Inorganic Chemistry
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pubs.acs.org/IC

Enhancing the Magnetic Coupling of Oxalato-Bridged $Re^{IV}{}_2M^{II}$ (M = Mn, Co, Ni, and Cu) Trinuclear Complexes via Peripheral Halide Ligand Effects

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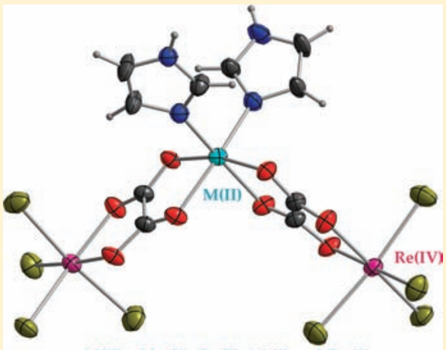
Supporting Information



M(II) = Mn (1), Co (2), Ni (3) and Cu (4)

ABSTRACT: Four heterotrinuclear $Re^{IV}{}_2M^{II}$ compounds of general formula $(NBu_4)_2[\{Re^{IV}Br_4(\mu\text{-ox})\}_2M^{II}(Him)_2]$ [$NBu_4{}^+$ = tetra-*n*-butylammonium cation, ox = oxalate, Him = imidazole; M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)] have been synthesized by using the novel mononuclear complex $[Re^{IV}Br_4(ox)]^{2-}$ as a ligand toward divalent first-row transition metal ions in the presence of imidazole. Compounds **1**−**4** are isostructural complexes whose structure contains discrete trinuclear $[\{Re^{IV}Br_4(\mu\text{-ox})\}_2M^{II}(Him)_2]^{2-}$ anions and bulky $NBu_4{}^+$ cations. The Re and M atoms are six-coordinated: four peripheral bromo and two oxalate-oxygens (at Re), and two cis-coordinated imidazole molecules and four oxygen atoms from two oxalate ligands (at M), build distorted octahedral surroundings. Two peripheral $[ReBr_4(ox)]^{2-}$ units act as bidentate ligands through the oxalate group toward the central $[M^{II}(Him)_2]$ fragment affording the trinuclear entities. The values of the intramolecular Re···M separation are 5.62(1) (**1**), 5.51(1) (**2**), 5.46(1) (**3**), and 5.55(1) Å (**4**). Magnetic susceptibility measurements on polycrystalline samples of **1**−**4** in the temperature range of 1.9−300 K show the occurrence of intramolecular antiferro- [$J = -1.1$ cm^{-1} (**1**)] and ferromagnetic interactions [$J = +3.9$ (**2**), +19.7 (**3**), and +14.4 cm^{-1} (**4**)], the Hamiltonian being defined as $\hat{H} = -J[\hat{S}_M(\hat{S}_{Re1} + \hat{S}_{Re2})]$. The larger spin delocalization on the oxalato bridge in **1**−**4** when compared to the trinuclear $Re^{IV}{}_2M^{II}$ complexes with chloro instead of bromo as peripheral ligands (**1′**−**4′**) accounts for the strengthening of the magnetic interactions in **1**−**4** [$J = -0.35$ (**1′**), +14.2 (**3′**), and +7.7 cm^{-1} (**4′**)]. An incipient frequency dependence of the out-of-phase ac signals of **3** at very low temperatures is reminiscent of a system with slow relaxation of the magnetization, a phenomenon characteristic of single-molecule magnet behavior.

■ INTRODUCTION

The complex as ligand strategy is one of the safest preparative routes of nuclearity-tailored heterometallic magnetic systems. It consists of using a stable paramagnetic unit as a ligand toward either fully solvated metal ions or preformed metal complexes whose coordination sphere is partially blocked. Some representative examples are the tris(oxalato)chromate(III),[1] tri-,[2,3] tetra-,[4] hexa-,[5] hepta-,[6] and octacyanometallate entities[7] and polyoxamate-containing metal complexes.[8] All of these paramagnetic precursors have in common the anionic character, the relative reluctance to exchange ligands, and the remarkable ability of the oxalate,[9] cyanide,[10] and oxamate[11] groups to mediate strong magnetic interactions when acting as bridges in the resulting polynuclear compounds. Most of these studies concern 3d−3d′ and 3d−4f mixed systems, whereas the 3d−4d and 3d−5d ones have received comparatively less attention. In particular, magnetostructural studies on heterometallic systems containing second and third row transition elements seem very appealing because of the opportunity they provide to investigate the effects of the spin−orbit coupling and covalency effects (more diffuse character of the 4d and 5d orbitals versus the 3d ones) on the magnetic properties. Illustrative examples are the building blocks $[Ru(ox)_3]^{3-}$,[12] $[ReCl_4(ox)]^{2-}$ (ox = oxalate),[13] *trans*-$[RuL_x(CN)_2]^-$ [L = dianion of *N*,*N*′-ethylenebis(salicylideneimine) or acetylacetonate with x = 1 and 2, respectively],[14] $[Re(triphos)(CN)_3]^-$ [triphos =1,1,1-tris(diphenylphosphinoethyl)methane],[15] and *trans*-$[ReCl_4(CN)_2]^{2-}$,[16] whose use as ligands has afforded a good number of heterometallic systems, with some of them exhibiting slow relaxation of the magnetization.

The stable and paramagnetic building block $[ReCl_4(ox)]^{2-}$ is especially appealing for the following reasons: (i) it has three unpaired electrons; (ii) it is quite reluctant to the ligand substitution; (iii) its terminal oxalate group can coordinate to

Received: March 15, 2011
Published: May 25, 2011

dx.doi.org/10.1021/ic200531s | *Inorg. Chem.* 2011, 50, 5731–5739

Table 1. Crystallographic Data for $(NBu_4)_2[\{Re^{IV}Br_4(\mu\text{-ox})\}_2M^{II}(Him)_2]$ with M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)

	compd			
	1	**2**	**3**	**4**
empirical formula	$C_{42}H_{80}Br_8N_6O_8Re_2Mn$	$C_{42}H_{80}Br_8N_6O_8Re_2Co$	$C_{42}H_{80}Br_8N_6O_8Re_2Ni$	$C_{42}H_{80}Br_8N_6O_8Re_2Cu$
fw	1863.74	1867.73	1867.51	1872.34
space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$
a, Å	11.1814(4)	11.202(1)	11.220(1)	11.2120(6)
b, Å	16.5320(4)	16.414(1)	16.3950(1)	16.3081(6)
c, Å	35.051(1)	34.732(4)	34.675(3)	34.781(1)
β, deg	96.651(1)	96.032(5)	95.935(5)	96.301(2)
V, Å^3	6435.5(3)	6350.1(1)	6344.5(9)	6321.2(5)
Z	4	4	4	4
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.924	1.954	1.955	1.967
T, K	293	293	293	293
μ(Mo Kα), mm^{-1}	8.958	9.141	9.185	9.257
R [a]	0.0371	0.0363	0.0327	0.0319
R_w [b]	0.0819	0.0870	0.0791	0.0686

[a] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_{w2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/[(w(F_o^2)^2\}]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [F_o^2 + 2F_c^2]/3$, a = 0.0334 (**1**), 0.0374 (**2**), 0.0362 (**3**), 0.0274 (**4**), and b = 18.37 (**1**), 22.04 (**2**), 20.00 (**3**), and 15.43 (**4**).

metal ions (or preformed complexes with easy leaving ligands) through its free carbonyl-carbon atoms adopting the bis-bidentate bridging mode; (iv) it has large magnetic anisotropy arising from spin–orbit coupling (second-order effects) associated with the third row transition metal ion. Indeed, this building block has been incorporated into a tetranuclear $[Re^{IV}{}_3Ni^{II}]$ compound that exhibits single-molecule magnet behavior at low temperature[13g,j] and also in low-dimensional homo- and hetero-bimetallic compounds with ferro-[13d,h] and anti-ferromagnetic interactions[13a,c,e,f,i] across the bridging oxalate.

Having in mind the diffuse character of the 5d orbitals and studying the influence of the peripheral ligands on the magnetic coupling between Re(IV) and 3d metal ions across the bridging oxalate, we have explored the use of the mononuclear species $(NBu_4)_2[ReBr_4(ox)]$ (**1**) (NBu_4^+ = tetra-*n*-butylammonium cation) as a ligand toward several divalent first-row transition metal ions whose coordination sphere is partially blocked with two imidazole ligands. In this work, we report the preparation and magnetostructural characterization of four oxalato-bridged trinuclear compounds of formula $(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2M^{II}(Him)_2]$ with Him = imidazole and M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**). An enhancing of the intramolecular magnetic coupling is achieved in this series when compared with the parent compounds which have terminal chloro instead of bromo atoms,[13h] the different electronegativity of the halogeno atoms accounting for this effect.

EXPERIMENTAL SECTION

Materials. All starting chemicals and solvents were purchased from commercial sources and used without further purification. The mononuclear precursor $(NBu_4)_2[ReBr_4(ox)]$ was prepared following the procedure described for the parent $(PPh_4)_2[ReBr_4(ox)]$ (PPh_4^+ = tetraphenylphosphonium cation) by using NBu_4Cl instead of PPh_4Cl as the precipitating agent.[17]

Synthesis of the Complexes. *$(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2M(Him)_2]$ [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu(**4**)].* Single crystals of **1**–**4** were prepared by slow diffusion in an H-shaped tube at room temperature of the concentrated solutions of corresponding chemicals. Only the details of the synthesis of **1** are provided as an illustrative example. Solid $(NBu_4)_2[ReBr_4(ox)]$ (107.9 mg (0.10 mmol)) dissolved in MeCN (2 mL) was introduced in one arm, whereas a mixture of $Mn(NO_3)_2 \cdot 4H_2O$ (12.60 mg, 0.05 mmol) and Him (6.80 mg, 0.05 mmol) dissolved in 2-propanol (1 mL) was placed in the other arm. The tube was filled by careful addition of 2-propanol in both arms and allowed to diffuse at room temperature. In a few days, X-ray quality crystals as green-yellowish hexagonal plates appeared in the bridge of the tube. The diffusion was completed within 2 weeks. Yield: ca. 60%. The nitrate salts of cobalt(II) and nickel(II) as hexahydrates and that of copper(II) as trihydrate were the sources of the 3d metal ions for **2**–**4**, respectively. Orange (**2**) and green (**3** and **4**) hexagonal plates were grown, the yields being 55 (**2**), 70 (**3**), and 75% (**4**). Anal. Calcd for $C_{42}H_{80}N_6Br_8O_8MnRe_2$ (**1**): C, 27.07; H, 4.33; N, 4.51. Found: C, 27.23; H, 4.31; N, 4.48%. Anal. Calcd for $C_{42}H_{80}N_6Br_8O_8CoRe_2$ (**2**): C, 27.01; H, 4.32; N, 4.50. Found: C, 27.25; H, 4.23; N, 4.44%. Anal. Calcd for $C_{42}H_{80}N_6Br_8O_8NiRe_2$ (**3**): C, 27.01; H, 4.32; N, 4.50. Found: C, 27.36; H, 4.30; N, 4.40%. Anal. Calcd for $C_{42}H_{80}N_6Br_8O_8CuRe_2$ (**4**): C, 26.94; H, 4.31; N, 4.49. Found: C, 27.12; H, 4.27; N, 4.40%. IR/cm^{-1}: peaks associated with the oxalato ligand appear at 1696 vs, 1664 vs, 805 s (**1**), 1695 vs, 1665 vs, 806 s (**2**), 1691 vs, 1662 vs, 809 s (**3**), and 1697 vs, 1686 vs, 805 s (**4**).

Physical Measurements. Elemental analyses (C, H, N) were performed on a CE Instruments EA 1110 CHNS analyzer. A 2:1 Re/M [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)] molar ratio was found by means of a Philips XL-30 scanning electron microscope (SEM) equipped with a system of X-ray microanalysis from the Central Service for the Support to Experimental Research (SCSIE) at the University of València. Infrared spectra were recorded with a Nicolet 320 FT-IR spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Magnetic measurements on polycrystalline samples of **1**–**4** were carried out with a Quantum Design SQUID magnetometer in the temperature range of 1.9–300 K and under an applied magnetic field of 1 T in the high-temperature range and 250 G at low temperatures in order to avoid any problem of magnetic saturation. Magnetization measurements of **1**–**4** were performed at 1.8 K in the 0–5 T field range starting at zero field. Alternating current magnetic susceptibility measurements were performed with an oscillating field of ±1 G and in an operating frequency range of 1–1000 Hz. All data were corrected for the diamagnetic contributions of the constituent atoms (estimated from Pascal's constants)[18] as well as for the sample holder.

X-ray Data Collection and Structure Refinement. Crystals of dimensions 0.03 × 0.10 × 0.12 (**1**), 0.08 × 0.12 × 0.14 (**2**), 0.08 × 0.12 × 0.18 (**3**), and 0.10 × 0.10 × 0.12 mm^3 (**4**) were used for data collection on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo Kα radiation. A summary of the crystallographic data and structure refinement is given in Table 1. The index ranges of data collection were $-15 < h < +15$, $-23 < k < +23$, $-49 < l < +48$ for **1**, $-15 < h < +14$, $-20 < k < +22$, $-46 < l < +46$ for **2**, $-14 < h < +14$, $-21 < k < +21$, $-45< l < +45$ for **3**, and $-14 < h < +14$, $-21 < k < +19$, $-45 < l < +46$ for **4**. Of the 9235 (**1**), 8236 (**2**), 7697 (**3**), and 7886 (**4**) measured independent reflections in the θ ranges of 1.17–29.87° (**1**), 2.21–28.74° (**2**), 1.18–28.12° (**3**), and 1.18–28.36° (**4**), 7086 (**1**), 6482 (**2**), 6204 (**3**), and 5949 (**4**) have $I > 2.0\ \sigma(I)$. All the measured independent reflections were used in the analysis. The data for compounds **1**–**4** were processed through the SAINT[19] reduction and SADABS[20] absorption software.

The structures of **1**–**4** were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL software package.[21] All non-hydrogen atoms were refined anisotropically, with the exception of some carbon atoms of the tetra-*n*-butylammonium cations with high thermal disorder. The hydrogen atoms were set in calculated positions and refined as riding atoms. Full-matrix least-squares refinements on $|F|^2$, carried out by minimizing the function $R_w(|F_o| - |F_c|)^2$, reached convergence with values of the discrepancy indices R/R_w for all data of 0.0572/0.0898 (**1**), 0.0519/0.0934 (**2**), 0.0455/0.0872 (**3**), and 0.0496/0.0777 (**4**) [those listed in Table 1 correspond to the data with $I > 2.0\ \sigma(I)$]. The final Fourier difference map showed maximum and minimum height peaks of 1.288 and −0.768 e $Å^{-3}$ for **1**, 1.289 and −0.849 e $Å^{-3}$ for **2**, 1.189 and −0.698 e $Å^{-3}$ for **3**, and 0.869 and −0.746 e $Å^{-3}$ for **4**. The values of the data/parameters are 9235/293 (**1**), 8236/293 (**2**), 7697/288 (**3**), and 7886/288 (**4**), whereas those of the goodness-of-fit are 1.092 (**1**), 1.076 (**2**), 1.102 (**3**), and 1.082 (**4**). Final geometrical calculations and graphical manipulations were carried out with the PARST97[22] and DIAMOND[23] programs. Selected bond distances and angles for **1**–**4** are listed in Table 2. Crystallographic data for the structure reported in this contribution has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 784922 (**1**), 784923 (**2**), 784924 (**3**), and 784925 (**4**). Copies of the data can be obtained free of charge on application to CCDC, Cambridge, U.K. (http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

Description of the Structures of $(NBu_4)_2[\{ReBr_4(\mu\text{-ox})\}_2M(Him)_2]$ [M = Mn (1), Co (2), Ni (3), and Cu(4)]. Compounds **1**–**4** are isostructural compounds whose structure is made up of $[\{ReBr_4(\mu\text{-ox})\}_2M(Him)_2]^{2-}$ trinuclear anions [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)] and tetra-*n*-butylammonium cations which are held by electrostatic forces, hydrogen bonds, and van der Waals interactions (see below). A perspective drawing of the anionic unit with the atomic numbering scheme is shown in Figure 1. Each $[\{ReBr_4(ox)\}_2M(Him)_2]^{2-}$ unit contains one central M(II) cation atom and two peripheral Re(IV) centers which are interlinked through two bis-bidentate oxalate ligands. Compounds **1**–**4** are isostructural species with the previously reported parent compounds with peripheral chloro ligands (compounds **1′**–**4′** hereafter) instead of the bromo ones.[13h]

Each rhenium atom in **1**–**4** exhibits a somewhat distorted octahedral environment which is built by two oxygen atoms from

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 1–4 [a]

	1	2	3	4
Re(1)–O(1)	2.064(3)	2.085(3)	2.088(3)	2.089(3)
Re(1)–O(2)	2.080(3)	2.078(3)	2.080(3)	2.066(3)
Re(1)–Br(2)	2.4219(6)	2.4505(6)	2.4560(6)	2.4421(6)
Re(1)–Br(3)	2.4477(5)	2.4509(5)	2.4507(5)	2.4618(5)
Re(1)–Br(4)	2.4799(5)	2.4826(6)	2.4842(6)	2.4952(6)
Re(1)–Br(1)	2.4838(6)	2.4852(6)	2.4842(6)	2.4946(6)
M(1)–N(1)	2.160(4)	2.061(4)	2.029(4)	1.983(3)
M(1)–O(4)	2.220(3)	2.140(3)	2.101(3)	2.350(3)
M(1)–O(3)	2.253(3)	2.170(3)	2.133(3)	2.067(3)
O(1)–Re(1)–O(2)	78.59(10)	78.63(11)	78.71(11)	78.54(10)
O(1)–Re(1)–Br(2)	172.57(8)	172.37(8)	172.28(8)	171.76(7)
O(2)–Re(1)–Br(2)	94.29(8)	94.06(8)	93.96(8)	93.51(8)
O(1)–Re(1)–Br(3)	91.08(7)	91.28(8)	91.28(8)	92.22(7)
O(2)–Re(1)–Br(3)	169.61(8)	169.82(8)	169.88(8)	170.66(8)
Br(2)–Re(1)–Br(3)	96.07(2)	96.07(2)	96.10(2)	95.773(19)
O(1)–Re(1)–Br(4)	89.13(9)	89.18(10)	89.32(10)	88.92(9)
O(2)–Re(1)–Br(4)	87.32(9)	86.54(10)	86.22(10)	86.44(9)
Br(2)–Re(1)–Br(4)	92.67(2)	92.61(2)	92.65(2)	92.75(2)
Br(3)–Re(1)–Br(4)	91.46(2)	92.03(2)	92.19(2)	92.11(2)
O(1)–Re(1)–Br(1)	85.92(9)	86.26(10)	86.02(10)	85.90(9)
O(2)–Re(1)–Br(1)	87.58(9)	88.46(10)	88.77(10)	89.08(9)
Br(2)–Re(1)–Br(1)	91.72(2)	91.38(2)	91.44(2)	91.89(2)
Br(3)–Re(1)–Br(1)	92.84(2)	92.26(3)	92.08(2)	91.61(2)
Br(4)–Re(1)–Br(1)	173.51(2)	173.81(2)	173.74(2)	173.74(2)
N(1)–M(1)–N(1a)	93.6(2)	93.5(2)	92.1(2)	92.3(2)
N(1)–M(1)–O(4a)	90.35(12)	91.84(13)	91.56(13)	91.03(12)
N(1)–M(1)–O(4)	102.54(13)	98.73(14)	97.68(14)	100.47(13)
O(4a)–M(1)–O(4)	161.24(15)	164.57(17)	166.70(16)	163.43(15)
N(1)–M(1)–O(3a)	164.7(1)	169.42(13)	171.19(13)	167.25(12)
O(4)–M(1)–O(3a)	92.1(1)	90.85(12)	90.57(11)	91.59(11)
N(1)–M(1)–O(3)	90.72(14)	90.61(15)	90.79(14)	91.56(14)
O(4)–M(1)–O(3)	74.4(1)	77.90(11)	79.80(11)	76.33(10)
O(3a)–M(1)–O(3)	88.95(17)	87.02(18)	87.60(17)	87.28(17)

[a] Symmetry code: (a) $-x + 1, y, -z + {}^1/_2$.

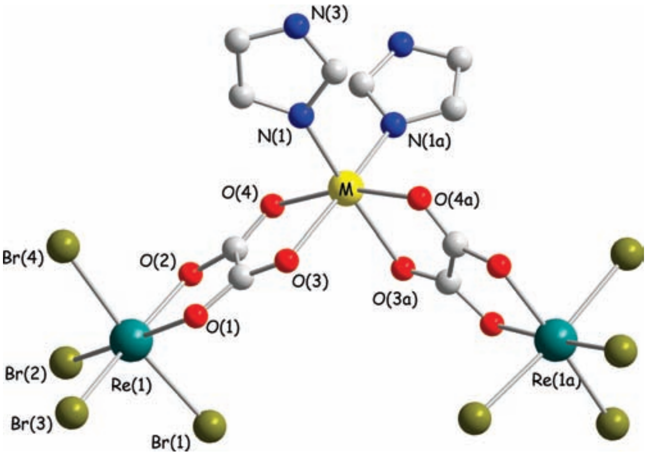


Figure 1. Perspective drawing of the heterotrinuclear unit of **1**–**4** [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)] showing the atom numbering of the non-carbon atoms. The hydrogen atoms have been omitted for clarity.

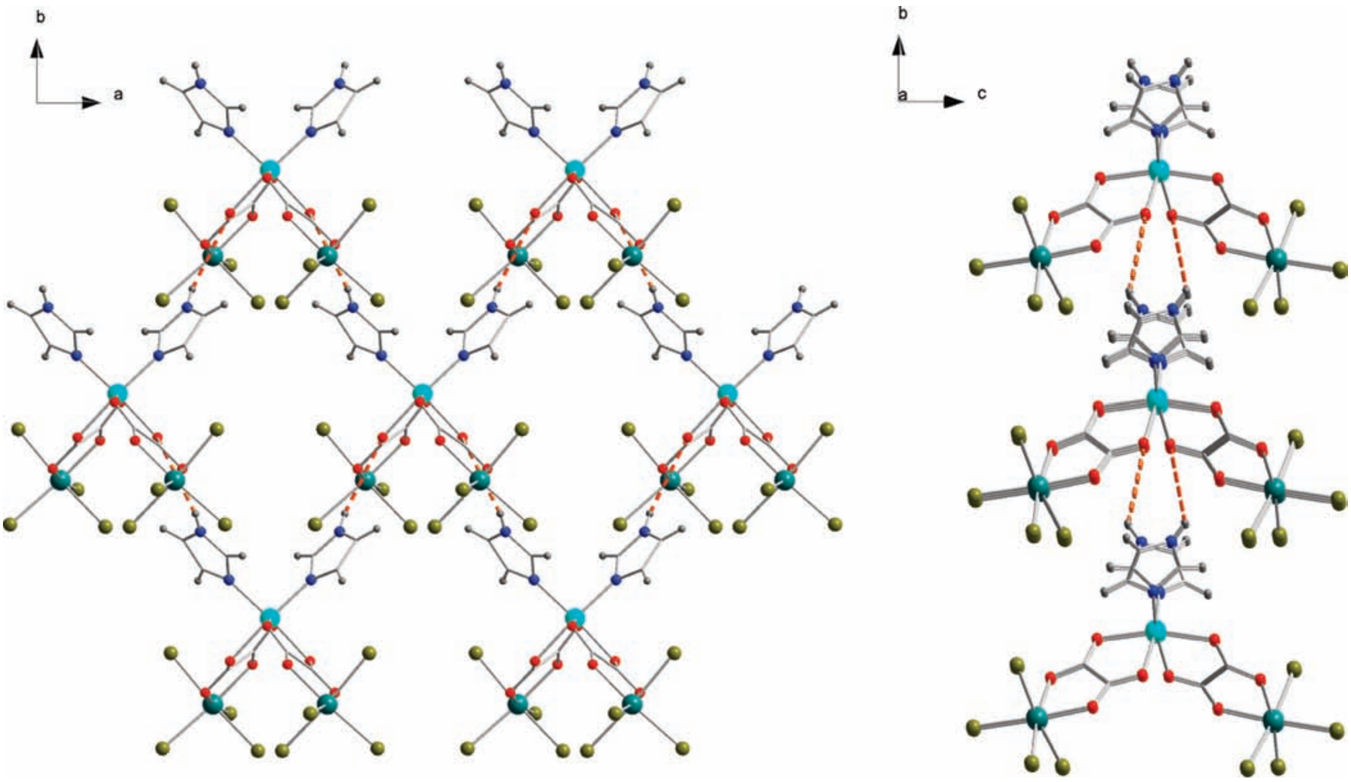


Figure 2. View along the *c*- (left) and *a*-axes (right) of a fragment of the layer formed by the interconnection of the $[\{ReBr_4(\mu\text{-}ox)\}_2M(Him)_2]^{2-}$ units through N−H···O type interactions in **1**−**4**. Color code: sky blue (M), gray (Re), deep blue (N), red (O), and green (Br).

a bridging oxalate and four peripheral bromo ligands. The small bite angle of the oxalate is the main cause of the distortion, the value of the angle subtended by this ligand at the rhenium atom [O(1)−Re(1)−O(2)] varying in the range from 78.6(1) (**2**, **3**) to 78.7(1)° (**1**, **4**). No significant differences were found in the Re−Br [values covering the range from 2.4466(5) (**4**) to 2.4866(6) Å (**1**)] and Re−O [minimum and maximum values being 2.059(3) (**4**) and 2.093(3) Å (**4**), respectively] bond distances in this family, and their average values agree with those found for the mononuclear species $(PPh_4)_2[ReBr_4(ox)]$, *cis*-$(EPh_4)_2[ReBr_2(ox)_2]$ (E = P and As) in the literature, and $[ReBr_4(bpym)]$ (bpym =2,2′-bipyrimidine).[17,24] The best equatorial plane around the rhenium atom in **1**−**4** is defined by the O(1)O(2)Br(2)Br(3) set of atoms, the largest deviation from planarity being 0.034(1) (**1**), 0.037(2) (**2**), and 0.0413(2) (**3**) Å at O(1) and 0.036(2) Å at O(2) in compound **4**. The Re atom effectively lies in this plane in the four compounds, the maximum deviation being 0.011(1) Å in **1**. The values of the dihedral angle between the equatorial plane and that of the oxalate group are 4.5(2) (**1**), 5.2(2) (**2**), 5.2(2) (**3**), and 5.6(2)° (**4**) [values varying between 4.78(7) and 5.6(2)° in **1′**−**4′**].

The M atoms are also six-coordinated with four oxalate oxygen atoms from two $[ReBr_4(ox)]^{2-}$ units and two imidazole nitrogen atoms from two terminal imidazole ligands in cis position, building somewhat distorted octahedral surroundings. As observed at the Re atom, the main source of distortion of the ideal octahedral geometry around the M atom is due to the reduced bite angle of the oxalate [the values of the O(3)−M(1)−O(4) angle covering the range from 74.6(1) (**1**) to 79.7(1)° (**3**)]. The M atom lies on a 2-fold axis. The values of the M−N(imidazole) bond length decreases in **1**−**4** when going from manganese(II) [2.165(4) Å] to copper(II) [1.977(4) Å] as expected because of the reduction of the ionic radii of the divalent first-row transition metal ions from left to right in the periodic system. They are very close to those observed in **1′**−**4′**.[13h] The $[ReBr_4(ox)]^{2-}$ unit exhibits quasi symmetrical (**1**−**3**) and asymmetrical (**4**) chelating modes of the oxalato at the M atom [$M-O_{ox}$ bond distances of 2.241(3) and 2.255(3) Å (**1**), 2.133(3) and 2.095(3) Å (**2**), 2.138(3) and 2.168(3) Å (**3**), and 2.353(3) and 2.059(3) Å (**4**)]. The values of the Re···M separation across the oxalate bridge are 5.62(1) (**1**), 5.51(1) (**2**), 5.46(1) (**3**), and 5.55(1) Å (**4**). Both the oxalate and Him ligands are planar. The minimum/maximum values of the dihedral angles of the ox/ox, Him/Him, and ox/Him pairs in **1**−**4** are 71.7(1) (**1**)/88.7(1)° (**1**), 71.7(3) (**1**)/77.0(3)° (**4**), and 83.7(2) (**1**)/86.9(2)° (**3**), respectively. The bond lengths and angles with the planar oxalate ligands are as expected, and those of the imidazole ring agree with the parameters reported for the free imidazole at 150 °C.[25]

The heterometallic trinuclear units of **1**−**4** are interconnected through weak N−H···O hydrogen bonds [the donor···acceptor N(3)···O(1b) distances being 2.937(6) (**1**), 2.984(7) (**2**), 2.993(6) (**3**), and 3.020(5) (**4**); $b = -x + {}^3/_2, y + {}^1/_2, -z + {}^1/_2$] leading to anionic layers which grow in the *ab* plane (see Figure 2) and which are separated from each other by organic layers of tetra-*n*-butylammonium cations. Weak $C-H\cdots O_{ox}$ type interactions between the trinuclear units occur within the inorganic layers. The shortest intermolecular Br···Br distances are 5.60(1) (**1**), 5.55(1) (**2**), 5.52(1) (**3**), and 5.52(1) Å (**4**), values which are beyond the sum of the van der Waals radii. The organic NBu_4^+ cation exhibits its usual tetrahedral shape, and,

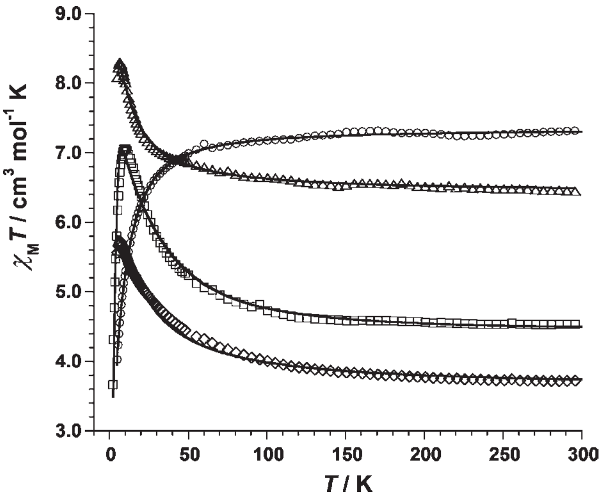


Figure 3. Thermal variation of the $\chi_M T$ product for **1** (○), **2** (Δ), **3** (□), and **4** (◇). The solid lines are the best-fit curves (see text).

interestingly, each cation interacts with the $[\{ReBr_4(ox)\}_2M(Him)_2]^{2-}$ units via very weak C−H···Br type contacts.

Magnetic Properties of 1−4. The magnetic properties for this family of complexes are shown in Figure 3 under the form of $\chi_M T$ vs T plot (χ_M being the magnetic susceptibility per $Re^{IV}{}_2M^{II}$ heterotrinuclear unit). At room temperature, the values of $\chi_M T$ are 7.4 (**1**), 6.4 (**2**), 4.5 (**3**), and 3.7 cm^3 mol^{-1} K (**4**). They are all as expected for one M(II) [$\chi_M T$ = 4.375 (M = Mn), 1.875 (M = Co), 1.0 (M = Ni), and 0.375 cm^3 mol^{-1} K (M = Cu) with S_{Mn} = 5/2, S_{Co} = 3/2, S_{Ni} = 1, and S_{Cu} = 1/2 and g_M = 2.0] and two Re(IV) ions magnetically isolated ($\chi_M T$ = ca. 2 × 1.60 = 3.2 cm^3 mol^{-1} K with S_{Re} = 3/2 and g_{Re} = 1.8−1.9),[13a] having in mind that an important orbital contribution is involved in the case of **2** because of the unquenched orbital momentum of the six-coordinated high-spin cobalt(II) ion. Upon cooling, $\chi_M T$ for **1** decreases first slowly and then faster, reaching a value of 4.0 cm^3 mol^{-1} K at 1.9 K. No maximum of the magnetic susceptibility is observed for **1** in the temperature range explored. Although most of the variation of $\chi_M T$ with T is due to the zero-field splitting of the Re(IV), a significant antiferromagnetic interaction between the Re(IV) and Mn(II) ions through the oxalato is supported by the value of $\chi_M T$ at low temperature (ca. 4.0 cm^3 mol^{-1}) which is certainly below the expected one for two Re(IV) and one Mn(II) magnetically isolated ($\chi_M T$ ca. 2 × 1.0 + 4.4 = 6.4 cm^3 mol^{-1} K). At that respect, it deserves to be noted that, at low temperatures, a magnetically isolated Re(IV) species can be regarded as an Ising-spin-1/2 system with a $\chi_{av} T$ value of ca. 1.0 cm^3 mol^{-1} K (χ_{av} being the average powder magnetic susceptibility with $g = g_\parallel = g_\perp$).[13a,26] The shape of the $\chi_M T$ vs T plot for **2**−**4** is typical of an overall ferromagnetic coupling. $\chi_M T$ for these three complexes continuously increases upon cooling to reach maximum values of 8.30 (**2**), 7.05 (**3**), and 5.75 cm^3 mol^{-1} K (**4**) at 7.0 (**2**), 10.0 (**3**), and 6.5 K (**4**), and it further decreases to 8.05 (**2**), 3.70 (**3**), and 5.60 cm^3 mol^{-1} K (**4**) at 1.9 K. The local anisotropy of the metal ions (zero-field splitting effects) and/or intermolecular antiferromagnetic interactions would account for the observed decrease of $\chi_M T$ in the very low temperatures domain.

In agreement with the trinuclear structure of **1**−**4**, and the above magnetic features, we have analyzed their magnetic data through the Hamiltonian of

$$\hat{H} = -J(\hat{S}_{Re1}\cdot\hat{S}_M + \hat{S}_{Re2}\cdot\hat{S}_M) + D_{Re1}[(\hat{S}^Z_{Re1})^2 - 5/4] + D_{Re2}[(\hat{S}^Z_{Re2})^2 - 5/4] + D_M[(\hat{S}^Z_M)^2 - n(n+2)/12] + \beta(\hat{S}_{Re1}g_{Re1} + \hat{S}_{Re2}g_{Re2} + \hat{S}_M g_M)\cdot H \quad (1)$$

where J is the exchange coupling parameter between each peripheral Re(IV) and the central M(II) local spins [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)], n is the number of unpaired electrons on M(II) [n = 5 (Mn), 3 (Co), 2 (Ni), and 1 (Cu)], $2D_{Re}$ and $2D_{Co}$ are the energy gaps between the M_S = ±3/2 and M_S = ±1/2 Kramers doublets [the zfs of Re(IV) and Co(II)], and D_{Ni} represents the energy gap between the sublevels M_S = 0 and M_S = ±1. The last term in eq 1 accounts for the Zeeman effects of the three metal ions. It deserves to be noted that this spin-Hamiltonian formalism is applicable only to metal ions with orbitally nondegenerate ground terms in an octahedral environment. This condition is not fulfilled by the Co(II) ion in **2** with a $^4T_{1g}$ ground term which is split into a sextet, a quartet, and a Kramers doublet by spin−orbit coupling. However, the fact that the orbital contribution to the $\chi_M T$ value in **2** should be lower than expected because of the distorted environment of the Co(II) at one hand and that the crystal field component of lower symmetry splits the T term giving a nondegenerate ground term would be at the origin of the successful application of eq 1 to this compound, affording physically reasonable values for the best-fit parameters (see Table 3). Finally, although the axial anisotropy is considered in the Hamiltonian used and with an effort to avoid the overparametrization because of the large number of variable parameters, we have assumed that $g = g_\parallel = g_\perp$ for the Re(IV) and M(II) ions. Due to the strong correlation observed in the fitting process between D_{Re} and D_M parameters, we have taken D_{Mn} and D_{Ni} as zero. Least-squares fit of the magnetic data of **1**−**4** by means of eq 1 through the VMPAG package[27] leads to the magnetic parameters listed in Table 3. As observed in Figure 3, the calculated curves reproduce well the experimental data in the whole temperature range investigated.

Table 3. Best-Fit Parameters for Compounds 1−4

	compd			
	1	**2**	**3**	**4**
J, cm^{-1}	−1.1	+3.9	+19.7	+14.4
$\lvert D_{Re}\rvert$, cm^{-1}	28.2	49.0	1.2	48.0
$\lvert D_M\rvert$, cm^{-1}	0	3.4	0	
g_{Re}	1.90	1.85	1.87	1.80
g_M	2.00	2.20	2.32	2.10
θ,[a] K			−1.5	−1.9
R [b] × 10^5	1.1	2.0	6.4	9.2

[a] Curie−Weiss term accounting for intermolecular interactions. [b] R is the agreement factor defined as $\Sigma_i\ [(\chi_M T)_i^{obsd} - (\chi_M T)_i^{calcd}]^2/[(\chi_M T)_i^{obsd}]^2$.

Prior to the discussion of the magnetic coupling parameters of **1**−**4** which are listed in Table 3, we comment on the meaning of the different values of the local zero-field splitting (D_{Re} and D_M) within this family. With respect to this, it deserves to be noted that the computed values of D_{Re} and D_M through the VMPAG program[27] are evaluated by considering that the local D values are collinear. This leads to an overestimation (that in some cases, it may be very large) of the D_S values of the different spin states. Of course, when these D_S values are very small, the program affords local D values which are smaller than the real ones. This can be the case of the $\mathrm{Re^{IV}{}_2Ni^{II}}$ derivative (compound **3**). The low computed value of D_{Re} in **3** is also a common feature in parent heterometallic $\mathrm{Re^{IV}}-\mathrm{Ni^{II}}$ compounds that we have previously investigated.[13g,j] This fact has to be attributed to a noncollinear situation of the local D_{Re} and D_{Ni} tensors as well as to possible different signs of D_{Re} and D_{Ni}. In addition, it has to be taken into account that intermolecular interactions and the local D values are strongly correlated.

Dealing with the results obtained by the analysis of the magnetic data of **1**−**4**, two points deserve to be discussed: (i) the nature and magnitude of the magnetic coupling between Re(IV) and M(II) through the oxalate bridge and (ii) the influence of electronegativity of the peripheral halo ligands on the magnitude of the magnetic coupling. As far as the first point is concerned, simple orbital considerations provide an easy explanation. For the sake of simplicity, we will limit our discussion to a binuclear Re(IV)−M(II) unit. The exchange coupling parameter J_{ReM} is expressed by means of the individual interactions J_{ij} after eq 2[28]

$$J_{\mathrm{ReM}} = (1/n_i n_j) \sum_{i,\,j} J_{ij} \qquad (2)$$

where n_i and n_j are the number of unpaired electrons on the Re(IV) ($n_i = 3$) and M(II) ions [$n_j = 1$ (Cu), 2 (Ni), 3 (Co), and 5 (Mn)]. The strict orthogonality between the magnetic orbitals of the Re(IV) ($\mathrm{d^3}$ electronic configuration with three unpaired electrons in $\mathrm{t_{2g}}$ type orbitals) and those of the Ni(II)/Cu(II) (two/one unpaired electrons in $\mathrm{e_g}$ type orbitals) accounts for the ferromagnetic coupling observed in **3** and **4**. However, as the number of unpaired electrons on the $\mathrm{t_{2g}}$ orbitals increases when going toward Co(II) ($\mathrm{t_{2g}{}^5e_g{}^2}$) and Mn(II) ($\mathrm{t_{2g}{}^3e_g{}^2}$), the possibilities of net overlap between interacting magnetic orbitals (and then the antiferromagnetic contributions) also increase. So, the antiferromagnetic terms become more important in **2** and **1**, and although the magnetic coupling is still ferromagnetic for **2**, it is already antiferromagnetic for **1**. The importance of the larger diffuseness of the magnetic orbitals of the 5d cations on the magnetic coupling when compared to the more contracted 3d orbitals is well-exemplified by the fact that the ferromagnetic coupling between Cr(III) ($\mathrm{3d^3}$ ion) and Ni(II) through the oxalate bridge in the tetranuclear compound $[\mathrm{Cr}(\mu\text{-ox})_3\{\mathrm{Ni}(\mathrm{Me_6}[14]\mathrm{ane\text{-}N_4})\}_3](\mathrm{ClO_4})_3$ ($\mathrm{Me_6}[14]\mathrm{ane\text{-}N_4}$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) is $J = +5.30\ \mathrm{cm^{-1}}$,[29] that is, a value less than one-third from that measured in the related trinuclear compound **3** ($J = +19.7\ \mathrm{cm^{-1}}$). These features concerning the oxalato-bridged Cr(III)−Ni(II) system are also supported by two recently reported trinuclear $\mathrm{Cr^{III}{}_2Co^{II}}$ compounds of formula $\{\mathrm{Co(Me_2bpy)[Cr(phen)(ox)_2]_2}\}\cdot 1.5\mathrm{H_2O}$ and $\{\mathrm{Co(Me_2phen)[Cr(bpy)(ox)_2]_2}\}$ ($\mathrm{Me_2bpy}$ = 6,6′-dimethyl-2,2′-bipyridine, phen = 1,10-phenanthroline, $\mathrm{Me_2phen}$ = 2,9-dimethyl-1,10-phenanthroline, and bpy = 2,2′-bipyridine) displaying intramolecular magnetic couplings of +2.34 and +1.81 $\mathrm{cm^{-1}}$, respectively.[30] Remarkably, the value of J_{ReCo} in **2** is about twice the values of J_{CrCo} in these two latter compounds.

Finally, dealing with the second point, a comparison of the magnetic couplings in **1**−**4** with the related isostructural trinuclear complexes with peripheral chloro (compounds **1′**−**4′**) instead of bromo ligands [$J = -0.35$ (**1′**), +14.2 (**3′**), and +7.7 $\mathrm{cm^{-1}}$ (**4′**)][13h] reveals a considerable strengthening of the magnetic coupling in the bromo series. The smaller electronegativity of the peripheral bromo ligands with respect to the chloro ones causes a greater spin density from the 5d orbitals on the oxalato bridge and, then, a stronger magnetic coupling. This phenomenon was analyzed in detail both from theoretical and experimental points of view in oxalato-bridged homodinuclear complexes involving only homometallic species with first-row transition metal ions,[31] but to our knowledge, this is the first time that this effect is observed in 5d−3d mixed systems. This feature appears then as an effective tool to be used when attempting to increase the magnetic coupling through a given bridge in systems containing heavier elements.

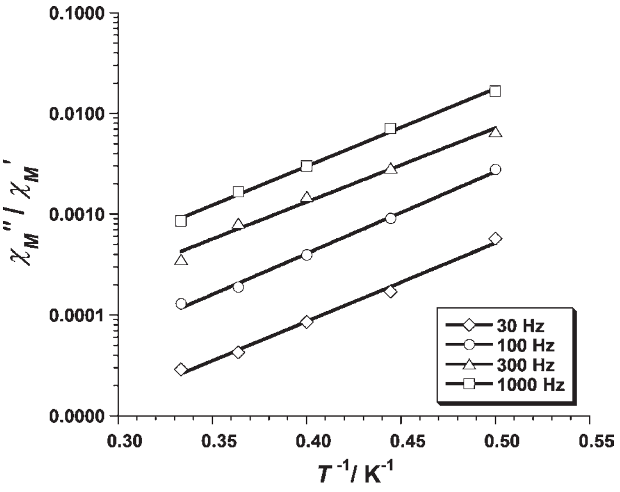


Figure 4. $\chi''_{\mathrm{M}}/\chi'_{\mathrm{M}}$ vs $1/T$ plot for **3** at four different frequencies (1−1000 Hz range). The solid lines are the best-fit curves (see text).

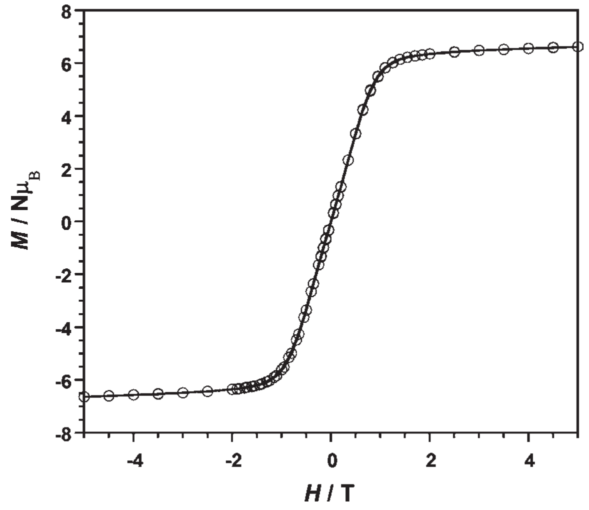


Figure 5. Variable-field magnetization data for **3** at 1.8 K. The solid line is an eye guide.

Interestingly, compound **3** exhibits an incipient frequency-dependent out-of-phase ac signals (χ''_{M}) at very low temperatures which is indicative of a system with slow relaxation of the magnetization (Figure S1 of the Supporting Information). This phenomenon was already observed by some of us in the parent tetranuclear complex $(\mathrm{NBu_4})_4[\mathrm{Ni}\{\mathrm{ReCl_4}(\mu\text{-ox})\}_3]$ which behaves as a single-molecule magnet (SMM).[13g,j] In this previously reported $\mathrm{Re^{IV}{}_3Ni^{II}}$ SMM, a shift of the χ''_{M} maxima toward higher temperatures occurs when an external direct current (dc) magnetic field is applied.[13g,j] This last fact is not observed in **3**, and no χ''_M maxima are detected above 2.0 K (Figure S1). Nevertheless, the values of the anisotropy energy barrier to magnetization reorientation (U) and the preexponential factor (τ_o) for **3** can be estimated from the χ''_M/χ'_M vs $1/T$ plot at a given frequency of the alternating current (ac) field and by assuming only a single relaxation time (Figure 4).[32] The best least-squares fit of these experimental data by means of the $\chi''/\chi' = 2\pi\nu\tau_o \exp(U/k_BT)$ expression led to ca. 18 K (12.5 cm^{-1}) and 4×10^{-10} s for U and τ_o, respectively, these values being in agreement with those found in the literature for systems displaying a low-lying $S = 4$ spin state.[33] Variable-field magnetization data collected for **3** at 1.8 K between −5 and +5 T reveal complete reversibility of the magnetization (Figure 5) and the maximum value of M per the $Re^{IV}_2Ni^{II}$ unit at the highest magnetic field available (5 T) is ca. 7.0 μ_B, a value which is as expected for a ferromagnetically coupled $S = 4$ system with $g \approx 1.8-1.9$.

CONCLUSIONS

In summary, a new series of hetero-trinuclear $Re^{IV}_2M^{II}$ compounds has been prepared by using for the first time the $[ReBr_4(ox)]^{2-}$ complex as a ligand toward M^{II} metal ions [M = Mn (**1**), Co (**2**), Ni (**3**), and Cu (**4**)] in the presence of imidazole. In the present work we show how the substitution of the peripheral chloro atoms from the $[ReCl_4(ox)]^{2-}$ complex by the less electronegative Br ligands causes a significant strengthening of the magnetic coupling between Re(IV) and M(II) ions across the oxalato bridge in the hetero-trinuclear $Re^{IV}_2M^{II}$ systems providing magnetochemists with a suitable tool to increase the magnetic coupling in systems containing heavier elements. An incipient slow relaxation of the magnetization is observed for the $Re^{IV}_2Ni^{II}$ derivative (**3**) which is reminiscent of a SMM behavior.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** X-ray crystallographic files (CIF) for compounds **1**−**4** and frequency-dependent out-of-phase ac plot (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Financial support from the Spanish Ministerio de Ciencia e Innovación (Grant CTQ2010-15364), the Consolider Ingenio in Molecular Nanoscience (Grant SD2007-00010), and the Italian Ministero dell'Istruzione, dell'Università e della Ricerca Scientifica, through the Centro di Eccellenza CEMIF.CAL (Grant CLAB01TYEF) is gratefully acknowledged.

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