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# First Magnetostructural Study on a Heterodinuclear 2,2′-Bipyrimidine-Bridged Complex

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*Supporting Information*

**ABSTRACT:** The use of the $[ReCl_4(bpym)]$ precursor as a ligand toward the fully solvated nickel(II) metal ion affords the first example of a 2,2′-bipyrimidine-bridged $Re^{IV}-Ni^{II}$ complex, $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$ (**1**), whose intramolecular ferromagnetic coupling has been substantiated from both experimental and theoretical studies.

One of the safest approaches to preparing polynuclear compounds with controlled nuclearity and magnetic properties consists of using stable paramagnetic building blocks as ligands toward either fully solvated metal ions or preformed partially blocked metal complexes.[1,2] Well-known and highly rewarding examples in the field of molecular magnetism and crystal engineering are, for instance, the bis- and tris(oxalato)-chromate(III)[1] or polycyanidometallate complexes,[2] the remarkable ability of the oxalate and cyanide to mediate strong magnetic interactions between the paramagnetic centers when acting as bridges being at the origin of their choice. Among the variety of the existing building blocks involving heavier metal ions,[3] those containing the $Re^{IV}$ center, such as $[ReX_4(ox)]^{2-}$ (X = Cl and Br)[4,5a] or $[ReCl_4(CN)_2]^{2-}$,[6] are especially appealing. The six-coordinated $Re^{IV}$ has three unpaired electrons ($S = {}^3/_2$ and ${}^4A_{2g}$ as the ground electronic term), a large magnetic anisotropy arising from spin−orbit coupling associated with the 5d metal ion, and the diffuse nature of the 5d orbitals, which results in stronger magnetic interactions.[5b] Their complex formation with first-row transition-metal ions has afforded new examples of mixed 5d−3d single-molecule magnets[4b,d,5b] and single-chain magnets,[6] respectively. Recently, the isolation, structural characterization, and electrochemical,[7] magnetic,[8] and antitumoral[9] investigation of the stable neutral $[ReX_4(bpym)]$ complexes (bpym = 2,2′-bipyrimidine and X = Cl and Br) has opened new gates for these heterometallic 3d−5d systems. In that respect, $[ReCl_4(bpym)]$ displays potent in vitro antiproliferative activity against selected cancer cells, and it exhibits a spin-canting behavior with a magnetic ordering below 7.0 K and values of the coercive field ($H_c$) and remnant magnetization ($M_r$) of 1750 G and 0.05 $\mu_B$, respectively.

Keeping in mind the well-known ability of the bpym molecule to mediate magnetic interactions [the largest reported value of the magnetic coupling through bpym-bridged copper(II) complexes being $J = -236\ \mathrm{cm}^{-1}$],[10] we underwent a systematic study of the complexing ability of the $[ReCl_4(bpym)]$ unit toward transition-metal ions in order to prepare new bpym-bridged 5d−*n*d (*n* = 3−5) assemblies. Here, we present our first results that deal with the preparation and magneto-structural characterization of the unprecedented bpym-bridged heterobimetallic $Re^{IV}Ni^{II}$ (5d−3d) compound of the formula $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$ (**1**), whose intramolecular ferromagnetic coupling has been substantiated by density functional theory (DFT)-type calculations. It deserves to be noted that only a few structures of heterodinuclear bpym-bridged complexes, mostly involving $Ru^{II}/Pd$[11] or M/Ln pairs (M = $Ru^{II}$, $Re^{I}$, $Pt^{II}$; Ln = trivalent lanthanide cation),[12] have been reported, the investigations focusing mainly on their luminescence properties.

Compound **1** was prepared by reacting $[ReCl_4(bpym)]$ and $NiBr_2\cdot H_2O$ dissolved in a $MeNO_2$/MeCN solvent mixture. Slow evaporation at room temperature of the resulting orange-yellowish solution afforded X-ray-quality crystals of **1**. The crystal structure of **1** is made up of heterobimetallic dinuclear neutral units $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$, which are held together by means of hydrogen-bonding, $\pi-\pi$-stacking, and van der Waals interactions. A perspective drawing of the structure of the dinuclear unit along with the atom numbering is depicted in Figure 1. Each $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$ entity contains $Re^{IV}$ and $Ni^{II}$ metal ions, which are interconnected through a bis-bidentate bpym ligand, with the Re···Ni distance across this bridge being 5.659(1) Å. Each rhenium atom is surrounded by two bpym nitrogen and four chloro atoms, building a distorted octahedral environment. The value of the Re−N bond length is 2.23(1) Å, while the bond distances for Re−Cl(1) and Re−Cl(2) are 2.399(8) and 2.216(10) Å, respectively. Both Re−N and Re−Cl bond lengths and angles within the $[ReCl_4(bpym)]$ fragment are in agreement with the values found in the mononuclear $[ReCl_4(bpym)]$ complex.[7]

The nickel atom in **1** is also six-coordinated, with two bpym nitrogen atoms, two bromine atoms in trans positions, and two oxygen atoms from two water molecules building a somewhat distorted octahedral surrounding. The value of the angle

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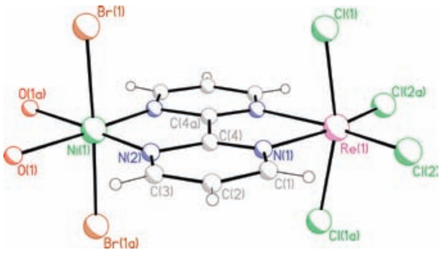

**Figure 1.** Perspective view of complex **1** along with the atom numbering of the metal environments. Symmetry code: (a) = 1 − *x*, 1 − *y*, *z*.

subtended at the nickel atom by the bpym ligand is 90.7(11)° [N(2)−Ni(1)−N(2a)], and the Ni−N and Ni−O bond lengths are 1.98(2) and 2.164(17) Å, respectively. These values are somewhat different from those found in the dinuclear $[\{Ni(H_2O)_4\}_2(\mu\text{-bpym})](NO_3)_4$ [79.2(1)° and 2.094(3) and 2.050(3) Å, respectively].[13] The Ni−Br bond length [2.533(2) Å] is the longest around this metal atom, as expected. The bpym molecule as a whole in **1** is close to planarity, with the value of the dihedral angle between the two planar pyrimidyl rings being only 2.0(6)° (to be compared with a value of 16.0(3)° in the mononuclear $[ReCl_4(bpym)]$ complex).[7] The value of the dihedral angle between the bpym ligand and the equatorial plane at the nickel atom is ca. 3°, whereas the bpym ligand and the equatorial plane at the rhenium atom are coplanar.

Adjacent $[ReCl_4(\mu\text{-bpym})NiBr_2(H_2O)_2]$ units are connected through hydrogen bonds involving the chloro atoms and the coordinated water molecules [3.7 Å for Cl(2)···O(1b); (b) = *x*, 1 − *y*, −0.5 + *z*] to generate pseudochains developing along the crystallographic *c* axis (Figure 2). Each bpym molecule within the chain forms with the nearest one a dihedral angle of ca. 67°. In addition, *π*−*π* interactions take place along the crystallographic *a* axis among pyrimidyl rings of the bpym ligands, leading to a supramolecular two-dimensional structure. The value of the interplanar distance is 3.78 Å, and that of the angle between the centroid−centroid vector from the facing pyrimidyl rings and their normal is 26(1)°. The resulting layers are interconnected through very weak C−H···Br-type interactions into a three-dimensional supramolecular arrangement (Figure S1 in the Supporting Information).

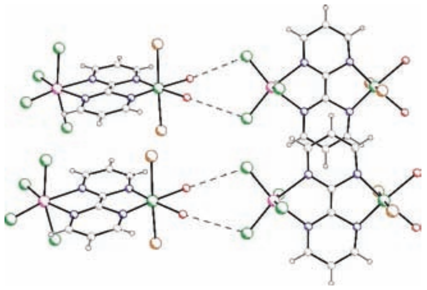

**Figure 2.** View of the Cl···H−O hydrogen bonds (dashed lines) and *π*−*π*-type interactions in **1**.

The magnetic properties of **1** under the form of a $\chi_M T$ versus $T$ plot (with $\chi_M$ being the magnetic susceptibility per heterodinuclear $Re^{IV}Ni^{II}$ unit) are shown in Figure 3. $\chi_M T$ at 250 K is ca. 2.65 $cm^3\ mol^{-1}$ K, a value that is very close to that expected for an uncoupled $Re^{IV}Ni^{II}$ pair [$\chi_M T = 2.77\ cm^3\ mol^{-1}$ K with $S_{Re} = {}^3/_2$, $g_{Re} = 1.86$, $S_{Ni} = 1$, and $g_{Ni} = 2.20$]. Upon cooling, this value practically follows a Curie law until 90 K, and then it decreases sharply to reach a minimum value of ca. 0.60 $cm^3\ mol^{-1}$ K at 1.9 K. No maximum of the magnetic susceptibility is observed for **1** in the explored temperature range. Most of the variation of $\chi_M T$ with $T$ is due to zero-field-splitting effects ($2D_{Re}$) resulting from the combined action of the second-order spin−orbit interaction and the tetragonal field of the six-coordinated $Re^{IV}$ [$2D_{Re}$ is the energy gap between the $M_S = \pm{}^3/_2$ and $M_S = \pm{}^1/_2$ Kramers doublets]. At low temperatures where $kT \ll |2D_{Re}|$, the $[ReCl_4(bpym)]$ entity can be regarded as an Ising spin ${}^1/_2$ system with a $\chi_{av}T$ value of 1.0 $cm^3\ mol^{-1}$ K (with $\chi_{av}$ being the average powder susceptibility with $g = g_\parallel = g_\perp$).[4a] Given that $\chi_M T$ for **1** at 1.9 K (ca. 0.60 $cm^3\ mol^{-1}$ K) is well below this value, significant antiferromagnetic interactions are also involved. The shape of the magnetization versus $H$ plot for **1** at 2.0 K is consistent with these features; the maximum value of $M$ at 5.0 T (the highest magnetic field available in our device) is only 1.7 $\mu_B$ (Figure S2 in the Supporting Information). Looking at the structure of **1**, two exchange pathways are possible: one being intramolecular (the bpym bridge) and the other intermolecular (Cl···H−O hydrogen bonds plus *π*−*π*-type interactions). Concerning the first one, the strict orthogonality between the magnetic orbitals of the interacting magnetic centers in octahedral symmetry [$t_{2g}{}^3$ ($Re^{IV}$) versus $e_g{}^2$ ($Ni^{II}$)] ensures a ferromagnetic interaction, a situation that is well documented for the parent oxalato-bridged $Re^{IV}Ni^{II}$ pair where the same topology for the exchange pathway occurs.[4,5]

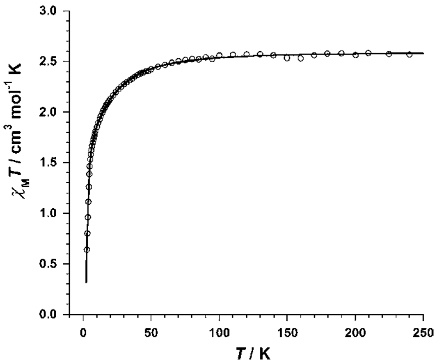

**Figure 3.** Thermal dependence of the $\chi_M T$ product (○) for **1**. The solid line is the best-fit curve.

As far as the intermolecular exchange pathways are concerned, they are especially relevant in the case of the rhenium(IV) compounds because of the significant spin delocalization on the peripheral donor atoms around the $Re^{IV}$ atom due to covalency effects of this 5d metal ion. The intermolecular contacts, usually of the type $Re^{IV}$−X···X−$Re^{IV}$ (with X being a halogen atom), mediate antiferromagnetic interactions between the paramagnetic centers.[14]

Keeping in mind these considerations, we have analyzed the magnetic data of **1** through the Hamiltonian of eq1

$$\hat{H} = -J\hat{S}_{Re}\cdot\hat{S}_{Ni} + D_{Re}[(\hat{S}^{Z}_{Re})^2 - 5/4] + D_{Ni}[(\hat{S}^{Z}_{Ni})^2 - 2/3] + (\hat{S}_{Re}g_{Re} + \hat{S}_{Ni}g_{Ni})\cdot \beta H \qquad (1)$$

where $J$ is the exchange-coupling parameter between the $Re^{IV}$ and $Ni^{II}$ local spins, $2D_{Re}$ is the energy gap between the $M_S$ =

$\pm{}^{3}/_{2}$ and $\pm{}^{1}/_{2}$ Kramers doublets [the zero-field splitting of $\mathrm{Re^{IV}}$], and $D_{\mathrm{Ni}}$ represents the energy gap between the sublevels $M_S = 0$ and $\pm1$ of the $\mathrm{Ni^{II}}$ ion. The last term in eq1 accounts for the Zeeman effects of the two metal ions. In order to reduce the large number of variable parameters, we have assumed that $g = g_{\parallel} = g_{\perp}$ for the $\mathrm{Re^{IV}}$ and $\mathrm{Ni^{II}}$ centers. The intermolecular interactions were considered in the fit by introducing a $\theta$ parameter as $T-\theta$. The best least-squares fit of the experimental magnetic data of **1** through eq 1 leads to the following parameters: $J_{\mathrm{ReNi}} = +5.8\ \mathrm{cm^{-1}}$, $|D_{\mathrm{Re}}| = 71.0\ \mathrm{cm^{-1}}$, $|D_{\mathrm{Ni}}| = 6.1\ \mathrm{cm^{-1}}$, $g_{\mathrm{Re}} = 1.81$, $g_{\mathrm{Ni}} = 2.15$, and $\theta = -5.5$ K with $zj = -1.3\ \mathrm{cm^{-1}}$. Taking into account that $z$ is 3, the $j$ value is ca. $-0.44\ \mathrm{cm^{-1}}$ (with $j$ being the average value for the intermolecular interactions among $[\mathrm{Re^{IV}Ni^{II}}]$ units). As shown in Figure 3, the calculated curve matches very well the experimental magnetic data.

In order to give additional support to the ferromagnetic interaction, we have performed DFT-type calculations on the experimental geometry of complex **1**. A ferromagnetic coupling between $\mathrm{Re^{IV}}$ and $\mathrm{Ni^{II}}$ of $+6.3\ \mathrm{cm^{-1}}$ was computed, together with antiferromagnetic interactions of −0.27, −0.48, and −0.16 $\mathrm{cm^{-1}}$ through the crystallographic *a*, *b*, and *c* axes, respectively. These values are $J_{\mathrm{eff}}$, and concerning the last one, which is referred to as the Cl···H−O pathway, it would correspond to $J = -0.58\ \mathrm{cm^{-1}}$ between the $\mathrm{Re^{IV}}$ and $\mathrm{Ni^{II}}$ ions. Although the quantitative evaluation of the intermolecular magnetic interactions is quite difficult, their antiferromagnetic nature, together with the zero-field-splitting effects of $\mathrm{Re^{IV}}$ and $\mathrm{Ni^{II}}$ metal ions, would compensate the intramolecular ferromagnetic interaction, accounting for the observed $\chi_M T$ vs $T$ variation. Thus, the theoretical calculations allow us to substantiate this unprecedented ferromagnetic coupling through bridging bpym in a mixed 3d−5d system.

In summary, the first ferromagnetically coupled heterodinuclear bpym-bridged complex of formula $[\mathrm{ReCl_4}(\mu\text{-bym})\mathrm{NiBr_2(H_2O)_2}]$ (**1**) has been prepared by using the $[\mathrm{ReCl_4(bpym)}]$ precursor as a ligand toward nickel(II) ion. This represents a new and rational strategy to prepare 5d(Re)−*n*d/4f (*n* = 3−5) mixed magnetic systems.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental, crystallographic, and computational details, crystallographic data (CIF file), and Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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