Inorg. Chem. **2003**, *42*, 1064–1069

Inorganic Chemistry

Article

Heterobimetallic Oxalato-Bridged $M^{II}Re^{IV}$ Complexes (M = Mn, Fe, Co, Ni): Synthesis, Crystal Structure, and Magnetic Properties

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Received October 2, 2002

Four rhenium(IV)–M(II) bimetallic complexes of formula $[ReCl_4(\mu\text{-ox})M(dmphen)_2]\cdot CH_3CN$ with M = Mn (**1**), Fe (**2**), Co (**3**), and Ni (**4**) (ox = oxalate anion, dmphen = 2,9-dimethyl-1,10-phenanthroline) have been synthesized and the crystal structures of **1** and **3** determined by single-crystal X-ray diffraction. **1** and **3** are isostructural and crystallize in the monoclinic system, space group $P2_1/c$, with $a = 16.008(4)$ Å, $b = 12.729(2)$ Å, $c = 18.909(5)$ Å, $\beta = 112.70(2)°$, and $Z = 4$ for **1** and $a = 15.998(4)$ Å, $b = 12.665(2)$ Å, $c = 18.693(5)$ Å, $\beta = 112.33(2)°$, and $Z = 4$, for **3**. The structure of **1** and **3** is made up of neutral $[ReCl_4(\mu\text{-ox})M(dmphen)_2]$ bimetallic units (M = Mn (**1**), Co (**3**)) and acetonitrile molecules of crystallization. M(II) and Re(IV) metal ions exhibit distorted octahedral coordination geometries being bridged by a bis(bidentate) oxalato ligand. The magnetic behavior of **1**–**4** has been investigated over the temperature range 2.0–300 K. A very weak antiferromagnetic coupling between Re(IV) and Mn(II) occurs in **1** ($J = -0.1$ cm^{-1}), whereas a significant ferromagnetic interaction between Re(IV) and M(II) is observed in **2**–**4** [$J = +2.8$ (**2**), +5.2 (**3**), and +5.9 cm^{-1} (**4**)].

Introduction

In the past few years, several research groups have thoroughly investigated two- and three-dimensional (*n*D) oxalato-bridged networks which were prepared by using anionic tris(oxalato)metalate units as ligands toward either univalent or divalent cations.[2−10] One of the main conclusions arising from these studies is that the dimensionality of the resulting compound is controlled by the nature of the cation. Bulky organic cations of the type ER_4^+ (E = N, P; R = *n*-alkyl, phenyl), or decamethylferricinium, lead to the formation of 2D structures of formula $ER_4[M^{II}M^{III}(ox)_3]$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn; M^{III} = Fe, Cr, Ru; ox = oxalate),[2−7] whereas the tris-chelated $[Z(bipy)_3]^{2+}$ cation (Z^{II} = Ru, Fe, Co, Ni, Zn; bipy = 2,2′-bipyridine) affords the chiral 3D structure with general formula $[Z(bipy)_3][M^IM^{III}(ox)_3]$ or $[Z(bipy)_3][M^{II}_2(ox)_3]$ (M^I = alkali metal,

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10.1021/ic0205942 CCC: $25.00

NH_4^+; M^{II} = Mn, Fe, Co, Cu; M^{III} = Cr, Fe).[8−10] Each layer in the 2D series contains M^{II} and M^{III} tris(oxalate) sites of opposite configuration (Δ and Λ), and the univalent cations are located between the anionic layers determining the interlayer separation. In the 3D family, the metal sites of the anionic network have the same configuration (Δ or Λ) and the tris-chelated cations are located in the cavities. Because of the flexibility of these cavities, monoanions X^- can be incorporated, leading to compounds of formulas $[Z^{III}(bipy)_3][X][M^IM^{III}(ox)_3]$ and $[Z^{III}(bipy)_3][X][M^{II}_2(ox)_3]$.[8c,9,10] Recently, the enantioselective synthesis of these *n*D ($n = 2$ and 3) compounds was performed by using resolved $[Cr(ox)_3]^{3-}$ and $[M(bipy)_3]^{2+}$ species as chiral building blocks.[11] The variety of the magnetic properties of these oxalato-bridged compounds (ferromagnets, ferrimagnets, or canted antiferromagnets) together with their enantioselective control have opened a new field of research in polyfunctional molecule-based materials.

To extend these studies to second and third row transition metal ions, we have explored the possibility of using mononuclear oxalato-containing rhenium(IV) species such as $[ReCl_4(ox)]^{2-}$ (three unpaired electrons on the Re(IV) ion) as a ligand toward a first row transition metal ion. So, the first examples of bimetallic $Re^{IV}Cu^{II}$ compounds were reported very recently.[12,13] In these studies, we found that the coordination mode of the $[ReCl_4(ox)]^{2-}$ complex is very sensitive to the nature of the other ligands in the coordination sphere of Cu(II). In fact, the rhenium(IV) precursor exhibits different coordination modes: it acts as a monodentate ligand in $[ReCl_4(ox)Cu(bipy)_2]$ and $[ReCl_4(ox)Cu(terpy)(CH_3CN)]$ (terpy = 2,2′:6,2″-terpyridine) (forming a long Cu−O axial bond of 2.65 and 2.40 Å, respectively), whereas it adopts a rather asymmetric bidentate binding mode in $[ReCl_4(ox)Cu(phen)_2]$ (phen = 1,10-phenanthroline) (two long Cu−O bonds, 2.32 and 2.41 Å) and a very asymmetric bidentate one in $[ReCl_4(ox)Cu(terpy)(H_2O)]$ (forming one short and one long Cu−O bond, 2.05 and 2.47 Å, respectively). Orthogonality between magnetic orbitals in these binuclear complexes (the electronic configurations of Re(IV) and Cu(II) in an octahedral environment are $t_{2g}{}^3$ and $t_{2g}{}^6e_g{}^3$, respectively) would lead to a ferromagnetic coupling. However, this kind of interaction was found only in $[ReCl_4(ox)Cu(terpy)(CH_3CN)]$ ($J = +5.6$ cm^{-1}). Distortions in the coordination geometry in all the other complexes introduce some orbital overlap, turning the interaction weakly antiferromagnetic.

In this work, we present the results obtained when $[ReCl_4(ox)]^{2-}$ is used as a ligand toward preformed complexes containing divalent first row transition metal ions other than copper(II). The preparation and magnetic characterization of a series of compounds of formula $[Re^{IV}Cl_4(ox)M^{II}(dmphen)_2]\cdot CH_3CN$ (M = Mn (**1**), Fe (**2**), Co (**3**), and Ni (**4**); dmphen = 2,9-dimethyl-1,10-phenanthroline) together with the crystal structures of the Mn and Co derivatives are included here. The formation of the tris-chelated $[M(phen)_3]^{2+}$ complexes is precluded by using dmphen instead of phen as a terminal ligand, thereby facilitating the binding of $[ReCl_4(ox)]^{2-}$ to the M(II) ions.

Experimental Section

Materials. The perchlorate salts $M(ClO_4)_2\cdot 6H_2O$ (M = Mn, Fe, Co, and Ni), dmphen ligand (Aldrich) and the organic solvents acetonitrile (MeCN) and dimethylformamide (DMF) were purchased from commercial sources and used as received. The complex $(NBu_4)_2[ReCl_4(ox)]$ was prepared as previously reported.[12]

Synthesis of the Complexes. $[ReCl_4(\mu\text{-}ox)Mn(dmphen)_2]\cdot CH_3CN$ (1). An acetonitrile solution (20 mL) of $(NBu_4)_2[ReCl_4(ox)]$ (45 mg, 0.05 mmol) was poured into a solution (20 mL) of manganese(II) perchlorate hexahydrate (17.9 mg, 0.05 mmol) and dmphen monohydrate (20.8 mg, 0.10 mmol) in the same solvent at room temperature. The resulting solution was allowed to stand in a closed container. A crystalline lemon green solid was formed slowly. After some days, it was filtered, washed with MeCN (2 × 2 mL), and dried in the air. Yield: ca. 80%. Anal. Calcd for $C_{32}H_{27}N_5Cl_4O_4MnRe$: C, 41.39; H, 2.93; N, 7.54. Found: C, 40.78; H, 2.93; N, 6.99. IR/cm^{-1}: peaks associated to the oxalato ligand appear at 1684vs, 1640w, and 802s. Crystals were very small but suitable for X-ray diffraction.

$[ReCl_4(\mu\text{-}ox)Fe(dmphen)_2]\cdot CH_3CN$ (2). This complex was prepared by using the same procedure described for **1** but substituting iron(II) perchlorate hexahydrate (18.1 mg, 0.05 mmol) for the manganese perchlorate. A brown microcrystalline solid was obtained. Yield: ca. 75%. Anal. Calcd for $C_{32}H_{27}N_5Cl_4O_4FeRe$: C, 41.35; H, 2.93; N, 7.53. Found: C, 40.94; H, 3.13; N, 7.51. IR/cm^{-1}: peaks associated to the oxalato ligand appear at 1684vs, 1645w, and 803s.

$[ReCl_4(\mu\text{-}ox)Co(dmphen)_2]\cdot CH_3CN$ (3). A solution of $(NBu_4)_2[ReCl_4(ox)]$ (45 mg, 0.05 mmol) in a MeCN−DMF (5:1 v/v, 15 mL) mixture was poured into a solution of the same mixed solvent (15 mL) containing cobalt(II) perchlorate hexahydrate (18.3 mg, 0.05 mmol) and dmphen monohydrate (20.8 mg, 0.10 mmol). Both solutions were very hot, close to boiling, before the mixing, and the resulting solution was left to cool slowly at room temperature in a closed container. After some days, a crystalline salmon-colored solid was formed. It was filtered, washed with MeCN (2 × 2 mL), and dried in the air. Yield: ca. 80%. Anal. Calcd for $C_{32}H_{27}N_5Cl_4O_4CoRe$: C, 41.22; H, 2.92; N, 7.51. Found: C, 40.89; H, 3.07; N, 7.51. IR/cm^{-1}: peaks associated to the oxalato ligand appear at 1683vs, 1647w, and 803s. Crystals of **3** were suitable for X-ray diffraction.

$[ReCl_4(\mu\text{-}ox)Ni(dmphen)_2]\cdot CH_3CN$ (4). This complex was prepared by using the same procedure described for **3** but with the solutions at room temperature and substituting the nickel(II) perchlorate hexahydrate (18.3 mg, 0.05 mmol) for the cobalt perchlorate. A green crystalline solid was obtained. Yield: ca. 90%. Anal. Calcd for $C_{32}H_{27}N_5Cl_4O_4NiRe$: C, 41.23; H, 2.92; N, 7.51. Found: C, 41.02; H, 2.97; N, 7.60. IR/cm^{-1}: peaks associated to the oxalato ligand appear at 1683vs, 1644w, and 805s.

Physical Techniques. The IR spectra (KBr pellets) were recorded with a Perkin-Elmer 1750 FTIR spectrometer. Magnetic susceptibility measurements (2−300 K) were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 1 T in the high-temperature range ($T > 50$ K) and only 50 G at

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Table 1. Crystal Data and Structure Refinement for $[ReCl_4(ox)M(dmphen)_2)]\cdot CH_3CN$ with M = Mn (**1**) and Co (**3**)[a]

compound	**1**	**3**
formula	$C_{32}H_{27}Cl_4MnN_5O_4Re$	$C_{32}H_{27}Cl_4CoN_5O_4Re$
M	928.53	932.52
a, Å	16.008(4)	15.988(4)
b, Å	12.729(2)	12.665(2)
c, Å	18.909(5)	18.693(5)
β, deg	112.70(2)	112.33(2)
V, Å^3	3554(1)	3501(1)
D_c, g cm^{-3}	1.735	1.769
μ, cm^{-1}	41.01	42.77
R1[b] $[I > 2\sigma(I)]$	0.0799	0.0746
wR2[c,d]	0.1714	0.1427

[a] Details in common: monoclinic $P2_1/c$ (No. 14), $T = 293(2)$ K and $Z = 4$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/[\sum(w(F_o^2)^2]\}^{1/2}$. [d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [F_o^2 + 2F_c^2]/3$, $a = 0.0854$ (**1**) and 0.0589 (**3**), $b = 0$ (**1** and **3**).

low temperatures to avoid any problem of magnetic saturation. The device was calibrated with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$. The corrections for the diamagnetism were estimated from Pascal constants.

X-ray Data Collection and Structure Refinement. Crystals of dimensions 0.10 × 0.21 × 0.23 (**1**) and 0.09 × 0.11 × 0.08 mm^3 (**3**) were mounted on a Bruker R3m/V automatic four circle diffractometer and used for data collection. Diffraction data were collected at room temperature by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with the $\omega - 2\theta$ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections in the 2θ range of 15−30°. A summary of the crystallographic data and structural parameters are listed in Table 1. Examination of two standard reflections, monitored after every 50 reflections, showed no sign of crystal deterioration. Lorentz-polarization and absorption correction through the XABS program[14] were applied for compounds **1** and **3**. The maximum and minimum transmission factors were 0.684 and 0.452 for **1** and 0.726 and 0.650 for **3**. A total of 6690 (**1**) and 6724 (**3**) reflections were measured in the 2θ range of 4−50° with index ranges $-19 \le h \le 17$, $0 \le k \le 15$ and $0 \le l \le 22$ (**1** and **3**). From these, 6291 (**1**) and 6185 (**3**) were observed ($I > 2\sigma(I)$) and used for the refinement of the structures.

The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. All non-hydrogen atoms (except the carbon atoms of the dmphen ligands) were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropically thermal parameter. Full-matrix least-squares refinements on F^2, carried out by minimizing the function $\Sigma w(|F_o|-|F_c|)^2$, reached convergence with values of the discrepancy indices given in Table 1. The goodness-of-fit is 1.093 for **1** and 1.063 for **3**. Solutions and refinements were performed with the SHELXTL NT system.[15] The final geometrical calculations were carried out with the PARST program.[16] The graphical manipulations were performed using the XP utility of the SHELXTL NT systems. The main interatomic bond distances and angles are listed in Table 2 (**1** and **3**).

Results and Discussion

Description of the Structures of $[ReCl_4(ox)M(dmphen)_2)]\cdot CH_3CN$ (M = Mn (1) and Co (3)). **1** and **3** are isostructural compounds whose structure is made up by neutral $[ReCl_4(ox)M(dmphen)_2)]$ (M = Mn (**1**) and Co (**3**)) heterodinuclear units and acetonitrile molecules of crystallization, which are linked through van der Waals forces. A perspective drawing, showing the atom numbering scheme, is depicted in Figure 1. Each $[ReCl_4(ox)M(dmphen)_2)]$ unit contains Re(IV) and M(II) ions bridged by a bis(bidentate) oxalato ligand. The Re(IV) is surrounded by two oxalate−oxygens and four chloride anions in a distorted octahedral geometry. No significant differences were found in the Re−Cl (average value 2.330(4) Å) and Re−O (2.07(1) Å) bond distances. Both Re−Cl and Re−O bond lengths are in agreement with those found for the $(ReCl_4(ox))^{2-}$ fragment in previous reports.[12,13] The O(1)O(2)Cl(1)Cl(2) set of atoms constitutes the equatorial plane around Re, the largest deviation from planarity being 0.012(5) Å for **3**. The Re atom lies in this plane for both compounds. The values of the dihedral angle between the equatorial plane and that of the oxalate are 8.3(5) (**1**) and 7.8(5)° (**3**). The short bite of the oxalate accounts for the large deviation from the ideal value of the angle subtended by this ligand at the Re atom (79.4(4) (**1**) and 78.5(4)° (**3**)).

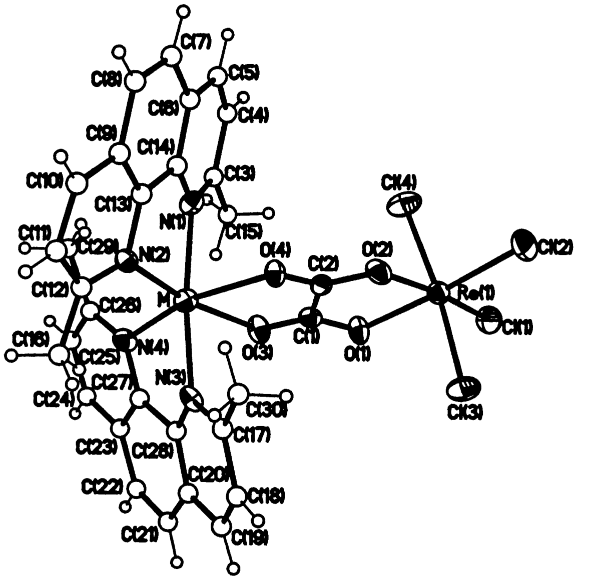

Figure 1. Perspective drawing of the $[ReCl_4(ox)M(dmphen)_2]$ heterobimetallic unit (M = Mn (**1**) and Co (**3**)) showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level.

The Mn (**1**) and Co (**3**) atoms are six-coordinated with two oxalate−oxygens and four nitrogen atoms from two chelating dmphen ligands describing a highly distorted octahedral surrounding around the metal atoms. The reduced values of the angle subtended at the metal atom by the ox (73.6(4) (**1**) and 76.1(4)° (**3**)) and dmphen (75.0(5) and 74.5(4)° for **1** and 79.3(5) and 78.1(5)° for **3**) ligands are the main factor for this distortion. The values of the M−O bond lengths (2.31(1) and 2.28(1) Å for **1** and 2.21(1) Å for **3**) are somewhat longer than those observed in other oxalato-bridged homodinuclear Mn(II) (average Mn−O$_{ox}$ value 2.18(1) Å) and Co(II) (average Co−O$_{ox}$ value 2.094(3) Å) compounds.[17] This lengthening is most likely due to the electron-withdrawing effect induced by the high valent

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Compounds **1** and **3**

	M = Mn (**1**)	M = Co (**3**)		M = Mn (**1**)	M = Co (**3**)
Re(1)−O(1)	2.059(10)	2.047(10)	M(1)−O(3)	2.315(11)	2.208(11)
Re(1)−O(2)	2.076(11)	2.074(10)	M(1)−O(4)	2.284(10)	2.211(9)
Re(1)−Cl(1)	2.324(4)	2.316(4)	M(1)−N(1)	2.292(12)	2.169(12)
Re(1)−Cl(2)	2.298(4)	2.306(5)	M(1)−N(2)	2.245(12)	2.080(12)
Re(1)−Cl(3)	2.328(4)	2.334(4)	M(1)−N(3)	2.261(11)	2.143(12)
Re(1)−Cl(4)	2.368(5)	2.363(5)	M(1)−N(4)	2.227(14)	2.119(12)
O(1)−Re(1)−O(2)	79.4(4)	78.5(4)	N(1)−M(1)−N(2)	75.0(5)	79.3(5)
O(1)−Re(1)−Cl(1)	93.2(3)	93.8(3)	N(1)−M(1)−N(3)	174.8(4)	173.2(4)
O(1)−Re(1)−Cl(2)	171.2(3)	171.1(3)	N(1)−M(1)−N(4)	109.0(4)	107.1(5)
O(1)−Re(1)−Cl(3)	88.5(4)	87.8(3)	N(1)−M(1)−O(3)	97.2(4)	95.7(4)
O(1)−Re(1)−Cl(4)	85.9(4)	86.4(3)	N(1)−M(1)−O(4)	81.4(4)	79.2(4)
O(2)−Re(1)−Cl(1)	172.5(3)	172.3(3)	N(2)−M (1)−N(3)	107.9(4)	103.8(5)
O(2)−Re(1)−Cl(2)	91.9(3)	92.6(3)	N(2)−M (1)−N(4)	108.1(5)	105.4(5)
O(2)−Re(1)−Cl(3)	90.1(4)	90.0(3)	N(2)−M(1)−O(3)	167.3(4)	168.4(4)
O(2)−Re(1)−Cl(4)	88.0(4)	87.7(3)	N(2)−M (1)−O(4)	95.1(4)	92.6(4)
Cl(1)−Re(1)−Cl(2)	95.6(2)	95.1(2)	N(3)−M (1)−N(4)	74.5(4)	78.1(5)
Cl(1)−Re(1)−Cl(3)	90.2 (2)	90.2(2)	N(3)−M(1)−O(3)	79.2(4)	80.1(4)
Cl(1)−Re(1)−Cl(4)	91.0(2)	91.3(2)	N(3)−M(1)−O(4)	93.9(4)	94.6(4)
Cl(2)−Re(1)−Cl(3)	91.6(2)	91.5(2)	N(4)−M(1)−O(3)	83.7(4)	86.0(4)
Cl(2)−Re(1)−Cl(4)	93.8(2)	94.0(2)	N(4)−M (1)−O(4)	156.2(4)	161.7(4)
Cl(3)−Re(1)−Cl(4)	174.3(2)	174.1(2)	O(3)−M(1)−O(4)	73.6(4)	76.1(4)

Re(IV) cation. The M−N bond lengths vary in the ranges 2.29(1)−2.23(1) Å (**1**) and 2.17(1)−2.08(1) Å (**3**). The best equatorial plane in **1** and **3** is defined by the O(3)O(4)-N(2)N(4) set of atoms (largest deviation 0.129(7) (**1**) and 0.063(7) Å (**3**) at the O(3) atom) with the Mn and Co atoms being practically in this plane. The values of the dihedral angle between this mean plane and that of the oxalate are 4.3(6) (**1**) and 2.25(6)° (**3**). The two dmphen ligands are planar, and the values of the dihedral angle between them are 63.2(2) (**1**) and 62.5(2)° (**3**). The bond lengths and angles within the planar oxalato ligand are as expected in both compounds. The Re atom lies 0.22(1) Å (**1** and **3**) out of this plane, whereas the Mn and Co atoms are shifted only by 0.07(2) Å. The values of the dihedral angle between the oxalate mean plane and those of the dmphen ligands are 62.7(4) and 66.0(4)° (**1**) and 61.5(4) and 66.5(4)° (**3**). The values of the Re···M separation through the bridging oxalato are 5.645(1) (**1**) and 5.552(2) Å (**3**).

The heterobimetallic units are well separated from each other, with the shortest intermolecular Re···M(1*a*) distances being 7.130(1) (**1**) and 7.147(2) Å (**3**) [(*a*) = *x*, *y* − 1, *z*]. The shortest interdimer Cl···Cl(1*b*) separation [broken lines in Figure S1; (*b*) = 1 − *x*, −*y*, −*z*] is 4.40(1) (**1**) and 4.50(1) Å (**3**). Significant $\pi-\pi$ off-set interactions (interplanar distance ca., 3.4 Å) between dmphen ligands from adjacent heterobimetallic units in **1** and **3** leads to a chain running along the *c* axis (Figure S2).

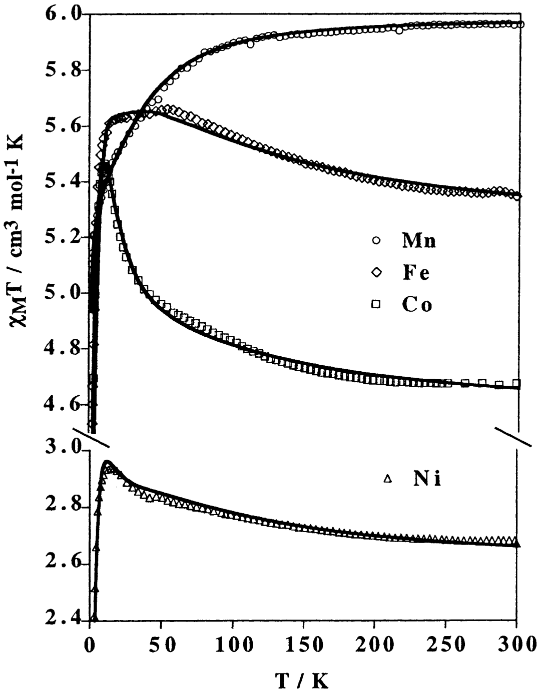

Figure 2. Thermal dependence of $\chi_M T$ for **1**−**4**. The solid lines are the calculated curves (see text).

Magnetic Properties. The magnetic properties of complexes **1**−**4** under the form of $\chi_M T$ versus *T* plot (χ_M being the magnetic susceptibility per $Re^{IV}M^{II}$ heterobimetallic unit) are shown in Figure 2. At room temperature, $\chi_M T$ for **4** is 2.67 cm^3 mol^{-1} K, a value which is as expected for an uncoupled $Re^{IV}(S_{Re} = {}^3/_2)-Ni^{II}(S_{Ni} = 1)$ pair. It increases very slowly upon cooling, reaching a maximum value of 2.94 cm^3 mol^{-1} K at about 15 K and decreases steeply at lower temperatures. The magnetic curves for complexes **2** and **3** are qualitatively very similar to that of **4**. A better defined maximum with $\chi_M T = 5.46$ cm^3 mol^{-1} K is reached at 10.5 K in the case of **3**, whereas the maximum in $\chi_M T$ is less pronounced for **2**, with a plateau at 5.62 cm^3 mol^{-1} K between 65 and 15 K. These features reveal a ferromagnetic coupling between Re(IV) and the 3d metal ion in **2**−**4**, the local anisotropy of the metal ions (ZFS effects) accounting for the steep decrease of $\chi_M T$ in the low-temperature range. Complex **1** exhibits a different magnetic behavior. At room temperature, $\chi_M T$ is equal to 5.96 cm^3 mol^{-1} K, the expected value for a uncoupled Re(IV)−Mn(II) pair ($S_{Mn} = {}^5/_2$). Upon cooling, it decreases first slowly and then faster, reaching a value of 5 cm^3 mol^{-1} K at 2 K. Most of this variation is due to zero field splitting of Re(IV), and most likely, a weak

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Table 3. Best-Fit Parameters for Complexes **1**−**4**

	1	**2**	**3**	**4**
J, cm^{-1}	−0.1	+2.8	+5.2	+5.9
D_{Re}, cm^{-1}	45	48	49	44
D_M, cm^{-1}	0	14	6.2	6.1
g_{Re}	1.85	1.83	1.85	1.82
g_M	2.0	2.20	2.49	2.08
R^a	1.1×10^{-5}	8.5×10^{-5}	3.5×10^{-5}	4.1×10^{-5}

[a] R is the agreement factor defined as $\sum_i [(\chi_M T)_i^{obsd} - (\chi_M T)_i^{calc}]^2/[(\chi_M T)_i^{obsd}]^2$).

antiferromagnetic coupling between the two metal ions is also involved.

Although the crystal structures of **2** and **4** have not been solved, the facts that **1** and **3** are isostructural compounds and that the IR spectra of the four complexes are identical strongly support the same structure for all the compounds in the series. So, we have analyzed theoretically the magnetic data with the same model, using the Hamiltonian of eq 1

$$\hat{H} = -J\hat{S}_{Re}\cdot S_M + D_{Re}[\hat{S}_{zRe}^{\ 2} - 5/4] + D_M[\hat{S}_{zM}^{\ 2} - n(n+2)/12] + \beta\,(\hat{S}_{Re}g_{Re} + \hat{S}_M g_M)\cdot H \quad (1)$$

where J is the exchange coupling parameter between the Re(IV) and M(II) local spins, n is the number of unpaired electrons on M(II), $2D_{Re}$ and $2D_{Co}$ are the energy gaps between the $M_S = \pm^3/_2$ and $M_S = \pm^1/_2$ Kramers doublets (the zero field splitting of Re(IV) and Co(II)), and D_{Ni} and D_{Fe} represent the energy gap between the sublevels $M_S = 0$ and $M_S = \pm 1$. The last term in eq 1 accounts for the Zeeman effects of the two metal ions. It should 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 satisfied by manganese(II), $^6A_{1g}$ (**1**), and nickel(II), $^3A_{2g}$ (**4**), but not by iron(II), $^5T_{2g}$ (**2**), and cobalt(II), $^4T_{1g}$ (**3**). To analyze the magnetic data for these two last compounds, it is necessary to introduce some simplifications. Actually, the orbital contribution to the $\chi_M T$ value should be lower than expected due to the distorted environment of the M(II) ions. The crystal field component of lower symmetry splits the T term giving a nondegenerate ground term. We have considered that this term reflects the electronic structure of the complex in all the temperature range investigated and that it is further split by second-order spin−orbit coupling, as for Re(IV). Obviously, this is correct only at very low temperatures. Least-squares fit through eq 1 leads to the parameters listed in Table 3. Although the axial anisotropy is considered in the Hamiltonian used, we assume $g_\parallel = g_\perp$ for the Re(IV) and M(II) metal ions in order to avoid overparametrization. A satisfactory match between the magnetic data and the calculated curves is obtained for all the compounds.

The nature and relative magnitude of the magnetic interaction in **1**−**4** can be understood, qualitatively at least, through orbital symmetry considerations.[18] Assuming an octahedral symmetry for the metal ions, Ni(II) (**4**) ($t_{2g}^6e_g^2$ configuration) holds two unpaired electrons in the e_g orbitals, which are orthogonal with the t_{2g} magnetic orbitals of Re(IV) (t_{2g}^3), and hence all the bielectronic interactions are ferromagnetic, giving a positive J value. High-spin Co(II) (**3**), $t_{2g}^5e_g^2$, has an additional unpaired electron in a t_{2g} orbital, and consequently, an antiferromagnetic interaction arises, which opposes the others, giving a less positive J value. The antiferromagnetic contribution is greater in **2,** since high-spin Fe(II) ($t_{2g}^4e_g^2$) has two unpaired electrons in t_{2g} orbitals. Eventually, in Mn(II) (**1**) ($t_{2g}^3e_g^2$) the number of antiferromagnetic contributions is greater than that of the ferromagnetic ones, leading to quasi-compensation and very small and negative J value results.

Up to now, these theoretical concepts have been applied nearly exclusively to transition metal compounds of the first series (3d),[12,19] and it was not obvious if they would be valid for systems involving 4d or 5d metal ions. Indeed, Kahn and co-workers have studied a series of compounds of formula $NBu_4[M^{II}Ru^{III}(ox)_3]$ (M = Mn, Fe, Cu), concluding that the presence of Ru(III) causes the breakdown of the symmetry rules governing the nature and magnitude of the interaction between magnetic ions.[19] However, our results here and in previous[12,13] works support the validity of the model for the Re(IV) compounds.

Upon dealing with the magnitude of the magnetic interactions in **1**−**4**, we expected that the greater diffuseness of 5d compared with 3d orbitals should produce stronger interactions. In fact, we have found a significant coupling, ferromagnetic in $[ReCl_4(ox)Cu(terpy)(CH_3CN)]$[13] and antiferromagnetic in $[ReCl_4(ox)Cu(bipy)_2]$,[12] whereas the interaction is negligible in a similar $Cr^{III}Cu^{II}$ complex, $[Cr(ox)_3Cu(bipy)_2]^-$,[20] where the same bridging mode of the oxalato ligand is involved. However, the J values of compounds **2**−**4** determined in the present work are not greater than others found in similar oxalato-bridged 3d−3d systems. So, a Cr(III)−Ni(II) ferromagnetic coupling of +5.3 cm^{-1} through bis(bidentate) oxalato ligand has been reported in the tetranuclear complex $[Cr(\mu\text{-}ox)_3Ni_3(Me_6[14]ane\text{-}N_4)_3](ClO_4)_3$ ($Me_6[14]ane\text{-}N_4$ = (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane).[21] The lack of structure of this compound precludes a detailed magneto-structural comparison with **4**. Clearly, more studies will be necessary on these and other systems involving different heavier transition metal ions to obtain a global picture of the phenomenon.

Safety Note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In the synthesis described here, we use only small amounts of material (preparations at the millimole scale) and the starting perchlorate salt was an aquo complex. The diluted solutions were handled with great care and evaporated slowly at room temperature in an open hood. (cf. *J. Chem. Educ.* **1973**, *50*, A335. *Chem. Eng. News* **1983**, *61*, (Dec 5), 4; **1963**, *41* (July 8), 47.) When noncoordinating agents are required, every

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attempt should be made to substitute anions such as the fluorosulfonates for the perchlorates.

Acknowledgment. Financial support from the Ministerio Español de Ciencia y Tecnología (Project BQU2001-2928), the Italian Ministero dell' Universitá e della Ricerca Scientifica e Tecnologica, the Comisión Sectorial de Investigación Científica (CSIC) de la Universidad de la República de Montevideo (Project N*o*. 601/215), the TMR Program of the European Union (Contract ERBFMRXCT98-0181), and the European Science Foundation through the Molecular Magnets Programme are gratefully acknowledged. R.C. and R.G. are indebted to the European Union for a grant (ALFA Program ALR/B7-3011/94.04-5.0273(9)).

Supporting Information Available: A perspective view of the neighboring heterobimetallic units (Figure S1), a view of the $\pi-\pi$ stacking interactions (Figure S2), and X-ray crystallographic files in CIF format, for **1** and **3**. This material is available free of charge via the Internet at htpp://pubs.acs.org.

IC0205942