Research Article

Synthesis, spectroscopic characterization and crystal structure of [ReV(O)₂(pyz)₄][ReII(NO)Br₄(pyz)] (pyz = pyrazine)

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Abstract: A novel Re(V)-Re(II) nitrosyl complex, [Re(O)₂(pyz)₄][Re(NO)Br₄(pyz)] (pyz = pyrazine) was prepared and characterized by X-ray diffraction, elemental analysis, infrared and ultraviolet-visible absorption spectra. This product is obtained in the initial steps of the reaction of (NBu₄)[Re(NO)Br₄(EtOH)] with pyrazine. Both, the cation and the anion are mononuclear complexes. The Re(V) atom in the cation is six-coordinate with four nitrogen atoms from pyrazine ligands, and two oxo ligands. The Re(II) anion is also six-coordinate, with four bromide ligands, a linear nitrosyl group and one nitrogen from pyrazine. The spectroscopic studies are discussed and compared with those already reported separately for the cation and the anion.

Supporting information: X-Ray (CIF file)

1. INTRODUCTION

Re(II) is probably the least explored oxidation state of rhenium. The easy oxidation to higher (and more stable) oxidation states as Re(V) and Re(VII) is the main reason of this poorly developed chemistry [1]. Stabilization of this d⁵ ion requires the reduction of the electron density at the metal ion by means of ligands with a strong capacity to attract electrons, like CN⁻, NO⁺ or ligands with P as donor atom. Complexes of Re(II) stabilized by nitrosyl ligands appear nowadays as an attractive field to study the properties of this oxidation state [2]. The complexes contain the core {Re(NO)}⁵ and exhibit a good stability. The strong spin-orbit coupling effects arising from the low-spin d⁵ configuration, gives rise to a significant magnetic anisotropy [3-5]. As a consequence, the magnetic properties of these compounds looks very interesting.

We have reported very recently the preparation of a series of complexes of general formula (NBu₄)[ReII(NO)Br₄(L)] (L = pyridine (py), pyrazine (pyz), pyrimidine (pym) and pyridazine (pyd)] [6]. The synthetic path to prepare them starts from (NBu₄)[ReII(NO)Br⁴(EtOH)]. The ethanol molecule, trans to the nitrosyl group, is easily replaced by L in ethanol using an excess of the incoming ligand (molar ratio pyz:Re complex 1.5). We have also found that previous to the formation of the main product, another solid crystallizes very quickly. The identification of this novel compound is the subject of this work. We report the synthesis, crystal structure, UV-Vis and FT-IR absorption properties of the complex [Re(O)₂(pyz)₄][Re(NO)Br₄(pyz)].

2. EXPERIMENTAL

2.1 Materials and measurements

All chemicals and solvents were purchased from commercial sources and used without further purification. (NBu₄)[Re(NO)Br₄(EtOH)] was prepared from KReO₄ and NO as formerly reported [6]. Elemental analyses (C, H, N) were performed using a Flash 2000 (Thermo Scientific) elemental analyzer. IR spectrum was recorded on a Bomen MB-102 FTIR spectrometer as KBr pellets. UV-Vis absorption spectrum (acetonitrile as solvent) was measured on a UV-1603 Shimadzu spectrophotometer.

2.2. Synthesis of [Re(O)₂(pyz)₄][Re(NO)Br₄(pyz)] (1)

73 mg (0.91 mmol) of pyrazine were added to a solution of (NBu₄)[Re(NO)Br₄(EtOH)] (0.060 mmol, 50 mg) dissolved in EtOH (10 mL). Then, another 10 mL of EtOH were added to the solution with stirring. A green-reddish polycrystalline solid of 1 usually appears after a few hours at room temperature. Some of these crystals were suitable for crystallographic studies. Longer crystallization times (usually one week) of the same solution produces the green main complex (NBu4)[Re(NO)Br4(pyz)]. Yield: 10-20 %. Anal. Calc. for Re₂O₃C₂₀H₂₀N₁₁Br₄: C, 20.81; H, 1.75; N, 13.75. Found: C, 21.07; H, 2.21; N, 12.97. Selected IR data (KBr, v_{max}/cm⁻¹): 2924 (w), 1778 (s), 1590(w), 1419(s), 1157(w), 1118(w), 1058(m), 830(m), 816(m), 653(w), 497(w),

461(w).

2.3. Single-crystal structure determination

X-ray diffraction data on a single crystal was collected with an Agilent SuperNOVA diffractometer with microfocus X-ray using Cu Kα radiation (λ = 1.54184 Å). CrysAlisPro [7] software was used to collect, index, scale and apply analytical absorption correction based on the faces of the crystal. The structure was solved by charge-flipping algorimth using Superflip program [8]. Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2014[9]. All non-hydrogen atoms have been refined anisotropically, and all hydrogen atoms have been placed in geometrically suitable positions and refined riding with isotropic thermal parameter related to the equivalent isotropic thermal parameter of the parent atom. The geometrical analysis of interactions in the structure was

performed with PLATON [10] and Olex2 [11] program. The hydrogen atoms were geometrically positioned with C-H = 0.93Å and Uiso(H) = 1.2 Ueq(C). Crystal data, collection procedures and refinement results are summarized in Table 1.

Crystallographic data for the structures reported in this contribution have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication 985452. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

3. RESULTS AND DISCUSSION

3.1. Synthesis

The reported synthesis of the Re(II) complex (NBu$_4$)[Re^{II}(NO)Br$_4$(pyz)] described the initial formation of a solid by-product which was discarded [6]. The formation of this solid is repetitive in all the synthesis, and we were interested in its isolation and characterization. We have found that crystallization of **1** is achievable during the first hours after preparation. The solid is only slightly soluble in most of the common solvents. The elemental analysis fits with the proposed formula [Re(O)$_2$(pyz)$_4$][Re(NO)Br$_4$(pyz)].

Some variations in the synthesis were assayed in order to optimize the yield of this product, such as the use of other polar solvents (methanol, isopropanol and acetonitrile, and various mixtures thereof), temperature raising and pre-drying of the solvents. We also attempted deliberate oxidation with oxygen stream in the mother solution without obtaining success. Hence, it should be considered as a side-product which is repetitively obtained during the synthesis.

3.2. Description of the crystal structure

The crystalline structure of the complex **1** (Figure 1) consists of discrete [Re(O)$_2$(pyz)$_4$]$^+$ cations and mononuclear [Re(NO)Br$_4$(pyz)]$^-$ anions held together by means of electrostatic attractions, van der Waals forces and hydrogen bonds. The complex crystallizes in a monoclinic crystal system with a space group
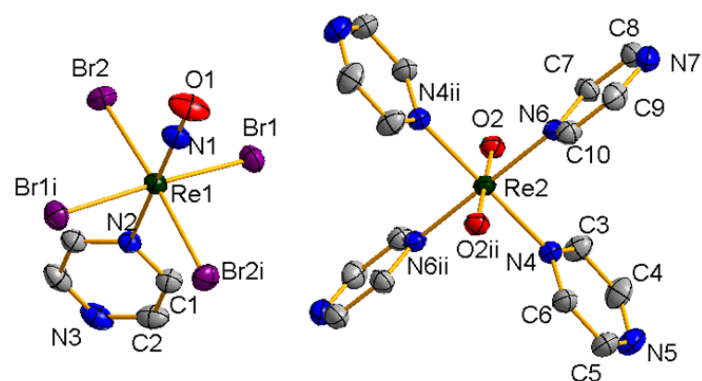
Table 1: Summary of the crystal data for compound **1**.

Chem. formula	Re$_2$O$_3$C$_{20}$H$_{20}$N$_{11}$Br$_4$
M	1154.51
Cryst. syst.	Monoclinic
Space group	C2/c
a/Å	11.8266(2)
b/Å	13.6009(2)
c/Å	19.1753(3)
α/deg	90.00
β/deg	97.371(2)
γ/deg	90.00
V/Å^3	3058.90(8)
2θ range/deg	9.3-146.8
Z	4
D_c/Kg m^{-3}	2.507
crystal dim./mm^3	0.15x0.07x0.02
F(000)	2124
μ(Cu Kα)/mm^{-1}	21.737
Reflections (collected/ unique, (Rint))	10420/3027/0.0359
Data / restraints/ Parameters	3027/0/185
R_1^{a}, wR_2 [$F^2>2\sigma(F^2)$] ^{b}	0.0263,0.0706
Goodness-of-fit on F^2	1.069
Largest diff. peak and hole (e Å^{-3})	0.86/-0.92

^{a}R$_1$=Σ||F$_0$|-|F$_c$||/Σ|F$_c$|, ^{b}wR$_2$={Σ[w(F$_0$^{2}-F$_c$^{2})2]/Σ[w(F$_0$^{2})^2}$^{1/2}$

Figure 1: Perspective drawing of the complex **1** showing the atom numbering. Atoms are plotted as thermal ellipsoids at 30% probability level. All H atoms are omitted for clarity. Color code: Re, green; Br, purple; O, red; N, blue; C, grey.

C2/c. Selected bond distances and angles for this complex are listed in Table 2.

The cationic entity contains a Re(V) atom in a squashed octahedral geometry, being coordinated by two oxo ligands in the axial positions. The equatorial plane is defined by the four N atoms belonging to four monodentate pyrazine ligands. The structure of this cation has been found and reported in the complex [Re(O)$_2$(pyz)$_4$][PF$_6$]×NaPF$_6$×2H$_2$O [12]. The Re=O distance in **1**, 1.760(3) Å, is in agreement with the previously reported (1.755(4) Å), and falls into the expected average for Re^V=O bonds, 1.761 Å [13]. This reflects the multiple bond character. Re-N distances (average 2.142(4) Å) in **1** are quite similar with those previously reported (average 2.141(5) Å) [12]. In spite of the similarities in the distances and angles of **1** compared to the same cation in [Re(O)$_2$(pyz)$_4$][PF$_6$]×NaPF$_6$×2H$_2$O, the relative positions of the pyrazine ligands is not the same. Pyrazine ligands in trans positions in **1** are coplanar. In the previously reported cation, the pyrazine ligands where tilted with respect to each other, forming angles of 54.7(5) and 25.5(5)° [12].

The anionic part of the compound is similar with the one previously reported by our group in the (NBu$_4$)[Re(NO)Br$_4$(pyz)] complex [6]. The Re(II) atom is in a distorted octahedral geometry, surrounded by four bromide ions in an equatorial plane, and two nitrogen atoms, one from the pyrazine ligand and the other from the nitrosyl ligand in the apical positions. The average Re-Br distance is 2.5257(6) Å, a value that is close to the mean value of the Re-Br distance (2.516 Å) in (NBu$_4$)[Re(NO)Br$_4$(pyz)]. The rhenium atom is shifted by 0.153 Å from the main plane towards the apical NO group. The Re-NO fragment is linear (Re1-N1-O1 angle 180°) and the set of three atoms is collinear to the N2 atom of the pyz ligand (N2-Re1-N1 angle 180°). The Re1-N1 and N1-O1 distances (1.750(7) and 1.116(9) Å, respectively) are in agreement with those found in other previous rhenium(II) nitrosyl complexes (*ca.* 1.76 Å and 1,15 Å
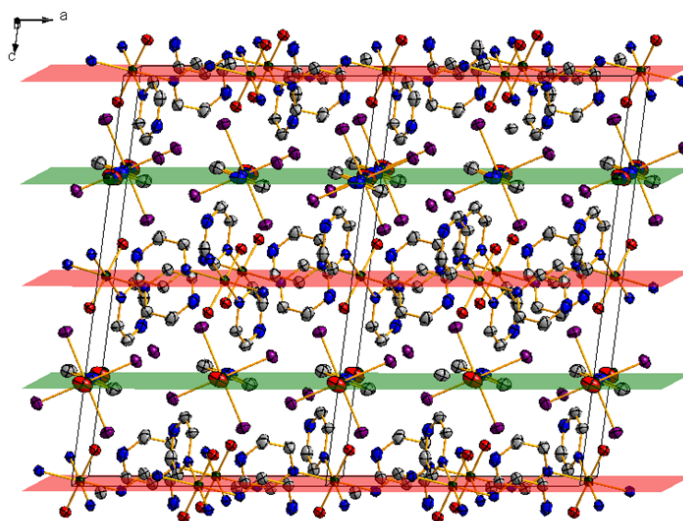

Figure 2: Crystal packing of **1** through *b* axis. Color code as in Figure 1. The layers of Re atoms in [ReO$_2$(pyz)$_4$]$^+$ are in red color. The layers of Re atoms in [Re(NO)Br$_4$(pyz)]$^-$ are in green color.

Table 2: Selected bond distances (Å) and angles (°) for compound **1**.

Distances	
Re1-N1	1.750(7)
Re1-Br1	2.5309(6)
Re1-Br2	2.5205(6)
Re1-N2	2.210(5)
N1-O1	1.116(9)
Re2-O2	1.760(3)
Re2-N4	2.145(4)
Re2-N6	2.138(4)
Angles	
Re1-N1-O1	180.0(2)
N1-Re1-N2	180.0(2)
N1-Re1-Br1	93.128(15)
N1-Re1-Br2	93.809(15)
Br1-Re1-Br2	90.32(2)
Br1-Re1-Br1^i	173.74(3)
O2-Re2-O2^{ii}	180.0(2)
N4-Re2-N6	88.72(14)
O2-Re2-N4	90.01(16)
N4-Re2-N4^{ii}	180.00(19)

Symmetry transformations used to generate equivalent atoms: i: 1-x, +y, 0.5-z: ii: 2-x, 1-y, 1-z.
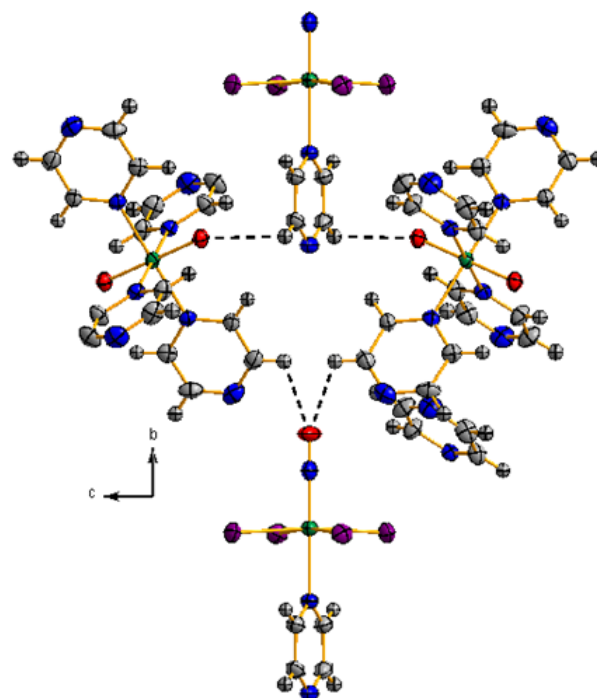

Figure 3: Hydrogen bonds (broken lines) in the crystal packing of compound **1**. Color code as in Figure 1.

respectively) [6]. The N1-Re-Br angles (93.128(15) ° and 93.809(15) ° for Br1 and Br2, respectively) provokes an additional distortion of the octahedron around the rhenium. This seems to be a consequence of the preference of bromide ions to be closer to the neutral ligand pyrazine.

The crystalline packing can be understood as alternating layers of $[ReO_2(pyz)_4]^+$ cations and $[Re(NO)Br_4(pyz)]^-$ anions perpendicular to c axis, as seen in Figure 2. Rhenium-rhenium distance (cation-anion) is then 7.155(3) Å. These layers also interact by two types of hydrogen bonds: (i) between O2 (ReO_2^+ core) in the cation and the H atom of C2 (O2-C2 distance 3.06 Å) and (ii) between O1 from a cationic residue and two H atoms bonded to C8 belonging to two independent $[ReO_2(pyz)_4]^+$ units O1-C8 distance 3.15 Å. This is shown in Figure 3.

3.3 Spectroscopic analysis

The IR spectra of $[Re(NO)Br_4(L)]^-$ ions (L = py, pyz, pym, pyd) are characterized by a strong absorption at *ca.* 1750 cm^{-1} corresponding to the stretching mode of the nitrosyl group [6]. This vibrational mode in the complex **1** (1778 cm^{-1}) shows an increased wavenumber respect to the reported complex $(NBu_4)[Re(NO)Br_4(pyz)]$ (1754 cm^{-1}), probably due to a change in the crystalline structure, as was observed in other Re(II) complexes when the cationic part was changed [2, 6]. The peak at 816 cm^{-1} is ascribed to the $v_{as}(O=Re=O)$ vibration in the cation $[ReO_2(pyz)_4]^+$. This is a fingerprint of the *trans*-dioxorhenium(V) core [14]. Characteristic pyrazine ring bands (from the cation and the anion) appears at 1590 cm^{-1} ("breathing mode"), 1419 cm^{-1} (v_{ring}), 1058 cm^{-1} (v_{Hbend}) and 461 cm^{-1} (v_{ring}) [15, 16].

The electronic spectrum of compound **1** in acetonitrile exhibits characteristic peaks of both the cationic and anionic cores (Figure 4). The lowest-energy broad peak at 467 nm seems to be characteristic of all *trans*-dioxorhenium(V) complexes, and is generally attributed to excitations between the $^1A_{1g}$ ground state

and the ^1E_g, (*d-d* spin-forbidden transition) [14, 17, 18]. Nonetheless, *d-d* transitions (or even LMCT) due to the Re(II) anion can be found in this region (as reported for $(NBu_4)[Re(NO)Br_4(pyz)]$ at 465 nm [6]), so the band observed can be a consequence of many electronic transitions [19, 20]. The strong bands at 373 nm and 409 nm are also observed in the $(NBu_4)[Re(NO)Br_4(pyz)]$ compound. They have been assigned to charge-transfer Re→Π$^*_{NO}$ transitions in some analogous complexes [2]. The UV absorptions at 256 nm and the shoulder at 272 nm are more difficult to assign. The Re(V) core usually present charge-transfer transitions (either from/to the Re atom to/from the oxo or pyrazine ligands) in this region, but also pyrazine exhibits strong absorptions at 270 nm in this solvent.

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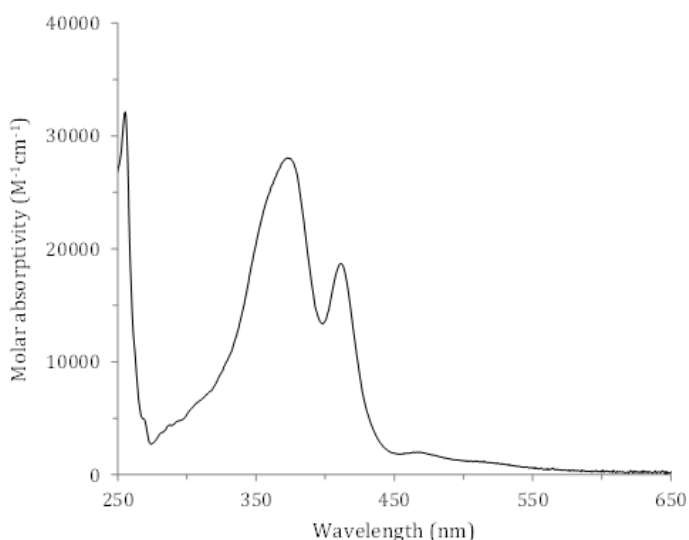
Figure 4: Uv-vis spectra of compound **1** in acetonitrile.

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