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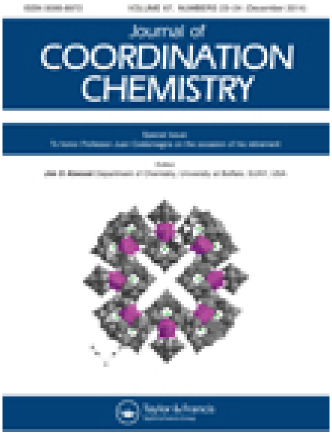

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Complex salts of $[\mathrm{Re^{II}(NO)Br_4(pyz)}]^-$: synthesis, crystal structures, and DFT studies

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Complex salts of $[Re^{II}(NO)Br_4(pyz)]^-$: synthesis, crystal structures, and DFT studies

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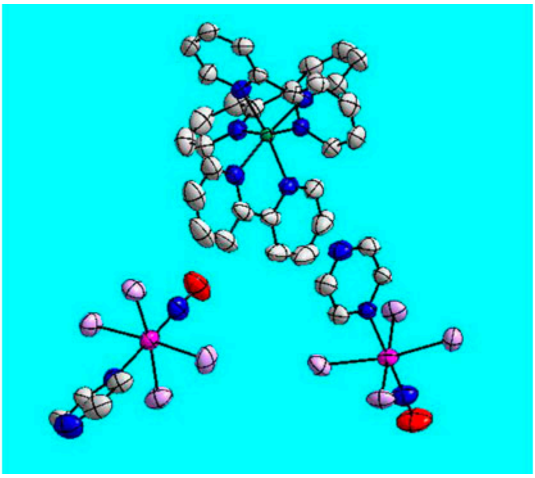

Two nitrosyl Re(II) complexes formulated as $[Ni(bipy)_3][Re(NO)Br_4(pyz)]_2$ and $[Cu(bipy)_2Br][ReNOBr_4(pyz)]$ (pyz = pyrazine, bipy = 2,2′-bipyridine) were synthesized and characterized by single-crystal X-ray diffraction. The pyrazine in $[Re(NO)Br_4(pyz)]^-$ was not able to act as bridge toward a second metal ion, and the two salts were obtained. Computational studies at the density functional level of theory show that the charge on the nitrogen, which could be available for bridging, is dramatically reduced to less than half, decreasing its capability to bind a second metal ion.

Keywords: Rhenium(II); Polynuclear complexes; Pyrazine; Nitrosyl complexes

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[1] Dedicated to Prof Juan Costamagna on the occasion of his retirement as professor of Inorganic Chemistry of Universidad de Santiago de Chile, Chile.

1. Introduction

We have been interested in the synthesis, structural characterization, and magnetic properties of polynuclear complexes containing Re(IV) or Re(II) and a first-row transition metal ion [1–4]. In the case of Re(IV) compounds, the synthetic approach involves the synthesis of stable mononuclear Re complexes which could act as ligands toward transition metal ions. This is the "complex as ligand" strategy, which was successfully used to prepare di-, tri-, tetra-, and pentanuclear compounds as well as chain-like compounds [5]. Different bridging ligands have been used, oxalato, malonato, pyrazine, 2-pyrazinecarboxylic acid, 2,2′-bipyrimidine, and thiocyanate, as reviewed [5]. The choice of the bridging ligand is a crucial point. It should have donors with enough electron density to bind simultaneously and efficiently to two metal ions, and they have to be arranged in an appropriate spatial disposition to avoid any steric hindrance.

We have reported very recently the preparation of a series of complexes of general formula $(NBu_4)[Re^{II}(NO)Br_4(L)]$ (L = pyridine (py), pyrazine (pyz), pyrimidine (pym), and pyridazine (pyd)) [4]. The rhenium in these complexes is six-coordinate, surrounded by a NO group, four bromides in the equatorial plane, and a diazine monodentate molecule *trans* to the nitrosyl group. The ligands pyz, pym, and pyd, bonded in this way, seem to be candidates to connect the Re(II) complex to a preformed complex of another metal ion with the coordination sphere partially blocked. With this in mind, we present in this work the results of the reaction of $(NBu_4)[Re^{II}(NO)Br_4(pyz)]$ with $[M(bipy)_2]^{2+}$ (M = Cu, Ni; bipy = 2,2′-bipyridine). The salts $[Ni(bipy)_3][Re^{II}(NO)Br_4(pyz)]_2$ and $[Cu(bipy)_2Br][Re^{II}(NO)Br_4(pyz)]$ were obtained. Pyrazine was not able to bridge the metal ions in this case. This result was studied by density functional theory (DFT) calculations in order to gain insight into the electronic properties of the complexes.

2. Experimental

2.1. *General procedure*

Reagents such as pyrazine, bipy, $Ni(ClO_4)_2{\cdot}6H_2O$, $Cu(CF_3SO_3)_2$, and solvents employed in the synthesis were purchased from commercial sources and used as received. $(NBu_4)[Re(NO)Br_4(pyz)]$ was prepared from $(NBu_4)[Re(NO)Br_4(EtOH)]$ and pyrazine as previously reported [4]. Elemental analyses (C, H, and N) were performed using a Flash 2000 (Thermo Scientific) elemental analyzer. IR spectra were recorded on a Bomen MB-102 FTIR spectrometer as KBr pellets.

2.2. *Synthesis of complexes*

2.2.1. $[Ni(bipy)_3][Re(NO)Br_4(pyz)]_2$ (1). $Ni(ClO_4)_2{\cdot}6H_2O$ (16 mg, 0.044 mM) and 2,2′-bipyridine (13 mg, 0.083 mM) were dissolved in 10 mL of a mixture of *i*-prOH/acetone (4 : 1 v/v). This solution was poured into a second solution prepared with 70 mg (0.082 mM) of $(NBu_4)[Re(NO)Br_4(pyz)]$ and 20 mL of the same mixture of *i*-prOH/acetone. After 9 days, a brown greenish crystalline solid was formed. Crystals were filtered and dried in the air. Some of them were suitable for X-ray diffraction. Yield: 25–30%. Anal. Calcd for $C_{38}N_{12}H_{32}O_2Br_8Re_2Ni$ (%): C, 25.95; H, 1.83; N, 9.55. Found: C, 25.62; H, 1.85; N, 9.12.

Selected IR data (KBr, ν_{max}/cm^{-1}): 2923 (w), 1752 (s), 1598 (m), 1471 (w), 1442 (m), 1417 (m), 1156 (w), 1127 (w), 1054 (w), 1019 (w), 802 (w), 767 (s), 735 (w), 459 (w).

2.2.2. [Cu(bipy)$_2$Br][ReNOBr$_4$(pyz)] (2). (NBu$_4$)[Re(NO)Br$_4$(pyz)] (26 mg, 0.030 mM) was dissolved in a mixture of 20 mL of EtOH and 5 mL of MeCN. This solution was poured into a second solution of 10 mL EtOH containing Cu(CF$_3$SO$_3$)$_2$ (5.4 mg, 0.015 mM) and 2,2′-bipyridine (4.8 mg, 0.031 mM) at room temperature. After 12 days, a green crystalline solid was formed. Crystals were filtered and dried in air. Some of them were suitable for X-ray diffraction. Yield: 15–20%. Anal. Calcd for $C_{24}N_7H_{20}OBr_5ReCu$ (%): C, 26.90; H, 1.88; N, 9.15. Found: C, 26.57; H, 2.41; N, 8.52. Selected IR data (KBr, ν_{max}/cm^{-1}): 1762 (s), 1596 (m), 1491 (m), 1442 (m), 1415 (m), 1313 (m), 1154 (w), 1057 (w), 768 (s), 731 (m), 461 (w).

2.3. *X-ray crystallography*

X-ray diffraction data on single crystals were collected with an Agilent SuperNOVA diffractometer with microfocus X-ray using Cu and Mo Kα radiation (λ = 1.54184 and 0.71073 Å, respectively). CrysAlisPro [6] software was used to collect, index, scale, and apply numerical absorption correction based on Gaussian integration over a multifaceted crystal model. The structures were solved by charge-flipping algorithm using the Superflip program [7]. Fourier recycling and least-squares refinement were used for the model completion with SHELXL-2014 [8]. All non-hydrogen atoms have been refined anisotropically, and all hydrogens have been placed in geometrically suitable positions and refined riding with

Table 1. Summary of the crystal data for [Ni(bipy)$_3$][Re(NO)Br$_4$pyz]$_2$ (**1**) and [Cu(bipy)$_2$Br][Re(NO)Br$_4$pyz] (**2**).

	1	**2**
Chemical formula	$C_{38}H_{32}Br_8N_{12}NiO_2Re_2$	$C_{24}H_{20}Br_5N_7OReCu$
M	1759.14	1071.76
Crystal system	Monoclinic	Monoclinic
Space group	*P 1 21/c1*	*P 1 21/n1*
a (Å)	11.18981 (12)	8.6987 (2)
b (Å)	30.0506 (3)	12.6273 (3)
c (Å)	15.30264 (16)	27.2338 (7)
α (°)	90.00	90.00
β (°)	105.3382 (11)	98.242 (2)
γ (°)	90.00	90.00
V (Å^3)	4962.39 (9)	2960.49 (12)
Z	4	4
D_{Calcd} (g cm^{-3})	2.355	2.405
F (0 0 0)	3272	2000
μ(Cu Kα), mm^{-1}	17.708	–
μ(Mo Kα), mm^{-1}	–	11.584
Reflections (collected/unique, (Rint))	42,293/8768/0.029	27,772/5231/0.028
Data/restrains/parameters	8768/0/568	5231/0/352
R_1[a], wR_2 [$F^2 > 2\sigma(F^2)$][b]	0.0370/0.0904	0.0218/0.0472
Goodness of fit on F^2	1.09	1.10
Largest diff. peak and hole (e Å^{-3})	2.63/−1.50	059/−0.69

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_c|$.
[b] $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)2]/\Sigma[w(F_0^2)^2\}^{1/2}$.

isotropic thermal parameters related to the equivalent isotropic thermal parameter of the parent atom. The geometrical analysis of interactions in the structure was performed with PLATON [9] and Olex2 [10] program. The hydrogens were geometrically positioned with C–H = 0.93 Å and Uiso(H) = 1.2 Ueq(C). Crystal data, collection procedures, and refinement results are summarized in table 1.

2.4. *Computational studies*

All computational studies have been undertaken at the DFT. The geometries of the complexes were optimized starting from the molecular structures determined by X-ray crystallography. It has been reported that PBE1PBE [11–13] in combination with the so-called STMIDI basis set (see below for details) is a good performer in describing geometries of rhenium complexes [14–17] with a very low computational cost. Therefore, we conducted optimizations with PBE1PBE/STMIDI in studying geometries and electronic properties at the minimum. The valence electrons for non-metal atoms in STMIDI were treated with MIDI! [18], those for the metal being described by a basis set (8s7p6d2f1g)/[6s5p3d2f1g] [19–21]. The core electrons were replaced by Stuttgart effective-core pseudopotentials [19–22]. STMIDI takes scalar relativistic effects into account, especially important when systems with heavy atoms are studied [23]. The nature of the stationary point was verified through a vibrational analysis (no imaginary frequencies). Natural population analysis (NPA) calculations were performed with the NBO code [24–27] included in the program package GAUSSIAN 09, Rev. A.01 [28], which has been used for all theoretical studies reported in this work.

3. Results and discussion

3.1. *Synthesis of the complexes*

The direct reaction of $[Re(NO)Br_4(pyz)]^-$, M(II), and bipy in a molar ratio 2 : 1 : 2 yields a crystalline product which fits the formula $[Ni(bipy)_3][Re(NO)Br_4(pyz)]_2$ (M = Ni) or $[Cu(bipy)_2Br][ReNOBr_4(pyz)]$ (M = Cu).

IR spectra of **1** and **2** are dominated by the characteristic absorption of the stretching mode of the nitrosyl group (1752 and 1762 cm^{-1}, respectively), as appears in other complexes containing the core $\{Re(NO)\}^{3+}$ [29]. This is almost unchanged if compared with the frequency of the parent compound $(NBu_4)[Re(NO)Br_4(pyz)]$ at 1754 cm^{-1} [4]. A sharp pyrazine ring band appears at 1598 cm^{-1} for **1** and 1596 cm^{-1} for **2**. This band is recognized as indicative of a terminal pyrazine group instead of a bridging mode. The latter situation would provoke a dramatic decrease in the intensity of this band [30, 31]. Other signals at *ca.* 1417 (ν_{ring}), 1054 (ν_{Hbend}) and 459 (ν_{ring}) cm^{-1} are probably a combination of different modes of pyrazine and 2,2′-bipyridine ligands, as they appear in the same region for the free ligands [32, 33].

3.2. *Description of the structures*

Compound **1** contains the $[Re(NO)Br_4(pyz)]^-$ anionic unit, packed with $[Ni(bipy)_3]^{2+}$ cations in 2 : 1 M ratio (figure 1). Selected bond distances and angles are listed in table 2.

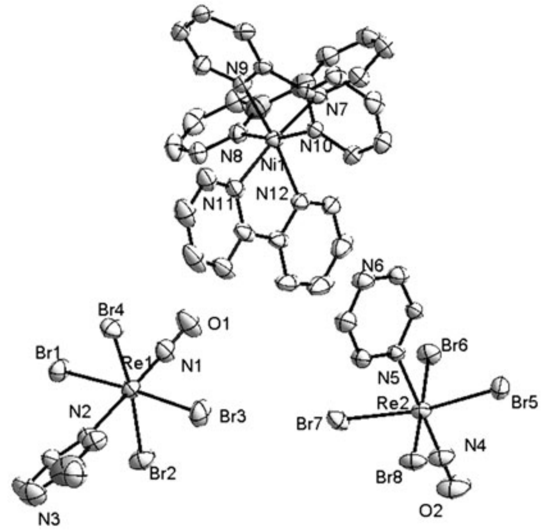

Figure 1. Perspective drawing of **1** showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level. Hydrogens have been omitted for clarity.

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

Distances					
Re(1)–Br(1)	2.5120(11)	Re(2)–Br(5)	2.5076(10)	Ni(1)–N(7)	2.120(5)
Re(1)–Br(2)	2.5217(10)	Re(2)–Br(6)	2.5095(10)	Ni(1)–N(8)	2.073(6)
Re(1)–Br(3)	2.5243(11)	Re(2)–Br(7)	2.5142(10)	Ni(1)–N(9)	2.065(5)
Re(1)–Br(4)	2.5038(10)	Re(2)–Br(8)	2.5243(10)	Ni(1)–N(10)	2.070(5)
Re(1)–N(1)	1.746(7)	Re(2)–N(4)	1.758(8)	Ni(1)–N(11)	2.100(6)
Re(1)–N(2)	2.245(6)	Re(2)–N(5)	2.233(5)	Ni(1)–N(12)	2.106(6)
N(1)–O(1)	1.171(10)	N(4)-O(2)	1.125(11)		
Angles					
Br(1)–Re(1)–Br(2)	88.98(3)	Br(5)–Re(2)–Br(6)	91.76(3)	N(8)–Ni(1)–N(7)	78.6(2)
Br(1)–Re(1)–Br(3)	175.81(4)	Br(7)–Re(2)–Br(5)	168.88(3)	N(8)–Ni(1)–N(11)	101.3(2)
Br(2)–Re(1)–Br(3)	89.32(4)	Br(7)–Re(2)–Br(6)	88.37(3)	N(8)–Ni(1)–N(12)	86.7(2)
Br(4)–Re(1)–Br(1)	90.65(3)	Br(7)–Re(2)–Br(8)	90.27(3)	N(9)–Ni(1)–N(7)	92.0(2)
Br(4)–Re(1)–Br(2)	169.92(4)	Br(8)–Re(2)–Br(5)	88.37(3)	N(9)–Ni(1)–N(8)	94.4(2)
Br(4)–Re(1)–Br(3)	90.35(4)	Br(8)–Re(2)–Br(6)	175.36(3)	N(9)–Ni(1)–N(10)	78.7(2)
N(1)–Re(1)–Br(1)	93.9(2)	N(4)–Re(2)–Br(5)	96.0(2)	N(9)–Ni(1)–N(11)	94.0(2)
N(1)–Re(1)–Br(2)	98.4(2)	N(4)–Re(2)–Br(6)	92.1(2)	N(9)–Ni(1)–N(12)	171.9(2)
N(1)–Re(1)–Br(3)	90.1(2)	N(4)–Re(2)–Br(7)	95.1(2)	N(10)–Ni(1)–N(7)	90.6(2)
N(1)–Re(1)–Br(4)	91.7(2)	N(4)–Re(2)–Br(8)	92.5(2)	N(10)–Ni(1)–N(8)	167.1(2)
N(1)–Re(1)–N(2)	176.8(3)	N(4)–Re(2)–N(5)	179.0(3)	N(10)–Ni(1)–N(11)	90.2(2)
N(2)–Re(1)–Br(1)	87.53(15)	N(5)–Re(2)–Br(5)	83.94(13)	N(10)–Ni(1)–N(12)	101.6(2)
N(2)–Re(1)–Br(2)	84.53(15)	N(5)–Re(2)–Br(6)	86.89(12)	N(11)–Ni(1)–N(7)	174.0(2)
N(2)–Re(1)–Br(3)	88.49(15)	N(5)–Re(2)–Br(7)	84.97(13)	N(11)–Ni(1)–N(12)	77.9(2)
N(2)–Re(1)–Br(4)	85.39(15)	N(5)–Re(2)–Br(8)	88.57(12)	N(12)–Ni(1)–N(7)	96.1(2)
O(1)–N(1)–Re(1)	175.9(7)	O(2)–N(4)–Re(2)	179.3(8)		

Despite the presence of two crystallographically non-equivalent $[Re(NO)Br_4(pyz)]^-$ units, the anions are structurally quite similar, in particular the coordination geometry around the rhenium (table 2). Each $[Re(NO)Br_4(pyz)]^-$ unit contains a Re(II) in a distorted octahedral environment, surrounded by four bromides, one NO group, and a monodentate pyz molecule in *trans* position. The Re–N(O) bond distances are 1.746(7) and 1.758(8) Å and Re–N (pyz) bond distances are 2.245(10) and 2.233(5) Å, respectively. The Re–Br bond distances fall within the range 2.5038(10)–2.524(10) Å. These values agree well with those found in the literature for other Re(II) nitrosyl compounds [4, 34–37]. The Re–NO group is practically linear with O(1)–N(1)–Re(1) angle of 175.9(7)° and O(2)–N(4)–Re(2) angle of 179.3 (8)°. The three atoms are also aligned with N(2) and N(5) of the pyridine ring, exhibiting N (1)–Re(1)–N(2) and N(4)–Re(2)–N(5) angles of 176.8(3)° and 179.0(3)°, respectively.

The cationic unit contains a nickel bound to six nitrogens from three bipy ligands (figure 1). The coordination around the metal exhibits a distorted octahedral geometry. The equatorial plane is defined by N(8), N(9), N(10), and N(12). The Ni is displaced 0.0316 Å from this plane towards N(11). The perpendicular axis N(11)–Ni(1)–N(7) is almost linear [174.0(2)°]. Ni-N(equatorial) distances (average 2.079 Å) are shorter than the Ni–N(axial), average 2.110 Å. Distortion of the geometry becomes evident also in other bonding angles like N(11)–Ni(1)–N(12) [77.9(2)°] or N(7)–Ni–N(11) [174.0(2)°] in the equatorial plane.

The crystalline packing of **1** is shown in figure 2. Besides the electrostatic anion–cation interaction, and hydrogen bonds in which bromide acts as acceptor, several π stacking interactions between pyz and bipy ligands are present. Centroid–centroid distance is 3.93 Å.

Compound **2** contains the $[Re(NO)Br_4(pyz)]^-$ anionic unit, packed with $[Cu(bipy)_2Br]^+$ cations in 1 : 1 M ratio (figure 3). The anion is structurally quite similar to that in **1**, as shown in table 3. The Re–NO bond distance is 1.743(4) Å and Re–N(pyz) bond distance is 2.238(3) Å. The Re–Br bond distances fall within the range 2.5048(5)–2.5344(7) Å.

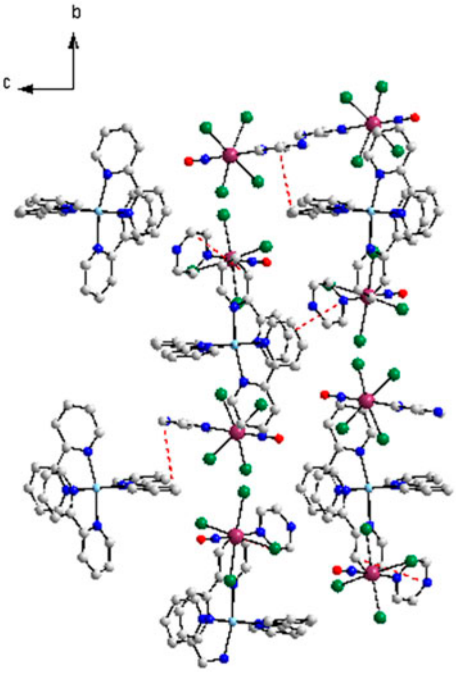

Figure 2. View of a fragment of the packing of **1** along the crystallographic *a*-axis. π stacking interactions are shown as broken red lines. Color code: rhenium, purple; bromine, green; oxygen, red; nitrogen, blue; and carbon, light gray. Hydrogens have been omitted for clarity (see http://dx.doi.org/10.1080/00958972.2014.959003 for color version).

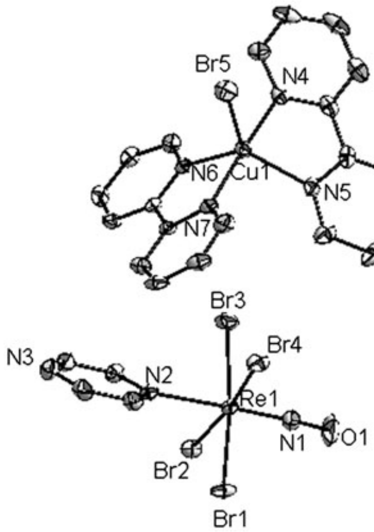

Figure 3. Perspective drawing of **2** showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level. Hydrogens have been omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) for **2**.

Distances			
Re(1)–Br(1)	2.5246(7)	Cu(1)–N(4)	1.980(3)
Re(1)–Br(2)	2.5194(5)	Cu(1)–N(5)	2.086(3)
Re(1)–Br(3)	2.5344(7)	Cu(1)–N(6)	2.120(3)
Re(1)–Br(4)	2.5048(5)	Cu(1)–N(7)	1.974(3)
Re(1)–N(1)	1.743(4)	Cu(1)–Br(5)	2.4451(6)
Re(1)–N(2)	2.238(3)		
O(1)–N(1)	1.166(5)		
Angles			
Br(1)–Re(1)–Br(3)	174.969(15)	Br(5)–Cu(1)–N(5)	125.45(7)
Br(2)–Re(1)–Br(1)	85.206(17)	Br(5)–Cu(1)–N(7)	92.05(8)
Br(2)–Re(1)–Br(3)	94.467(16)	N(4)–Cu(1)–Br(5)	91.64(8)
Br(4)–Re(1)–Br(1)	94.691(19)	N(4)–Cu(1)–N(5)	80.36(12)
Br(4)–Re(1)–Br(2)	173.909(16)	N(4)–Cu(1)–N(7)	176.13(12)
Br(4)–Re(1)–Br(3)	85.100(19)	N(5)–Cu(1)–N(7)	96.54(12)
N(1)–Re(1)–Br(1)	82.29(18)	N(6)–Cu(1)–Br(5)	118.44(8)
N(1)–Re(1)–Br(2)	95.45(15)	N(6)–Cu(1)–N(4)	99.65(11)
N(1)–Re(1)–Br(3)	102.74(18)	N(6)–Cu(1)–N(5)	116.11(10)
N(1)–Re(1)–Br(4)	90.56(15)	N(6)–Cu(1)–N(7)	79.59(11)
N(1)–Re(1)–N(2)	176.71(18)		
N(2)–Re(1)–Br(1)	97.27(11)		
N(2)–Re(1)–Br(2)	81.26(10)		
N(2)–Re(1)–Br(3)	77.73(11)		
N(2)–Re(1)–Br(4)	92.72(10)		
O(1)–N(1)–Re(1)	174.2(5)		

Copper is bound to one bromide and four nitrogens from two bipy ligands (figure 3). The coordination around copper can be described as trigonal bipyramidal, the geometric τ factor being 0.84 (the τ values for square pyramidal and trigonal bipyramidal metal

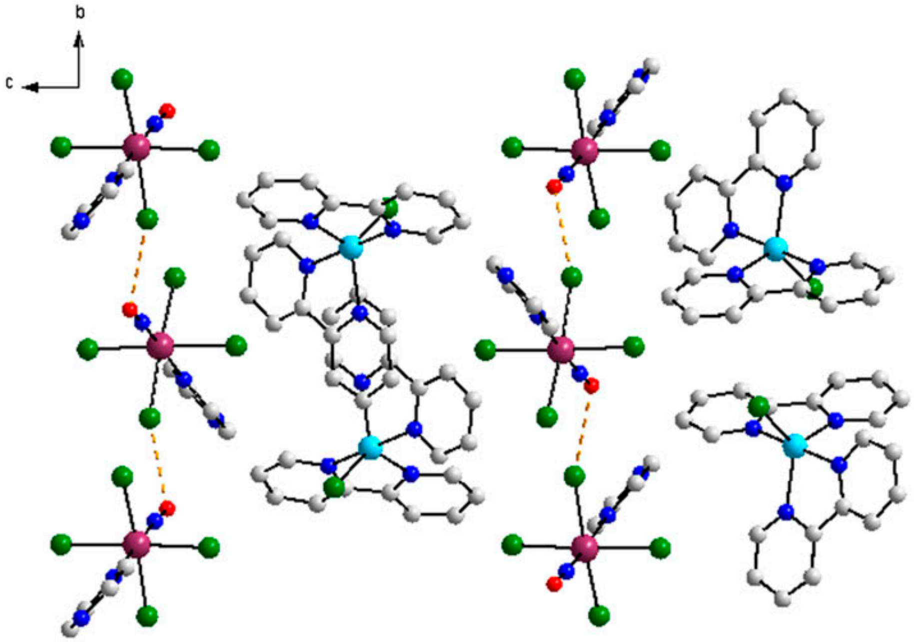

Figure 4. Partial view of the packing in **2** along the *a*-axis. Short Br–O contacts are shown as broken lines. Color code: rhenium, purple; bromine, green; oxygen, red; nitrogen, blue; and carbon, light gray (see http://dx.doi.org/10.1080/00958972.2014.959003 for color version).

environments are 0 and 1, respectively) [38]. The almost linear N(4)–Cu–N(7) moiety [176.13(12)°] appears as the axis in a rough trigonal bipyramid, with equatorial positions occupied by N(5), N(6), and Br(5). In this case, Cu–N(axial) distances [average 1.997(3) Å] are shorter than Cu–N(equatorial) ones [average 2.103(3) Å], while Cu–Br(5) distance is 2.4451(6) Å. A slight distortion of the ideal geometry becomes evident in other bond angles, like N(5)–Cu–Br(5) [125.45(7)°], and N(4)–Cu–N(5) [80.36(12)°].

The crystal packing is shown in figure 4. Hydrogen bonds between hydrogens of the organic ligands in the cation and bromides in the anion stabilize the 3-D lattice. Of particular importance are the short Br(3)–O(1) contacts of a contiguous anionic unit at 3.2994(38) Å, which form chain-like aggregates, as shown in figure 4.

3.3. *DFT calculations*

Pyrazine can bridge metallic centers [39], forming polymeric complexes with many divalent cations such as Cu(II) [40–42], Mn(II), Fe(II), Co(II) [43], and Pt(II) [44]. A Re(IV)–Cu(II) heteropolymetallic complex containing a pyrazine bridge has also been characterized [45]. Pyrazine is currently used to build molecular rectangles (reviewed in [46]). This is not the case in the anionic compound $[Re(NO)Br_4(pyz)]^-$. In the presence of divalent cations as Cu(II) or Ni(II), only complex salts are obtained as demonstrated in the crystal structures **1** and **2**. In consequence, we performed DFT calculations to understand the electronic reasons for this peculiar behavior. Full geometry optimizations of pyz and the related ligands pyd and pym were performed with PBE1PBE/STMIDI, as well as the complexes $[Re^{II}(NO)Br_4(L)]^-$ (L = pyz, pyd, pym). In the optimized structures, the remaining electronic charge

Table 4. Selected NPA results of free ligands and the complexes $[Re^{II}(NO)Br_4(L)]^-$ (L = pyz, pyd, pym).

Compound	N	Re	Coordinated N	Free N	Nitrosyl N
pyz	−0.384				
$[Re^{II}(NO)Br_4(pyz)]^-$		+0.222	−0.171	−0.190	+0.117
pyd	−0.211				
$[Re^{II}(NO)Br_4(pyd)]^-$		+0.220	−0.078	−0.070	+0.111
pym	−0.444				
$[Re^{II}(NO)Br_4(pym)]^-$		+0.222	−0.222	−0.229	+0.116

Table 5. Selected geometric parameters calculated for $[Re^{II}(NO)Br_4(pyz)]^-$ by using PBE1PBE/STMIDI (T = 298 K).[a]

Complex salt	Bond	d (Å)	Angle	∠ (°)
1	$Re–N_{NO}$	1.732 (1.752[b])	Re–N–O	179.9 (174.9[b])
	Re–Br	2.511 (2.515)	$Br–Re–N_{NO}$	94.6 (93.5[b])
	$Re–N_{pyz}$	2.237 (2.239[b])	$N_{NO}–Re–N_{pyz}$	180.0 (176.8[b])
			$Br–Re–N_{pyz}$	85.4 (86.36[b])
2	$Re–N_{NO}$	1.732 (1.582)	Re–N–O	179.9 (174.2)
	Re–Br	2.511 (2.676[b])	$Br–Re–N_{NO}$	94.6 (92.69[b])
	$Re–N_{pyz}$	2.237 (2.054)	$N_{NO}–Re–N_{pyz}$	180.0 (176.71)
			$Br–Re–N_{pyz}$	85.4 (86.00[b])

[a] Experimental values in parentheses (this work).
[b] Average value.

on nitrogen was evaluated. The results are summarized in table 4. The charge on N, which could be available for bridging, is reduced to less than half in the three cases. In particular, for pyz, the remaining charge changes from −0.384 to −0.190, quenching the basicity of the potential donor in this particular mononuclear complex. This is even worse for pyd and pym, avoiding the binding to a second metal ion.

Besides the study of the electronic features of the title complexes, it is also our aim to test the reliability of PBE1PBE/STMIDI in studying geometric features of complexes with rhenium in low oxidation states bearing different donor atoms. Therefore, we decided to include herein a discussion of structures of $[Re^{II}(NO)Br_4(L)]^-$ (L = pyz, pyd, and pym) optimized with PBE1PBE/STMIDI. Selected metric parameters are summarized in table 5 for $[Re^{II}(NO)Br_4(pyz)]^-$ (taken as example), the ones for $[Re^{II}(NO)Br_4(pyd)]^-$ and $[Re^{II}(NO)Br_4(pym)]^-$ are included in Supplementary material.

The geometry of $[Re^{II}(NO)Br_4(pyz)]^-$ optimized with PBE1PBE/STMIDI exhibits a slightly distorted octahedral rhenium featured by parameters in good agreement with the experimental findings reported in this work. The theoretical results for $[Re^{II}(NO)Br_4(pyd)]^-$ and $[Re^{II}(NO)Br_4(pym)]^-$ also match the experimental evidence [4] (for further details, see tables S1 and S2, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.959003).

4. Conclusion

The Re(II) complexes $[Ni(bipy)_3][Re(NO)Br_4(pyz)]_2$ and $[Cu(bipy)_2Br][Re(NO)Br_4(pyz)]$ were prepared by direct reaction of $[Re(NO)Br_4(pyz)]^-$, a salt of Cu(II)/Ni(II), and bipy as auxiliary ligand in 2 : 1 : 2 M ratio. Both were fully characterized by single-crystal X-ray diffraction. The structures show the presence of unchanged Re(II) anion and a cation formed by the second metal ion coordinated by bipy. In spite of the well-known ability of pyrazine to bridge metal centers and to form polynuclear complexes, we did not observe this behavior in $[Re(NO)Br_4(pyz)]^-$. This fact was analyzed by computational studies at the DFT. Calculated metric parameters of $[Re^{II}(NO)Br_4(pyz)]^-$ with PBE1PBE/STMIDI were in agreement with the crystallographic data obtained in this work. Thus, PBE1PBE in combination with STMIDI could be confidently employed in studying complexes of Re(II) with diazine-type ligands keeping the computational cost very low. Secondly, the calculations show that the charge on the N atom, which could be available for bridging, is reduced to less than half. This seems to be the reason of the inability of pyrazine to bind a second metal ion when participating in $[Re^{II}(NO)Br_4(pyz)]^-$.

Supplementary material

Tables S1 and S2 give selected geometric parameters calculated for $[Re^{II}(NO)Br_4(pyd)]^-$ and $[Re^{II}(NO)Br_4(pym)]^-$. Crystallographic data for the structures reported in this contribution have been deposited with the Cambridge Crystallographic Data Center as supplementary publication 997021-997022. Copies of the data can be obtained free of charge on application to the CCDC, Cambridge, UK (http://www.ccdc.cam.ac.uk/).

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