

Novel Zwitterionic Oxorhenium(V) Complexes: Synthesis, Characterization and Crystal Structure of $[\text{ReOX}_2(\text{Hdhp})(\text{PPh}_3)]$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{H}_2\text{dhp} = 2,3\text{-Dihydroxypyridine}$)

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Dois novos complexos zwitteriônicos de oxorrênio(V), $[\text{ReOCl}_2(\text{Hdhp})(\text{PPh}_3)]$ (**1**) e $[\text{ReOBr}_2(\text{Hdhp})(\text{PPh}_3)]$ (**2**) ($\text{H}_2\text{dhp} = 2,3\text{-dihidroxipiridina}$), foram sintetizados e caracterizados por espectroscopia de absorção no infravermelho, ressonância magnética nuclear de ^1H e ^{31}P , análise elementar e determinação da estrutura cristalina e molecular por difração de raios X em monocristais. Os complexos apresentam geometria de coordenação octaédrica bastante distorcida, com os dois ligantes haletois arranjados em posições *cis* equatoriais, o ligante trifenilfosfina em posição *trans* a um dos haletois e o ligante Hdhp^- coordenado de forma bidentada através de seus átomos de oxigênio, sendo um em posição *trans* ao ligante oxo e o outro em posição *trans* com relação ao outro haleto. Este ligante tem seu átomo de nitrogênio protonado. Os compostos **1** e **2** apresentam empacotamento cristalino bastante diferente, influenciado em ambos os casos por ligações de hidrogênio intermoleculares dos tipos $\text{N-H}\cdots\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) e $\text{N-H}\cdots\text{O}$.

Two novel zwitterionic oxorhenium(V) complexes, $[\text{ReOCl}_2(\text{Hdhp})(\text{PPh}_3)]$ (**1**) and $[\text{ReOBr}_2(\text{Hdhp})(\text{PPh}_3)]$ (**2**) ($\text{H}_2\text{dhp} = 2,3\text{-dihydroxypyridine}$), were synthesized and characterized by infrared spectroscopy, ^1H and ^{31}P nuclear magnetic resonance, elemental analysis and crystal and molecular structure determination by X-ray diffraction on single crystals. Both complexes show distorted octahedral coordination geometry, with the halide ligands arranged in equatorial *cis* positions, the triphenylphosphine ligand in a *trans* position to one of the halides and the Hdhp^- ligand coordinated in a bidentate form through its oxygen atoms, one in *trans* position to the oxo-ligand and the other in *trans* position to the second halide. The nitrogen atom of this ligand is protonated. Compounds **1** and **2** show quite different crystal packing, both influenced by hydrogen bonds of the types $\text{N-H}\cdots\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{N-H}\cdots\text{O}$.

Keywords: oxorhenium(V), zwitterionic complexes, 2,3-dihydroxypyridine

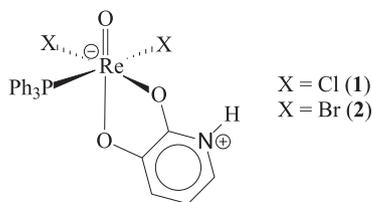
Introduction

The ability of 2,3-dihydroxypyridine (H_2dhp) to act as a chelating ligand is well known. Previous X-ray diffraction studies showed a bidentate coordination via the oxygen atoms, as Hdhp^- , in complexes with the trivalent ions Al^{3+} , Cr^{3+} and Fe^{3+} . The pyridine nitrogen atoms in these examples remain protonated, resulting in zwitterionic structures.^{1,2} To the best of our knowledge no rhenium complex was

reported so far involving the Hdhp^- anion as a ligand. In a recent work we described new zwitterionic rhenium complexes containing 2-hydroxypyridine as ligand.³

This work describes the synthesis, characterization and the X-ray crystal structure of novel rhenium complexes with Hdhp^- ligands. The zwitterionic $[\text{ReOX}_2(\text{Hdhp})(\text{PPh}_3)]$ ($\text{X} = \text{Cl}, \text{Br}$) complexes contain monoanionic, chelating Hdhp^- ligands, which are coordinated *via* their oxygen atoms. They formally possess a positive charge at the protonated nitrogen atom and a negative charge at the rhenium(V) center.

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Experimental

Reagents and apparatus

The rhenium starting complexes $[\text{ReOX}_3(\text{PPh}_3)_2]$ ($X = \text{Cl}, \text{Br}$) were prepared as previously described.⁴ 2,3-Dihydroxypyridine was used as purchased (Aldrich) without further purification. Solvents of analytical grade were degassed by purging with argon for about 15 minutes prior to use. Melting points were measured on a Melt-Temp II apparatus. Microanalytical data for C, H and N were obtained on a CHNS analyzer, FISON model EA 1108. IR spectra were recorded on a BOMEM MICHELSON FT BM 102 spectrophotometer, using CsI pellets, within the 4000–200 cm^{-1} range. NMR spectra were recorded at room temperature, in CD_2Cl_2 solutions, on a Varian Mercury Plus spectrometer, 7.05 T, operating at 300.07 MHz for ^1H and 121.47 MHz for ^{31}P . The ^1H spectra were internally referenced to TMS and $^{31}\text{P}\{^1\text{H}\}$ spectra were externally referenced to H_3PO_4 (85%, δ 0). The data collections for crystal structure determinations were performed on a NONIUS KAPPA CCD diffractometer, equipped with Mo- $\text{K}\alpha$ radiation (71.073 pm) and graphite monochromator, applying standard procedures.

Preparation of $[\text{ReOCl}_2(\text{Hdhp})(\text{PPh}_3)]$ (**1**)

H_2dhp (33.3 mg, 0.30 mmol) was added to a suspension of $[\text{ReOCl}_3(\text{PPh}_3)_2]$ (249.9 mg, 0.30 mmol) in degassed dichloromethane (25 mL). The mixture was stirred and heated to reflux for 3 h. After cooling, the green precipitate was filtered off and washed with dichloromethane followed by hexane. Yield: 92% (176 mg, 0.27 mmol). Melting point 178–181 °C (dec.). Anal. Calc. for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{Cl}_2\text{PRe}$ (645.50 g mol^{-1}): C, 42.80; H, 2.97; N, 2.17%. Found: C, 43.09; H, 3.16; N, 2.59%.

IR (CsI) $\nu_{\text{max}}/\text{cm}^{-1}$: 3266 $\nu(\text{N-H})$, 1627 $\nu(\text{C=O})$, 1599 and 1542 $\nu(\text{C=C} + \text{C=N})$, 1186 $\nu(\text{C-O})$, 1482 and 1435 $\nu(\text{C=C}, \text{PPh}_3)$, 1096 $\nu(\text{P-C})$, 692 $\gamma(\text{ring C}_6\text{H}_5, \text{PPh}_3)$, 978 $\nu(\text{Re=O})$, 335 $\nu(\text{Re-Cl})$. ^1H NMR: δ 6.166 (t, J 7.5 Hz, 1H, Hdhp⁻), 6.599 (d, J 7.5 Hz, 1H, Hdhp⁻), 6.765 (m, 1H, Hdhp⁻), 7.35 – 7.73 (m, 15H, PPh₃), and 10.7 (br, 1H, NH). $^{31}\text{P}\{^1\text{H}\}$ NMR (ppm, CD_2Cl_2): -21.06 (s, Re-PPh₃).

Preparation of $[\text{ReOBr}_2(\text{Hdhp})(\text{PPh}_3)]$ (**2**)

The reaction was conducted as described for **1**, but using $[\text{ReOBr}_3(\text{PPh}_3)_2]$ (298.8 mg, 0.30 mmol). After the reflux time, the partially precipitated product was separated by filtration and washed with dichloromethane and hexane. Addition of more hexane (10 mL) and storing overnight at -15 °C resulted in more product. Overall yield: 80% (176.6 mg, 0.24 mmol). Melting point 169–172 °C (dec.). Anal. Calc. for $\text{C}_{23}\text{H}_{19}\text{NO}_3\text{Br}_2\text{PRe}$ (734.40 g mol^{-1}): C, 37.62; H, 2.61; N, 1.91%. Found: C, 38.67; H, 2.74; N, 1.90%.

IR (CsI) $\nu_{\text{max}}/\text{cm}^{-1}$: 3224 $\nu(\text{N-H})$, 1627 $\nu(\text{C=O})$, 1605 and 1546 $\nu(\text{C=C} + \text{C=N})$, 1197 $\nu(\text{C-O})$, 1482 and 1435 $\nu(\text{C=C}, \text{PPh}_3)$, 1097 $\nu(\text{P-C})$, 693 $\gamma(\text{ring C}_6\text{H}_5, \text{PPh}_3)$, 978 $\nu(\text{Re=O})$, 273 $\nu(\text{Re-Br})$. ^1H NMR: δ , 6.219 (t, J 7.5 Hz, 1H, Hdhp⁻), 6.651 (d, J 7.5 Hz, 1H, Hdhp⁻), 6.900 (m, 1H, Hdhp⁻), 7.36 – 7.90 (m, 15H, PPh₃), and 11.1 (br, 1H, NH). $^{31}\text{P}\{^1\text{H}\}$ NMR: d -20.60 (s, Re-PPh₃).

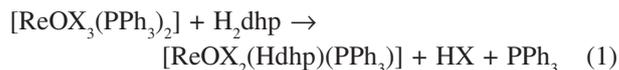
Crystal structure determinations

Suitable single crystals of **1** and **2** were obtained in the form of green needles by crystallization from dichloromethane. The cell constants were calculated from 33906 reflections for **1** and 77905 reflections for **2**. Direct methods⁵ were used for the solution of the structures. Except for the hydrogen atoms, which were calculated at idealized positions, all other atoms were refined with anisotropic displacement parameters.⁶ Complex **1** crystallizes in the trigonal crystal system, space group $\text{R}\bar{3}$, with one complex molecule in the asymmetric unit. Complex **2** crystallizes in the triclinic system, space group $\text{P}\bar{1}$, with two complexes in the asymmetric unit. This compound presented radiation damage which prevented the acquisition of an ideally complete data set. Additional information on the crystal structure analyses is given in Table 1.

Results and Discussion

Synthesis of the complexes

Complexes **1** and **2** are formed in good yields by reactions starting from $[\text{ReOX}_3(\text{PPh}_3)_2]$ ($X = \text{Cl}, \text{Br}$) and H_2dhp , with elimination of HX and PPh_3 , after 3 h of stirring under reflux.



The complexes were isolated as green precipitates of good purity and could be obtained also in the crystalline

Table 1. Crystal data and structure refinement for [ReOCl₂(Hdph)(PPh₃)] (**1**) and [ReOBr₂(Hdph)(PPh₃)] (**2**)

Complex	1	2
Empirical formula	C ₂₃ H ₁₉ Cl ₂ NO ₃ PRE	C ₂₃ H ₁₉ Br ₂ NO ₃ PRE
Formula weight / g mol ⁻¹	645.46	734.38
Temperature / °C	20(2)	20(2)
Crystal System	Trigonal	Triclinic
Space group	R3	P1
<i>a</i> / pm	3652.3(1)	993.90(9)
<i>b</i> / pm	3652.3(1)	1521.7(2)
<i>c</i> / pm	962.60(3)	1772.3(2)
α / °	90	110.714(4)
β / °	90	98.726(7)
γ / °	120	98.346(7)
Volume / nm ³	11.1201(7)	2.4202(4)
Chemical units per cell, Z	18	4
Absorption coefficient / mm ⁻¹	5.222	8.413
F(000)	5616	1392
Crystal size / mm ³	0.18 × 0.02 × 0.02	0.145 × 0.020 × 0.016
Crystal description	green needle	green needle
θ range for data collection / °	2.95 - 24.99	2.71 - 21.83
Index ranges (h, k, l)	-43→h→43, -42→k→43, -11→l→9	-10→h→10, -15→k→15, -18→l→18
Reflections collected	33123	9707
Independent reflections / <i>R</i> _{int}	4344 / 0.1003	5675 / 0.0515
Reflections observed [I>2 σ (I)]	3194	4296
Absorption correction	multi-scan ¹²	Gaussian ¹³
Max. and min. transmission	0.754 and 0.731	0.903 and 0.704
Refinement method	full-matrix least-squares on F ²	full-matrix least-squares on F ²
Hydrogen treatment	riding model	riding model
Final R-factors [I>2 σ (I)]	<i>R</i> ₁ = 0.0408; <i>wR</i> ₂ = 0.0871	<i>R</i> ₁ = 0.0382; <i>wR</i> ₂ = 0.0699
Final R-factors (all data)	<i>R</i> ₁ = 0.0685; <i>wR</i> ₂ = 0.0973	<i>R</i> ₁ = 0.0594; <i>wR</i> ₂ = 0.0763
“Goodness-of-fit, S, on F ² ”	1.051	1.022
Final peak and hole in the last difference map	1.725 and -0.793 e Å ⁻³	1.070 and -0.958 e Å ⁻³
Software used	SHELXS97 ⁵ and SHELXL ⁵	SHELXS97 ⁵ and SHELXL ⁶

form by crystallization from their dichloromethane solutions. The air stable compounds are moderately soluble in dichloromethane, but only slightly soluble in chloroform.

Spectroscopic characterization

The IR spectra of **1** and **2** are very similar in the range between 4000 and 400 cm⁻¹, which excludes the absorption bands related to $\nu(\text{Re-X})$ (X = Cl in **1** and Br in **2**), indicating that they have an analogous coordination sphere. The $\nu(\text{Re=O})$ bands appear at 978 cm⁻¹ for both complexes. The *O,O*-coordination mode of the Hdhp⁻ ligand is indicated by shifts of the $\nu(\text{C=O})$ (1627 cm⁻¹ for **1** and **2**) and $\nu(\text{C-O})$ bands (1186 cm⁻¹ for **1** and 1197 cm⁻¹ for **2**) with respect to the values found in uncoordinated H₂dhp (1663 cm⁻¹ and 1188 cm⁻¹). The $\nu(\text{C=C} + \text{C=N})$ bands are found at 1599 cm⁻¹ and 1542 cm⁻¹ in **1** and at 1605 and 1546 in **2**, respectively. The $\nu(\text{N-H})$ bands at 3266 cm⁻¹ for **1** and at 3224 cm⁻¹ for **2** are consistent with the zwitterionic structure of the complexes. The presence of the triphenylphosphine ligands in the complexes is evidenced by the presence of

characteristic bands at 1482 cm⁻¹ and 1435 cm⁻¹ ($\nu(\text{C=C})$), and 1096 cm⁻¹ and 1097 cm⁻¹ ($\nu(\text{P-C})$) for **1** and **2**, respectively. The $\nu(\text{Re-Cl})$ band appears at 335 cm⁻¹ for **1**, while a band at 273 cm⁻¹ was tentatively assigned for $\nu(\text{Re-Br})$ for **2**.

The ¹H-NMR spectra of **1** and **2** (for details see the Experimental Section) are consistent with the structures determined in the solid state. The ³¹P{¹H}-NMR spectra show predictable singlet peaks for the phosphorus donor atoms at -21.06 ppm and -20.60 ppm for **1** and **2**, respectively.

Crystal structures of **1** and **2**

Complexes **1** and **2** possess a similar arrangement of the ligands around the hexacoordinate rhenium(V) centers. The coordination spheres of the rhenium atoms are distorted octahedra, each one formed by one oxo ligand, two halides (Cl⁻ for **1** and Br⁻ for **2**), a triphenylphosphine and two oxygen atoms of the Hdhp⁻ ligand, which coordinates as a *O,O*-chelate. The pyridine nitrogen atom of the chelating ligands is protonated. The halides have a *cis* arrangement

to each other. The triphenylphosphine ligand is in *trans* position to one of the halides. One of the oxygen donor atoms from Hdhp⁻ is located *trans* to the oxo ligand, while the other is *trans* to the second halide. The molecular structure of **1** is shown in Figure 1. The molecular structures of the two independent molecules of **2** are virtually identical and essentially the same as **1**, and are therefore not shown here. Selected bond lengths and angles for both compounds are given in Table 2. The molecular labeling scheme of **1** has also been adopted for the bromo complex.

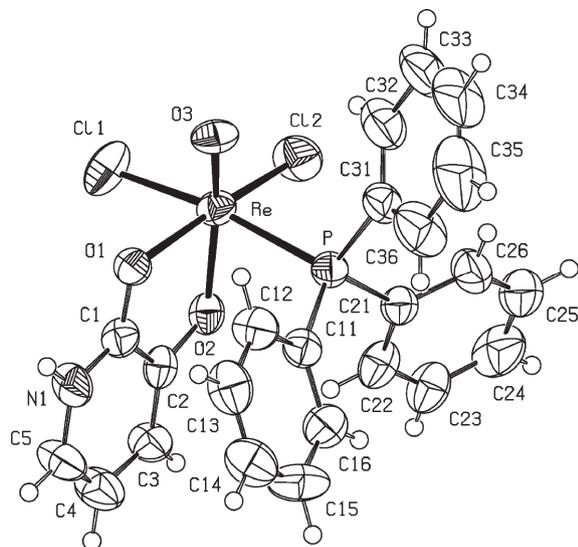


Figure 1. Ellipsoid representation¹⁴ of **1**, with the thermal ellipsoids representing 50% probability.

Table 2. Selected bonds (pm) and angles (°) for [ReOCl₂(Hdhp)(PPh₃)] (**1**) and [ReOBr₂(Hdhp)(PPh₃)] (**2**)

	1		2 *
Re–O(3)	167.0(5)	Re–O(3)	169.1(5)
Re–O(1)	213.5(5)	Re–O(1)	212.5(5)
Re–O(2)	200.5(5)	Re–O(2)	203.9(5)
Re–X(1)	241.7(2)	Re–X(1)	253.30(10)
Re–X(2)	232.0(2)	Re–X(2)	247.13(11)
Re–P	245.1(2)	Re–P	246.1(2)
O(1)–C(1)	128.4(8)	O(1)–C(1)	127.2(10)
O(2)–C(2)	133.9(9)	O(2)–C(2)	135.7(10)
N(1)–C(1)	132.8(9)	N(1)–C(1)	134.5(11)
N(1)–C(5)	135.5(10)	N(1)–C(5)	137.4(11)
C(2)–C(3)	135.3(10)	C(2)–C(3)	134.6(11)
C(3)–C(4)	140.5(11)	C(3)–C(4)	139.1(13)
C(4)–C(5)	132.9(11)	C(4)–C(5)	135.2(11)
O(1)–Re–X(1)	86.16(15)	O(1)–Re–X(1)	85.23(14)
O(1)–Re–X(2)	169.21(14)	O(1)–Re–X(2)	167.42(14)
O(2)–Re–X(1)	87.10(15)	O(2)–Re–X(1)	85.62(15)
O(2)–Re–X(2)	94.50(14)	O(2)–Re–X(2)	91.48(16)
O(3)–Re–X(1)	99.54(19)	O(3)–Re–X(1)	100.48(19)
O(3)–Re–X(2)	103.2(2)	O(3)–Re–X(2)	103.0(2)
O(1)–Re–P	94.64(15)	O(1)–Re–P	93.63(16)
O(2)–Re–P	82.07(14)	O(2)–Re–P	81.49(15)
O(3)–Re–P	91.85(19)	O(3)–Re–P	92.5(2)
Cl(1)–Re–P	168.61(7)	Cl(1)–Re–P	166.97(6)
Cl(2)–Re–P	89.57(8)	Cl(2)–Re–P	89.61(6)
Cl(2)–Re–X(1)	87.77(8)	Cl(2)–Re–X(1)	88.87(4)

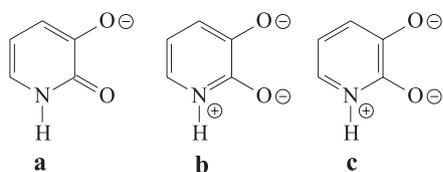
* The molecular labeling scheme was adopted from **1** given in Figure 1; values correspond to two complex molecules in the asymmetric unit of **2**.

Two crystal structures of complexes with ReO₃Cl₂P coordination spheres, in similar modes as observed in **1**, have been reported previously, namely [ReOCl₂(acac)(PPh₃)]⁷ (**3**) and [ReOCl₂(benzac)(PPh₃)]⁸ (**4**) (acac⁻ = acetylacetonate, benzac⁻ = benzoylacetonate).

As in **1**, in **4** the chlorine atoms are disposed in *cis* positions, while the structure of **3** presents these ligands in *trans* positions. No crystallographic data were found in the literature for a complex with a ReO₃Br₂P coordination sphere, as observed in **2**.

As observed in **4**, the Re–Cl bond in **2** is longer for the chloro ligand *trans* to PPh₃. This results from the *trans*-stabilizing effect of the phosphine ligand. The Re–O bonds *trans* to the oxo ligands are shorter than those *trans* to the chloro ligands in **1** and in **4**. This phenomenon is also observed in other rhenium complexes with similar coordination spheres and is assigned to delocalization of π -electron density from the oxo bonds to the *trans*-situated Re–O bonds.^{9–11} The Re–O and Re–P bond lengths in **2** are similar to the values observed in **1**. The distances between the rhenium atoms and the oxo ligands correspond to values normally found for Re=O double bonds in oxorhenium(V) complexes.⁹

The bond lengths in the Hdhp⁻ ligands in **1** and **2** do not differ significantly from the values found for the uncoordinated H₂dhp, which is also protonated at the nitrogen atom.¹ The following resonance structures (**a**, **b** and **c**) should best represent the structure of the Hdhp⁻ ligands in **1** and **2**.



The C(1)-O(1) bond is expectedly shorter than C(2)-O(2), showing a larger double bond character. This results from the contribution of the resonance structure **a**. The N-C(1) and N-C(5) distances, however, are similar and have considerable double bond character, showing that the zwitterionic resonance structures **b** and **c** also give significant contributions to the resonance hybrid.

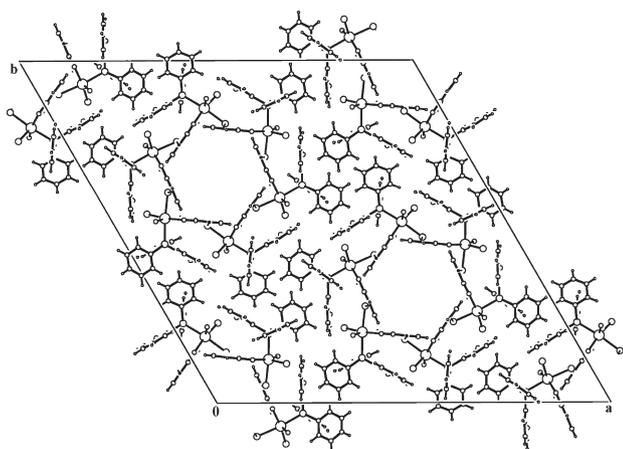


Figure 2. View of the unit cell of **1** in the direction $[001]$.¹⁴ The molecules are linked by H-bonds of the type N-H...Cl, forming channels in the crystal structure, which are parallel to the crystallographic c axis. N(1)-H(1) = 86.0 pm, H(1)...Cl(1)^(x-y, x-1, -z+1) = 232.6 pm, N(1)...Cl(1)^(x-y, x-1, -z+1) = 317.6 pm, N(1)-H(1)...Cl(1)^(x-y, x-1, -z+1) = 169.76°.

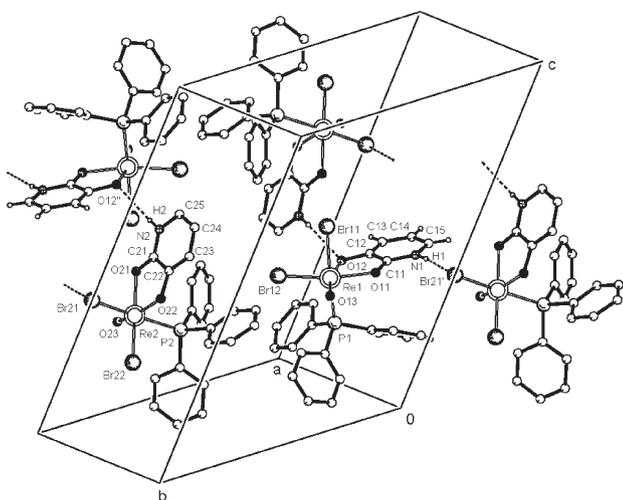


Figure 3. Perspective view¹⁴ of the unit cell of **2**, showing the interconnection of the complex molecules by H-bonds of the type N-H...Br and N-H...O. N(1)-H(1) = 86.0 pm, H(1)...Br(21)^(-x, -y, -z+1) = 244.6 pm, N(1)...Br(21)^(x, -y, -z+1) = 330.3 pm, N(1)-H(1)...Br(21)^(-x, -y, -z+1) = 173.90°; N(2)-H(2) = 86.0 pm, H(2)...O(12)^(x-1, y, z) = 227.5 pm, N(1)...O(12)^(x-1, y, z) = 301.2 pm, N(1)-H(1)...O(12)^(x-1, y, z) = 143.64°.

Crystal packings in **1** and **2** are quite different, being apparently influenced by the type of intermolecular H-bonds involved in each structure. The trigonal structure of **1** contains channels formed by groups of six molecules, as shown in Figure 2, which are arranged in a cyclic form by N-H...Cl hydrogen bonds. No solvent molecules were found in these voids. In the triclinic structure of **2**, N-H...Br and N-H...O H-bonds give rise to a network of molecules, as seen in Figure 3.

Conclusions

The zwitterionic complexes **1** and **2** can be prepared in good yields and purities following a relatively simple procedure. A distorted octahedral $\text{ReO}_3\text{X}_2\text{P}$ coordination (X = Cl in **1** and Br in **2**) is observed for them. The crystal structures of the compounds show different kinds of complex molecular packing, influenced by intermolecular hydrogen bonds.

Acknowledgments

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Supplementary Information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary material (deposition numbers CCDC 610190 and 610191 for **1** and **2**, respectively). Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK ; fax: +44 1223 336033 ; or e-mail: deposit@ccdc.cam.ac.uk).

The ellipsoid representation of **2** with the thermal ellipsoids representing 50% probability is available free of charge at <http://jbc.sbj.org.br>, as PDF file.

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