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A Chiral, Photoluminescent, and Spin-Canted $\{Cu^{I}Re^{IV}{}_2\}_n$ Branched Chain

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Supporting Information

ABSTRACT: A new heteroleptic 1D $Cu^{I}-Re^{IV}$ coordination polymer of the formula $\{Cu^{I}Re^{IV}Cl_4(\mu\text{-}Cl)(\mu\text{-}pyz)[Re^{IV}Cl_4(\mu\text{-}bpym)]\}_n\cdot n MeNO_2$ (**1**; pyz = pyrazine, bpym = 2,2′-bipyrimidine) has been prepared through the Cu^{I}-mediated self-assembly of two different Re^{IV} metalloligands, namely, $[ReCl_5(pyz)]^-$ and $[ReCl_4(bpym)]$. **1** consists of chiral branched chains with an overall rack-type architecture displaying photoemission and magnetic ordering. These results constitute a first step toward making new multifunctional magnetic materials based on mixed 3d−5d molecular systems.

The combination of magnetism and chirality in a molecular compound can permit access to new properties such as magnetochiral dichroism and chiral magnetostructural effects with potential applications in magnetooptical devices.[1] Luminescence is another significant property that is attracting an increasing interest because of its potential applications in optical storage,[2] switching,[3] and sensing.[4] Molecular systems that can exhibit this interesting all-embracing function, that is, the coexistence of chirality, magnetism, and photoluminescence, are particularly appealing.

Polynuclear transition-metal complexes have been investigated for their photoluminescence properties because of their application in the area of luminescent materials, especially the compounds with d^{10} metal centers.[5] These systems can also display magnetic properties when they contain a paramagnetic d^n ion. However, quenching of the d^{10} metal luminiscence by metal-promoted energy and/or electron transfer may occur depending on the nature of the paramagnetic d^n metal.[5] Compounds of this type involving 4d and 5d metal ions have been scarcely reported despite exhibiting more diffuse magnetic orbitals, which could enhance the magnetic interactions of 3d analogues.[6] In this context, the Re^{IV} ($5d^3$) ion is very appealing because of the high magnetic anisotropy that the mononuclear Re^{IV} complexes exhibit.[7]

Most of the polynuclear Re^{IV} compounds studied so far are based on mononuclear Re^{IV} complexes with potential bridging ligands, such as oxalate (ox^{2-}),[7,8] cyanide (CN^-),[9] or malonate (mal^{2-}),[10] which have afforded a family of metalloligands that have been used as ligands toward both transition-metal ions and lanthanides,[11] making them excellent building blocks for the synthesis of molecule-based magnetic materials.[7−9] In comparison, the use of Re^{IV} complexes with aromatic polyimines, such as $[ReCl_4(bpym)]$ (bpym = 2,2′-bipyrimidine) and $[ReCl_5(pyz)]^-$ (pyz = pyrazine), has been much less explored.[12−14] Nevertheless, the simultaneous use of $[ReCl_4(bpym)]$ and $[ReCl_5(pyz)]^-$ as metalloligands toward fully solvated metal ions seems to be a rather tempting strategy to get heteropolynuclear systems displaying versatile structures and multiple properties.

Herein we present our first result based on this new synthetic route, which provided us with a new 1D complex of the formula $\{Cu^{I}Re^{IV}Cl_4(\mu\text{-}Cl)(\mu\text{-}pyz)[Re^{IV}Cl_4(\mu\text{-}bpym)]\}_n\cdot n MeNO_2$ (**1**; Figure 1), where the chirality, magnetic ordering, and photoluminescence properties coexist. **1** is an example of a chiral compound based on the Re^{IV} ion displaying spin canting and photoemission.

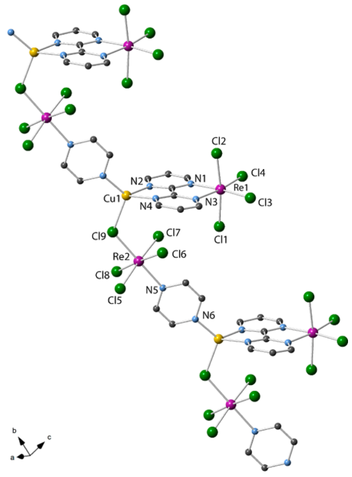

Figure 1. View of a fragment of the neutral chain in **1**. Hydrogen atoms and solvent molecules have been omitted for clarity.

The stoichiometric reaction of $NBu_4[ReCl_5(pyz)]$ (NBu_4^+ = tetra-*n*-butylammonium cation), $[ReCl_4(bpym)]$, and $Cu(CF_3SO_3)$ (1:1:1 molar ratio) in a $CH_2Cl_2/MeNO_2/MeCN$ mixture of solvents gives brown-orange crystals of **1** after slow evaporation at room temperature (see the Supporting

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Information, SI). **1** crystallizes in the noncentrosymmetric $P2_12_12_1$ space group of the orthorhombic system. The circular dichroism (CD) spectrum confirmed its chirality and also the fact that **1** is an enantiomerically pure Cu^I-Re^{IV} species (Figure S1 in the SI).

The structure of **1** consists of neutral bimetallic $Cu^IRe^{IV}_2$ branched chains with alternating chloro and pyz bridges growing along the crystallographic *b* axis and bpym bridges at the branches (Figure 1). $MeNO_2$ lattice solvent molecules are also present, lying in the voids between the chains. The intrachain Re⋯Cu distances through pyz and bpym are 6.89(1) and 5.62(1) Å, respectively, whereas that across the single chloro bridge is 4.11(1) Å. The intrachain Re⋯Re distance is ca. 6.47 Å, and the Re−Cl−Cu angle is 120(1)°.

The two crystallographically independent Re1 and Re2 atoms from the $[ReCl_4(bpym)]$ and $[ReCl_5(pyz)]^-$ units of **1** are six-coordinate in slightly distorted octahedral surroundings, which are built by four (Re1) and five (Re2) chloro atoms and two bpym (Re1) and one pyz (Re2) nitrogen atoms. No significant differences are observed in the Re−Cl and Re−N bond lengths, with the average values being 2.34(1) and 2.09(1) Å, respectively, which are very similar to those previously reported for polynuclear complexes containing these mononuclear Re^{IV} complexes.[13,14] Interestingly, the pyz ring is not oriented along the Cl−Re−Cl equatorial interbond directions, but it almost bisects them. The dihedral angle between the mean plane of the pyz ring and the Re2−Cl6−Cl8−Cl9 plane is 141(1)°. Moreover, the pyz ring exhibits a relevant offset from the plane bisecting the bpym ligand, defined by the Re1−Cu1−Re2 set of atoms. The dihedral angle between the pyz ring and that plane is 10(1)° (see Figure S2 in the SI). Because of the presence of only one type of enantiomer, the resulting branched chain of **1** is chiral. That orientation is most likely stabilized by intrachain Cl⋯H−C(pyz) interactions.

The four-coordinate, distorted tetrahedral environment at the Cu1 atom of **1** is built by two nitrogen atoms (N2 and N4) from the bpym ligand of the $[ReCl_4(bpym)]$ terminal unit and one nitrogen atom (N6a) from one bis(monodentate) pyz ligand and one chloro atom (Cl9) from the two adjacent $[ReCl_5(pyz)]^-$ bridging units. The Cu−N bond lengths involving the bpym ligand (average value of ca. 2.07(4) Å for Cu1−N2 and Cu1−N4) are somewhat longer than that of the pyz ligand [1.92(5) Å for Cu1−N6a], with all of them being very close to those found for the Cu^I ion in a similar tetrahedral geometry.[15] The neutral chiral branched chains growing along the *b* axis of **1** have an overall rack-type architecture,[16] where the $[Re^{IV}Cl_4(bpym)]$ units, playing the role of platforms, are linked to the Cu^I ions of the linear $[Cu^IRe^{IV}Cl_5(pyz)]_n$ motif acting as a rung. In addition, two neighboring chains of identical chirality related by a screw axis are further interconnected through edge-on Cl⋯π interactions, involving the Cl4 atom and the pyrimidine rings of the bpym ligand from adjacent $[ReCl_4(bpym)]$ peripheral units [Cl4b⋯C3 = 3.221(9) Å], in such a way that they constitute a molecular zipper (Figure S3 in the SI). The shortest interchain Re⋯Re and Re⋯Cu distances are 6.371(8) and 6.294(8) Å, respectively. In the crystal of **1**, additional Cl⋯Cl contacts between different zippers [Cl2⋯Cl3 = 3.60(1) Å] occur. A 3D supramolecular framework results through weak edge-on Cl⋯π interactions involving Cl5 and Cl6 atoms and the pyz rings (Figure S4 in the SI).

The direct-current (dc) magnetic properties of **1** under the form of a χ_MT versus T plot are shown in Figure 2. At room temperature, the χ_MT value is ca. 2.44 $cm^3\ mol^{-1}\ K$, which is somewhat smaller that that expected for two magnetically isolated Re^{IV} ($5d^3$, $t_{2g}{}^3$, $S_{Re} = {}^3/_2$) ions,[7−14] with the Cu^I ($3d^{10}$, $t_{2g}{}^6e_g{}^4$, $S_{Cu} = 0$) ion being diamagnetic. Upon cooling, χ_MT values decrease first slowly and then faster, reaching a minimum value of 1.15 $cm^3\ mol^{-1}$ K at 10 K. Then χ_MT values exhibit an abrupt increase and a further decrease at lower temperatures. This increase of χ_MT is more pronounced at lower dc magnetic fields (see the inset in Figure 2) because saturation effects are thus minimized.

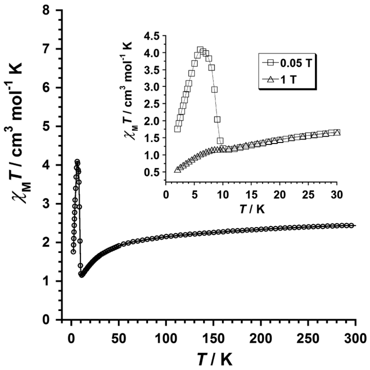

Figure 2. χ_MT versus T plot for **1**. The inset shows the temperature and field dependences of the χ_MT product in the temperature range 2−30 K and under the indicated dc fields. The solid lines are only guides for the eye.

The magnetic behavior of **1** in the high-temperature range is governed by the zero-field splitting of the Re^{IV} ions and/or the antiferromagnetic interactions between these 5d metal ions (Figure S5 in the SI). The abrupt increase of the χ_MT values in the low-temperature domain can be attributed to spin canting because of the weak intra- and interchain interactions that are mainly transmitted through Cl⋯Cl contacts. Indeed, a characteristic hysteresis loop of weak ferromagnets is observed at 2.0 K for **1** with values of the remnant magnetization (M_r) and coercive field (H_c) of 0.065 μ_B and 1200 G, respectively (Figure S6 in the SI). The great anisotropy of the Re^{IV} ion and the occurrence of a noncentrosymmetric space group in **1** account for this phenomenon, as previously observed in related Re^{IV} systems.[12b,17] Evaluation of the canting angle (α) can be performed through the equation $\sin\alpha = M_w/M_s$, where M_w is the magnetization induced by a very weak magnetic field, as observed in the FCM curve using $H = 100$ G (see Figure S7 in the SI), and M_s is the saturation magnetization. Although no saturation is reached in the M versus μ_0H plot (M being the molar magnetization and H the applied dc field; Figure S6 in the SI), a value of 1.1° for α can roughly be estimated by assuming extrapolated values of M_s and $M_w \approx 0.07\ \mu_B$ at 2.0 K. This α value for **1** is within the range of those usually reported for Re^{IV}-based compounds behaving as weak ferromagnets.[12b,17]

Next, the alternating-current (ac) magnetic properties of **1** in zero dc field were also investigated in the temperature range 2.0−18.0 K and with a variable frequency of the 3.5 G ac field (ν = 500−1000 Hz). A sharp peak was observed at ca. 10 K in both the $\chi_M{}'$ and $\chi_M{}''$ versus T plots (Figure S8 in the SI), and no prominent frequency dependence was observed, confirming the occurrence of long-range magnetic ordering in **1**.

Finally, we have investigated the excitation and emission spectra of an acetonitrile solution of **1** by using λ_{exc} = 295 nm and setting the absorbance at 0.20. **1** shows a strong emission band at λ_{em} = 355 nm (Figure 3) of higher intensity and wavelength than the emission displayed by the $[Cu^ICl(bpym)]$ model compound

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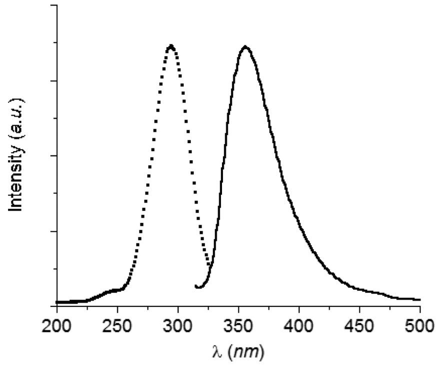

Figure 3. Excitation (dashed line) and emission (solid line) spectra for **1** collected in CH_3CN at room temperature. The concentration of **1** was adjusted to $A = 0.20$ at $\lambda = 295$ nm.

(see Figure S10 in the SI). The observed luminescence in **1** was unexpected because of the presence of the Re^{IV} ion, a paramagnetic center, which commonly would act as a quencher of emission by the electron-transfer process. The luminescence in **1** is then assigned to a $\pi^* \rightarrow \pi$ transition of the bpym bridging molecule, similar to other aromatic nitrogen heterocycles found to exhibit identical intense emission bands at $\lambda_{em} = 340$ nm in acetonitrile.[18]

In summary, **1** is a chiral chain that exhibits magnetic ordering below 10 K through spin canting. In addition, **1** displays fluorescence emission at $\lambda_{em} = 355$ nm. It is well-known that Cu^I systems generally show photoluminescence properties both in the solid state and in solution; a typical Cu^I emission appears in the visible range in the solid state and in solution as well,[19] but no luminescence from the Cu^I centers was detected for **1**. The persistence and mandate of the fluorescence of the bpym ligand in **1** even though coordinated to the paramagnetic quencher Re^{IV} ion and the absence of an emission band from the Cu^I chromophore are rather complicated, and their investigation is still underway. In any case, the coexistence of chirality, magnetic ordering, and luminescence in **1** reveals that our Re^{IV}-based synthetic route, by using two different Re^{IV} precursors simultaneously, constitutes an alternative and straightforward procedure to prepare new multifunctional *n*d−5d systems in the near future.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data in CIF format, preparation of **1**, Table S1, and Figures S1−S10. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00502.

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Notes

The authors declare no competing financial interest.

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