have a general pattern. Two main absorptions were present, one in the UV region (around 250 nm) and the other (around 440 nm) in the visible range. It has been suggested that these peaks are characteristic of a *trans* dioxo arrangement around the Re(V) center [12]. The peaks at higher energies correspond to a ligand to metal charge transfer and the other to a *d*–*d* transition [13, 14].

HPLC retention times (see Experimental) confirmed the positive charge of the complexes in solution. Compounds **(3)** and **(4)** showed a single peak in the chromatograms. On the other hand, complexes **(1)**, **(2)** and **(5)** showed the presence of at least two components. This suggests a mixture of isomers or conformers is present in solution. Moreover, when a suspension of complex **(1)** or **(2)** in methanol was stirred for 10 hours, the remaining solid had the same composition (identical found percentage of C, H and N compared to the original solid) but in the chromatogram only one peak was observed (around 4.5 min). This fact can be explained based on the conversion of one isomer to the other during the treatment in methanol.

TABLE II Formation constants of the species $[ReO_2(tren)_2]^+/M(II)$ (M=Ni, Cu) at 25°C and I = 0.5 M in KCl

System	*Titrations*	*pH range*	*Exp. points*	σ	*Log* K_{11}	*Log* K_{21}
Re-tren/Ni(II)	4	1.4–5.0	174	0.9	6.23 ± 0.02	4.04 ± 0.04
Re-tren/Cu(II)	4	1.4–4.0	232	3.3	7.45 ± 0.06	3.7 ± 0.1

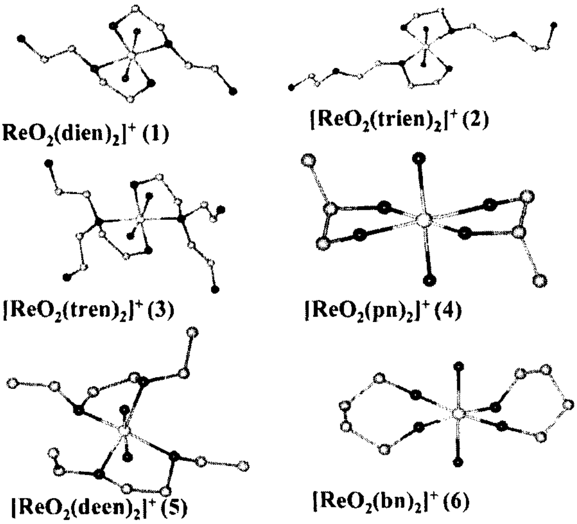
Results of the protonation studies performed on complexes **(1)**–**(5)** are depicted in Table I. The experimental potentiometric data of the complexes **(1)**–**(4)**, analyzed by means of the SUPERQUAD program showed a process of two successive protonations. However, basicity (represented by log K_1) of complexes with dien, trien and is clearly higher than that for the pn complex. On the other hand, **(5)** was the weaker base of this series and only shows one protonation in the pH range studied.

The results of the interaction of $[ReO_2(tren)_2]^+$ with Ni(II) and Cu(II) are shown in Table II. As in the case of protonation, divalent metals can associate with the Re complex in a two-step process. According to K_1 and K_2 values, this interaction is comparable with that for H^+, in spite of the double charge of the cations.

DISCUSSION

The formation of Re(V) dioxo complexes of general formula $[ReO_2(amine)_2]^+$ is supported by the results obtained in this work. Figure 1 shows the proposed spatial arrangement for these complexes.

Taking into account the existence of the $[ReO_2]^+$ core and the composition of the solids, it is clear that different isomers and conformers can be obtained for each complex. This situation arises from the presence of different substituents on the chelating ring. In compounds **(1)**, **(2)** and **(3)**, since there are two amine ligands per Re atom, they should be bidentate. Assuming that the ligand will be bonded by one primary amine (the most basic group) and the closest one (necessarily a secondary or tertiary amine) the complex will have at least two free amine groups per cation. These pendant arms can adopt different spatial arrangements (*cis* or *trans*, above or below the equatorial plane, *etc.*). Similarly, the methyl and ethyl groups in **(4)** and **(5)**, respectively, can be arranged in different ways. The presence of these groups lowers the symmetry in the complexes, activating the symmetric stretching vibration of the core. For compounds **(1)** and **(2)**, the charge transfer bands show a high value of ε. This also suggests a lower symmetry of these complexes in solution. Another consequence is the



$[ReO_2(dien)_2]^+$ (1)

$[ReO_2(trien)_2]^+$ (2)

$[ReO_2(tren)_2]^+$ (3)

$[ReO_2(pn)_2]^+$ (4)

$[ReO_2(deen)_2]^+$ (5)

$[ReO_2(bn)_2]^+$ (6)

FIGURE 1 Proposed stereochemical arrangements for complexes (1)–(6). Only one possibility is shown (see Discussion).

presence of more than one species in solution as found in the chromatograms. In complex (6), the formation of a less stable seven-membered ring seems to cause the low stability.

The IR spectra do not disclose significant structural differences among the complexes. However, the lower value of ν_{as} (784 cm^{-1}) in (5) suggests a weaker Re═O bond. This can be attributed to the steric hindrance of the deen ligand.

It has been previously reported that $[ReO_2(amine)_2]^+$ species in aqueous solution undergo successive protonations of the oxo groups [4]. Hence, $[ReO_2(amine)_2]^+$, $[ReO(OH)(amine)_2]^{2+}$ and $[Re(OH)_2(amine)_2]^{3+}$ species exist in solution. Theoretical calculations showed that the most basic point of the complex was the oxo group [5]. The complex with pn follows this behavior. K_1 and K_2 values are in line with those for en and tn complexes (see Tab. I). The successive protonations involved in the titrations are:

$$[ReO_2(pn)_2]^+ + H^+ \rightleftarrows [ReO(OH)(pn)_2]^{2+} \quad K_1$$

$$[ReO(OH)(pn)_2]^{2+} + H^+ \rightleftarrows [Re(OH)_2(pn)_2]^{3+} K_2$$

On the other hand, the complex with deen only shows one protonation. Moreover, the K_1 value indicates that protonation is more difficult in this cation. The presence of four ethyl groups seems to represent a severe steric hindrance for the protonation process. This is in line with the IR spectrum (see above).

For complexes with dien, trien and tren, the results are different. These are stronger bases towards the proton. As stated above, these complexes have free amino groups, *i.e.*, not coordinated to the rhenium atom. It is expected that these groups are the most basic points of the molecule ($\log K_1$ and $\log K_2$ values for free dien, trien and tren are higher than 9.0). Hence K_1 values are markedly higher. For example, in the case of **(3)** the protonations proposed are:

$$[ReO_2(tren)_2]^+ + H^+ \rightleftarrows [ReO_2(Htren)(tren)]^{2+} K_1$$

$$[ReO_2(Htren)(tren)]^{2+} + H^+ \rightleftarrows [ReO_2(Htren)_2]^{3+} K_2$$

Figure 2 shows the species distribution diagram for complexes **(3)** and **(4)**. As can be seen, at physiological pH **(3)** is a mixture of $[ReO_2(Htren)(tren)]^{2+}$ and $[ReO_2(tren)_2]^+$ while **(4)** behaves as a single cation ($[ReO_2(pn)_2]^+$).

Having in mind the spatial disposition of the ligand in **(3)**, we decided to study the interaction of this complex with Ni(II) and Cu(II). As can be seen in Figure 1, the Retren complex, acting as ligand, has a similar spatial arrangement to free dien. According to the potentiometric results, the association is as follows (L denotes complex **(3)**):

$$L^+ + M^{2+} \rightleftarrows ML^{3+} K_{11}$$

$$ML^{3+} + M^{2+} \rightleftarrows M_2L^{5+} K_{21}$$

K_{11} values show the formation of stable binuclear species. The presence of pendant arms in **(3)** with free amino groups allows the interaction with Cu(II) and Ni(II). K_{11} values can be compared with those for Cu-dien and Ni-dien complexes in similar experimental conditions ($\log K_{11} = 16.0$, $\log K_{21} = 5.3$ for Cu(II) and $\log K_{11} = 10.7$, $\log K_{21} = 8.2$ for Ni(II)) [14]. Values for Re-tren are lower, as can be expected for a charged ligand. A comparison of $\log K_{11}$ between Cu and Ni complexes follows a similar trend. This is a consequence of the well-known affinity of Cu(II) with ligands having nitrogen donor atoms. The relative stability is inverted for the second association. This can be due to the fact that the Cu(II) ion is Jahn-Teller distorted [16].

Figure 3 shows the species distribution diagram for M = Cu. When the L/Cu molar ratio is 2/1, complex **(3)** is bonded to Cu^{2+}, forming

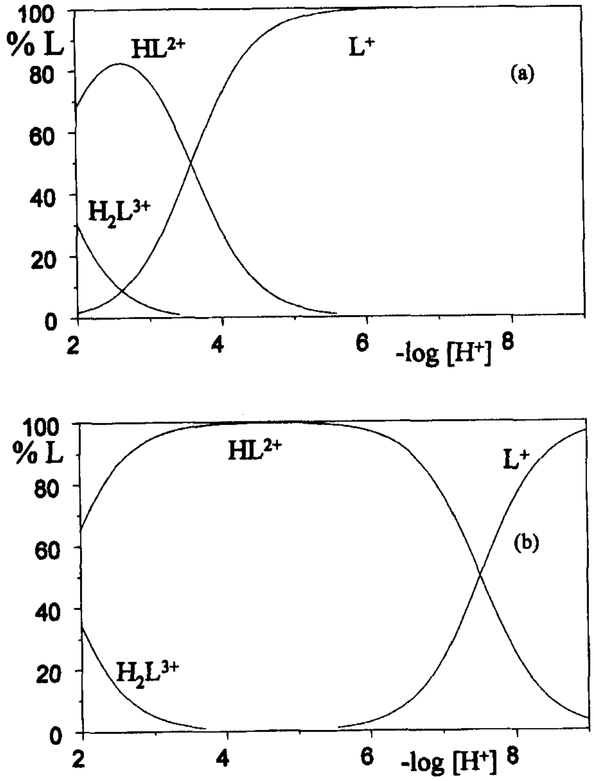


FIGURE 2 Species distribution diagrams for: (a) complex (4) and (b) complex (3) (25°C, $I=0.5\,M$ in KCl). In both cases, complex concentration is 2 mM. L^+ represents the species $[ReO_2(amine)_2]^+$.

predominantly a binuclear species. If the L/Cu molar ratio is 1/1, Cu_2L^{5+} and HL^{2+} species compete at low pH values. However, if the pH is raised CuL^{3+} is formed according to:

$$Cu_2L^{5+} + HL^{2+} \rightleftharpoons 2CuL^{3+} + H^+ \quad \log K = 3.68$$

Similar behavior is observed for Ni(II).

The new Re(V) complexes reported here, proved to be much more reactive in solution, compared with the well known $[ReO_2(en)_2]^+$ and $[ReO_2(tn)_2]^+$. The pendant arm provided by free amino groups can be protonated in saline solutions, changing the net charge of the species. In addition, it is possible to form stable dinuclear species with other transition metals. This result opens the study of these Re(V) complexes, with an enhanced reactivity, as potential therapeutic radiopharmaceuticals.

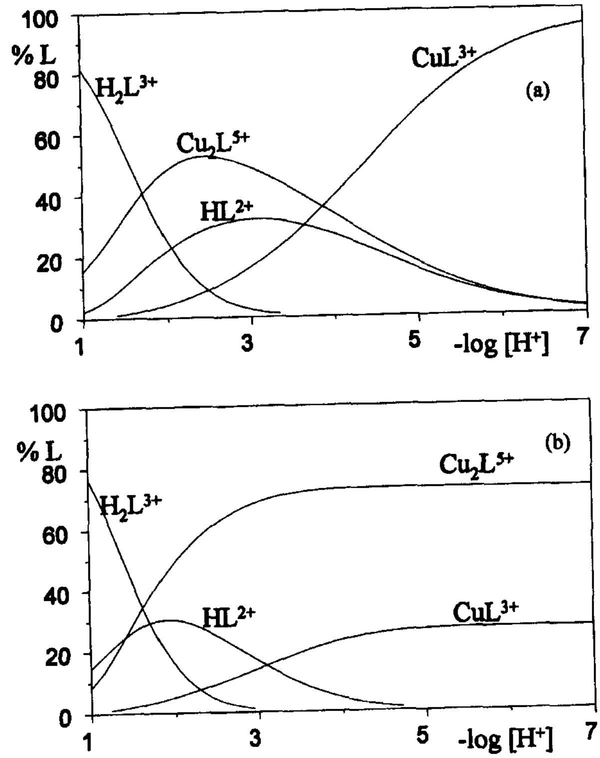


FIGURE 3 Species distribution diagram for the system Re-tren/Cu(II), 25°C, $I = 0.5\,M$ KCl. (a) $[ReO_2(tren)_2]^+$ and Cu(II) concentration 2 mM; (b) $[ReO_2(tren)_2]^+$ concentration is 2 mM and Cu(II) concentration 4 mM. L^+ denotes $[ReO_2(tren)_2]^+$ 4 mM.

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