Heterobimetallic Oxalato-Bridged Cu^{II}Re^{IV} Complexes. Synthesis, Crystal Structure and Magnetic Properties

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Three copper(II)−rhenium(IV) bimetallic complexes of formula [ReCl$_4$(μ-ox)Cu(phen)$_2$] (**1**), [ReCl$_4$(μ-ox)-Cu(phen)$_2$]·CH$_3$CN (**2**), and [ReCl$_4$(μ-ox)Cu(terpy) (H$_2$O)][ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)] (**3**) (ox = oxalate anion, phen = 1,10-phenanthroline, and terpy = 2,2′:6,2″- terpyridine) have been synthesized and their crystal structures determined by single-crystal X-ray diffraction. Complex **1** crystallizes in the triclinic system, space group *P*(−1), with *a* = 9.776(2), *b* = 11.744(3), *c* = 14.183(3) Å, α =102.09(2)°, β = 109.42(2)°, γ = 107.11(2)°, and *Z* = 2, whereas **2** and **3** crystallize in the monoclinic system, space groups *P*2$_1$/*n* and *P*2$_1$/*c*, respectively, with *a* = 12.837(3), *b* = 17.761(4), *c* = 12.914(3) Å, β = 91.32(2)°, and *Z* = 4 for **2**, and *a* = 8.930(2), *b* = 18.543(4), *c* = 27.503(6) Å, β = 94.67(2)°, and *Z* = 4 for **3**. The structures of **1** and **2** are made up of neutral [ReCl$_4$(μ-ox)Cu(phen)$_2$] bimetallic units. Re(IV) and Cu(II) metal ions exhibit distorted octahedral coordination geometries, being bridged by a bis(bidentate) oxalato ligand. The presence of acetonitrile molecules of crystallization in **2** causes a somewhat greater separation between the bimetallic complexes and a different packing of these units in the crystal structure with respect to **1**. The copper−rhenium separation across oxalato is 5.628(2) in **1** and 5.649(3) Å in **2**. The structure of **3** is made up of two different and neutral bimetallic units, [ReCl$_4$(μ-ox)Cu(terpy)(H$_2$O)] and [ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)]. In the first one, the oxalate group behaves as a bis(bidentate) ligand occupying one equatorial and one axial position in the elongated octahedral environment of Cu(II). The water molecule is axially coordinated. In the second one, the oxalate group behaves as a bidentate/monodentate ligand occupying the axial position in the square pyramidal environment of Cu(II). The acetonitrile molecule occupies a basal coordination position around the copper atom. These units are arranged in such a way that a chlorine atom of the first unit (Cl(1)) points toward the copper atom (Cu(2))of the second one (3.077(2) Å for Cl(1)···Cu(2)), forming a tetranuclear species. The copper−rhenium separation across bis(bidentate) oxalato is 5.504(3) Å, whereas that through bidentate/monodentate oxalato is 5.436(2) Å. The magnetic behavior of **2** and **3** has been investigated over the temperature range 1.8−300 K. A very weak and nearly identical antiferromagnetic coupling between Re(IV) and Cu(II) through bis(bidentate) oxalato occurs in **2** (*J* = −0.90 cm^{-1}) and **3** (*J* = −0.83 cm^{-1}); it is ferromagnetic in **3** through both the bidentate−monodentate oxalato (*J* = +5.60 cm^{-1}) and the chloro (*J* = +0.70 cm^{-1}) bridges.

Introduction

We are interested in the synthesis, structural characterization, and magnetic properties of polynuclear complexes containing Re(IV) (a 5d^3 ion) and first-row transition metal ions. Our approach involves the synthesis of stable mononuclear Re(IV) complexes which can act as ligands toward transition metal ions. In a recent report dealing with the synthesis and magnetostructural characterization of the mononuclear oxalato complex of Re(IV) of formula (AsPh$_4$)$_2$[ReCl$_4$(ox)] and of the ferrimagnetic chain [ReCl$_4$(μ-ox)Cu(bipy)$_2$] (AsPh$_4$ = tetraphenylarsonium and bipy = 2,2′-bipyridine), weak antiferromagnetic interactions between Re(IV) and Cu(II) through oxalato and single chloro bridges were observed for the latter compound.[2]

Three main points emerged from this work: (i) the zero-field splitting is very important in Re(IV) complexes, (ii) the oxalate ligand is reluctant to bridge Re(IV) and Cu(II), and (iii) strong magnetic interaction between Re(IV) and Cu(II) would be mediated by a good bridging ligand.

Zero-field splitting has usually been neglected in the analysis of the magnetic properties of Re(IV) complexes. Thus, the decrease of $\chi_M T$ when decreasing temperature in the hexahalo mononuclear complexes [ReX$_6$]$^{2-}$ has been attributed to intermolecular antiferromagnetic interactions.[3] These interactions are precluded in the crystal structure of (AsPh$_4$)$_2$[ReCl$_4$(ox)] because the paramagnetic complex anions are well separated from each other by the bulky tetraphenylarsonium cations. The high value of the zero-field splitting of the ^{4}A$_2$ ground term (2*D* = 60 cm^{-1}) of Re(IV) in this compound accounts for the variation of $\chi_M T$ with *T* in the low-temperature range. Even in the more symmetric (cat)$_2$[ReCl$_6$] species, the only consideration of a

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Scheme 1
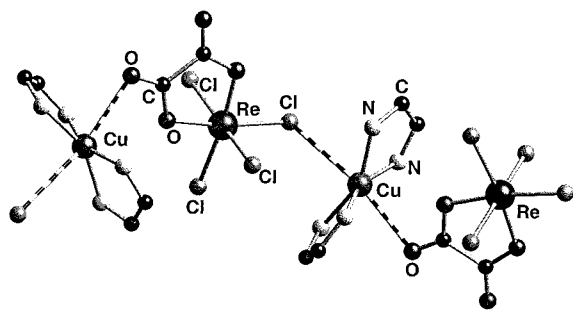
zero-field splitting of ca. 13 (cat = tetrabutylammonium, NBu$_4^+$) and 9 cm^{-1} (cat = AsPh$_4^+$) allows a very good match of the magnetic susceptibility data.[2] It should be noted that a value of 2D = 127 cm^{-1} was reported for Cs$_2$[ReF$_6$] from a study of its electronic absorption spectrum.[4]

The oxalate dianion is a well-known ligand which usually adopts the bis(bidentate) coordination mode when acting as a bridge in its metal complexes. Bimetallic complexes with di-, [Ni$_2$(ox)$_5$]$^{6-}$,[5] tri-, [Cr$_2$(ox)$_5$]$^{4-}$,[6] and [Fe$_2$(ox)$_5$]$^{4-}$,[7] and tetravalent, [Zr$_2$(ox)$_7$]$^{6-8}$ metal ions have been characterized. In these complexes both metal ions have the same oxidation state. The tendency of oxalate to act as a bridge decreases considerably when the metals involved exhibit different oxidation states. A series of compounds with extended oxalato bridges NBu$_4$-[M^{II}M^{III}(ox)$_3$] (M^{II} = Mn, Fe, Co, Ni, Cu, Zn, and M^{III} = Cr, Fe, Ru)[9] are known, but it appears that the counterion is essential in maintaining the polymeric structure. The synthesis and structure of another polymeric compound of formula K$_2$[UMn(ox)$_4$], where the oxalato bridges U(IV) and Mn(II) cations, has been reported very recently,[10] but as far as we know, [ReCl$_4$(μ-ox)Cu(bipy)$_2$] is the first compound with an oxalato ligand bridging M(IV) and M(II) transition metal ions. The complex [ReCl$_4$(ox)]$^{2-}$ has a low affinity for Cu(II) and most likely for any other divalent metal ion of the first transition series. Thus, [ReCl$_4$(μ-ox)Cu(bipy)$_2$] is the only isolated compound in the [ReCl$_4$(ox)]$^{2-}$−Cu^{2+}−bipy system even working at a 1:1 Cu^{2+} to bipy molar ratio. In this compound, the oxalate anion is coordinated to Re(IV) as a bidentate ligand but only as monodentate ligand to Cu(II), forming a very long axial bond, 2.65 Å for Cu−O (Scheme 1). No significant magnetic interaction is expected with such a bridge in a bimetallic complex with first-row transition metal ions. In fact, [ReCl$_4$(μ-ox)Cu(bipy)$_2$] behaves as a ferrimagnetic chain with significant intra- (through oxalato) and intermolecular (through chloro bridges, Cu−Cl = 3.35 Å) antiferromagnetic interactions (see Scheme 1). This behavior reflects the greater diffuseness of the 5d orbitals of Re(IV). Indeed, DFT calculations show an important spin density on the bridging atoms.[2] However, a strong

antiferromagnetic interaction is not expected in a bimetallic oxalato bridged Cu(II)Re(IV) complex. The orthogonality between magnetic orbitals (the electronic configuration of the metal ions is t$_{2g}^6$e$_g^3$ and t$_{2g}^3$, respectively, in an octahedral environment) would lead to a ferromagnetic coupling. Distortions in the coordination geometry can introduce some orbital overlap, but always small, turning the interaction to weak antiferromagnetic.

Given the well-known plasticity of the coordination sphere of Cu(II),[11] it seemed interesting to investigate the influence of the other ligands on the coordination modes of [ReCl$_4$(ox)]$^{2-}$. In our first attempt, we substituted 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy) for bipy, and we obtained three new heterobimetallic Re(IV)−Cu(II) complexes, [ReCl$_4$(μ-ox)-Cu(phen)$_2$] (**1**), [ReCl$_4$(μ-ox)Cu(phen)$_2$]·CH$_3$CN (**2**), and [ReCl$_4$-(μ-ox)Cu(terpy)(H$_2$O)][ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)] (**3**). Their syntheses, crystal structures, and variable-temperature magnetic properties are reported here.

Experimental Section

Materials. The copper(II) trifluoromethanesulfonate salt (Fluka), phen and terpy ligands (Aldrich) as well as the organic solvents acetonitrile (MeCN), dimethylformamide (DMF), and nitromethane (MeNO$_2$) were purchased from commercial sources and used as received. The complex (NBu$_4$)$_2$[ReCl$_4$(ox)] was prepared as previously reported.[2]

Synthesis of the Complexes. [ReCl$_4$(μ-ox)Cu(phen)$_2$] (1) and [ReCl$_4$(μ-ox)Cu(phen)$_2$]·CH$_3$CN (2). A solution of 45 mg of (NBu$_4$)$_2$-[ReCl$_4$(ox)] (0.05 mmol) in 30 mL of a MeCN-DMF (5:1) mixture was added to a solution of 18 mg of copper(II) trifluoromethane-sulfonate (0.05 mmol) and 20 mg of phen (0.10 mmol) in 30 mL of the same mixed solvent. Both solutions were very hot, nearly boiling, before the mixing, and the resulting solution was left to cool slowly at room temperature in a closed container. After a week, a mixture of a few well formed green (**1**) and a lot of blue−green (**2**) crystals was formed and manually separated. Both kinds of crystals were suitable for X-ray diffraction studies. Anal. Calcd for C$_{26}$H$_{16}$N$_4$Cl$_4$O$_4$CuRe (**1**): C, 37.18; H, 1.92; N, 6.67%. Found: C, 37.31; H, 1.98; N, 6.62%. IR: bands associated to the oxalato ligand appear at (cm^{-1}) 1697 vs, 1673 m, and 794 s. Anal. Calcd for C$_{28}$H$_{19}$N$_5$Cl$_4$O$_4$CuRe (**2**): C, 38.17; H, 2.17; N, 7.95%. Found: C, 38.06; H, 1.85; N, 7.92%. IR: bands associated to the oxalato ligand appear at (cm^{-1}) 1694 vs, 1669 m, and 800 s. Compound **2** can be isolated in a high yield as the only product using MeCN as solvent. The procedure is as follows: a solution of 45 mg of (NBu$_4$)$_2$[ReCl$_4$(ox)] (0.05 mmol) in 20 mL of MeCN was added to a solution of 18 mg of copper(II) trifluoromethanesulfonate (0.05 mmol) and 20 mg of phen (0.10 mmol) in 30 mL of MeCN. A solid appeared immediately, and precipitation was complete after a few hours. The crystalline solid was filtered, washed with MeCN (2 × 2 mL), and dried in the air. Yield: 70%.

[ReCl$_4$(μ-ox)Cu(terpy)(H$_2$O)][ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)] (3). A hot solution of 45 mg of (NBu$_4$)$_2$[ReCl$_4$(ox)] (0.05 mmol) in 45 mL of MeCN was added to a hot solution of 18 mg of copper(II) trifluoromethanesulfonate (0.05 mmol) and 11.6 mg of terpy (0.05 mmol) in 45 mL of MeCN. A crystalline solid separated immediately. The mixture was left undisturbed overnight. The green crystals were filtered and washed with MeCN (2 × 2 mL). Yield: 23.6 mg (64%). Polyhedral green single crystals of **3** suitable for X-ray diffraction studies were obtained by the slow mixing of solutions of both reagents in MeNO$_2$:MeCN (8:1) at room temperature. Anal. Calcd for C$_{18}$H$_{13.5}$N$_{3.5}$Cl$_4$O$_{4.5}$CuRe (**3**): C, 29.12; H, 1.83; N, 6.60%. Found: C, 29.06; H, 1.53; N, 6.62%. IR: bands associated to the oxalato ligand appear at (cm^{-1}) 1709 vs, 1692 vs, 1649 m, 1630, 1369, and 803 s.

Physical Techniques. The IR spectra (KBr pellets) were recorded with a Perkin-Elmer 1750 FTIR spectrometer. Magnetic susceptibility

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Table 1. Summary of Crystal Data[a] for [ReCl$_4$(ox)Cu(phen)$_2$] (**1**), [ReCl$_4$(ox)Cu(phen)$_2$]·CH$_3$CN (**2**), and [ReCl$_4$(ox)Cu(terpy)(H$_2$O)][ReCl$_4$(ox)Cu(terpy) (CH$_3$CN)] (**3**)

	1	**2**	**3**
chem formula	C$_{26}$H$_{16}$Cl$_4$CuN$_4$O$_4$Re	C$_{28}$H$_{19}$Cl$_4$CuN$_5$O$_4$Re	C$_{36}$H$_{27}$Cl$_8$Cu$_2$N$_7$O$_9$Re$_2$
M	840.0	881.0	1484.7
cryst syst	triclinic	monoclinic	monoclinic
space group	P($-$1)	P2$_1$/n	P2$_1$/c
a, Å	9.776(2)	12.837(3)	8.930(2)
b, Å	11.744(3)	17.761(4)	18.543(4)
c, Å	14.183(3)	12.914(3)	27.503(6)
α, deg	102.09(2)	90	90
β, deg	109.42(2)	91.32(2)	94.67(2)
γ, deg	107.11(2)	90	90
V, Å^3	1379.8(5)	2943(1)	4539(2)
Z	2	4	4
D$_c$/Kg m^{-3}	2.022	1.988	2.173
F(000)	808	1704	2832
μ(Mo Kα) cm^{-1}	55.82	52.39	67.72
refln unique/obs	4888/3852	5203/3049	8050/3946
R^b	0.040	0.097	0.053
Rw^c	0.043	0.107	0.052
S^d	1.06	2.03	1.30

[a] Details in common: $T = 25$ °C, $I > 3\sigma(I)$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $Rw = [\sum w(||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2}$. [d] Goodness of fit = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

measurements (1.8–300 K) were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 1 T at high temperature and only 50 G at low temperature to avoid any problem of magnetic saturation. The device was calibrated with (NH$_4$)$_2$Mn(SO$_4$)$_2$·6H$_2$O. The corrections for the diamagnetism were estimated from Pascal constants.

X-ray Data Collection and Structure Refinement. Crystals of dimensions 0.45 × 0.37 × 0.09 (**1**), 0.12 × 0.20 × 0.22 (**2**), and 0.20 × 0.10 × 0.12 mm (**3**) were mounted on a Siemens 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°. Information concerning crystallographic data collection and structure refinements is summarized in Table 1. Examination of two standard reflections, monitored after every 98 reflections, showed no sign of crystal deterioration. Lorentz-polarization and G-scan absorption correction [12] were applied for compound **1**, whereas the data of compounds **2** and **3** were corrected by the XABS program. [13] The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. All non-hydrogen atoms (except the acetonitrile carbon atom C(28) in **2** and all the terpy carbon atoms in **3**) were refined anisotropically. The hydrogen atoms of the acetonitrile molecules in **2** and **3** and the water molecule in **3** were not defined. The other hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. The refinement was performed on F against 4888 (**1**), 5203 (**2**), and 8050 (**3**) reflections. The residual maxima and minima in the final Fourier-difference maps were 1.28 and −1.28 e Å^{-3} for **1**, 4.52 and −4.93 e Å^{-3} for **2** (the first six residual maxima are near Re(1) atom), and 1.34 and −1.41 e Å^{-3} for **3**. Solutions and refinements were performed with the SHELXTL PLUS system. [13] The final geometrical calculations were carried out with the PARST program. [14] The graphical manipulations were performed using the XP utility of the SHELXTL PLUS system. Main interatomic bond distances and angles are listed in Tables 2 (**1**), 3 (**2**), and 4 (**3**).

Results and Discussion

Description of the Sructures. [ReCl$_4$(μ-ox)Cu(phen)$_2$] (1) and [ReCl$_4$(μ-ox)Cu(phen)$_2$]·CH$_3$CN (2). Both compounds **1**

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Table 2. Selected Bond Distances (Å) and Bond Angles (Deg) for Compound **1**

Distances			
Re(1)−O(1)	2.055(7)	Re(1)−O(2)	2.062(5)
Re(1)−Cl(1)	2.312(2)	Re(1)−Cl(2)	2.307(4)
Re(1)−Cl(3)	2.358(3)	Re(1)−Cl(4)	2.325(4)
Cu(1)−N(1)	1.987(8)	Cu(1)−N(2)	2.071(5)
Cu(1)−N(3)	2.001(8)	Cu(1)−N(4)	2.107(7)
Cu(1)−O(3)	2.355(6)	Cu(1)−O(4)	2.465(8)

Angles			
O(1)−Re(1)−O(2)	78.9(2)	O(1)−Re(1)−Cl(2)	171.6(1)
O(1)−Re(1)−Cl(1)	92.0(1)	O(1)−Re(1)−Cl(3)	87.9(2)
O(1)−Re(1)−Cl(4)	88.1(2)	O(2)−Re(1)−Cl(2)	92.9(2)
O(2)−Re(1)−Cl(1)	169.5(2)	O(2)−Re(1)−Cl(3)	85.0(2)
O(2)−Re(1)−Cl(4)	91.4(2)	Cl(2)−Re(1)−Cl(1)	96.4(1)
Cl(2)−Re(1)−Cl(3)	92.8(1)	Cl(2)−Re(1)−Cl(4)	90.7(1)
Cl(1)−Re(1)−Cl(3)	89.6(1)	Cl(1)−Re(1)−Cl(4)	93.4(1)
Cl(3)−Re(1)−Cl(4)	175.1(1)	N(1)−Cu(1)−N(2)	82.2(3)
N(1)−Cu(1)−N(3)	179.2(2)	N(1)−Cu(1)−N(4)	97.3(3)
N(1)−Cu(1)−O(3)	92.8(3)	N(1)−Cu(1)−O(4)	89.2(3)
N(2)−Cu(1)−N(3)	98.5(3)	N(2)−Cu(1)−N(4)	124.6(3)
N(2)−Cu(1)−O(3)	155.1(3)	N(2)−Cu(1)−O(4)	86.4(2)
N(3)−Cu(1)−O(3)	86.6(3)	N(3)−Cu(1)−O(4)	91.1(3)
N(3)−Cu(1)−N(4)	82.1(3)	N(4)−Cu(1)−O(3)	80.2(3)
N(4)−Cu(1)−O(4)	148.8(2)	O(3)−Cu(1)−O(4)	69.0(2)

and **2** contain neutral [ReCl$_4$(ox)Cu(phen)$_2$] dinuclear units. The substantial difference is the presence of acetonitrile molecules of crystallization in **2**. Perspective drawings showing the atom numbering are shown in Figures 1 (**1**) and S1 (**2**). Each [ReCl$_4$(ox)Cu(phen)$_2$] unit contains Re(IV) and Cu(II) ions bridged by a bis(bidentate) oxalato ligand. The Re(IV) ion is in a distorted octahedral geometry, being bonded to the oxalate group and four chloride anions. No significant differences were found in the Re−Cl [mean values 2.325(4) (**1**) and 2.329(8) Å (**2**)] and the Re−O [average values 2.058(6) (**1**) and 2.06(2) Å (**2**)] bond distances. Both Re−Cl and Re−O bond lengths are in agreement with those found in the literature.[2] The O(1)O(2)-Cl(1)Cl(2) set of atoms constitutes the equatorial plane around Re, the largest deviation from planarity being 0.085(6) Å for

(13) SHELXL PLUS, Version 4.11/V, Siemens Analytical X-ray Instruments Inc., Madison WI, 1990.
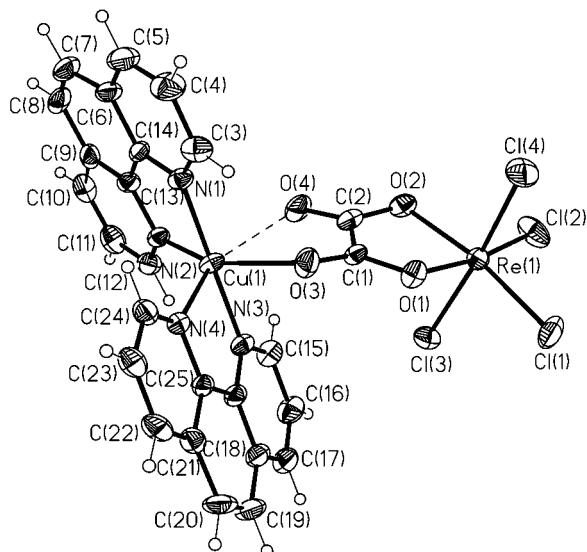(14) Nardelli, M. *Comput. Chem.*, **1983**, *7*, 95.

Figure 1. Perspective drawing of dinuclear complex in **1** showing the atom numbering. Thermal ellipsoids are plotted at 30% probability level.

Table 3. Selected Bond Distances (Å) and Bond Angles (Deg) for Compound **2**

Distances			
Re(1)−O(1)	2.07(2)	Re(1)−O(2)	2.05(2)
Re(1)−Cl(1)	2.325(9)	Re(1)−Cl(2)	2.303(8)
Re(1)−Cl(3)	2.370(8)	Re(1)−Cl(4)	2.317(7)
Cu(1)−N(1)	1.98(2)	Cu(1)−N(2)	2.10(2)
Cu(1)−N(3)	2.00(2)	Cu(1)−N(4)	2.12(2)
Cu(1)−O(3)	2.41(2)	Cu(1)−O(4)	2.32(2)
Angles			
O(1)−Re(1)−O(2)	78.9(7)	O(1)−Re(1)−Cl(2)	169.3(5)
O(1)−Re(1)−Cl(1)	96.3(5)	O(1)−Re(1)−Cl(3)	86.3(6)
O(1)−Re(1)−Cl(4)	89.1(6)	O(2)−Re(1)−Cl(2)	90.3(5)
O(2)−Re(1)−Cl(1)	173.8(5)	O(2)−Re(1)−Cl(3)	84.2(5)
O(2)−Re(1)−Cl(4)	93.1(5)	Cl(2)−Re(1)−Cl(1)	94.5(3)
Cl(2)−Re(1)−Cl(3)	93.1(3)	Cl(2)−Re(1)−Cl(4)	91.1(3)
Cl(1)−Re(1)−Cl(3)	91.6(3)	Cl(1)−Re(1)−Cl(4)	90.7(3)
Cl(3)−Re(1)−Cl(4)	175.1(2)	N(1)−Cu(1)−N(2)	82.1(8)
N(1)−Cu(1)−N(3)	176.0(8)	N(1)−Cu(1)−N(4)	99.7(7)
N(1)−Cu(1)−O(3)	96.1(7)	N(1)−Cu(1)−O(4)	88.6(7)
N(2)−Cu(1)−N(3)	94.4(8)	N(2)−Cu(1)−N(4)	111.8(7)
N(2)−Cu(1)−O(3)	171.7(7)	N(2)−Cu(1)−O(4)	100.8(7)
N(3)−Cu(1)−O(3)	87.6(7)	N(3)−Cu(1)−O(4)	93.9(7)
N(3)−Cu(1)−N(4)	79.7(7)	N(4)−Cu(1)−O(3)	76.5(7)
N(4)−Cu(1)−O(4)	147.2(7)	O(3)−Cu(1)−O(4)	71.0(7)

O(2) in **1** and 0.06(1) Å for O(1) in **2**. The Re atom is only 0.038(1) (**1**) and 0.040(1) Å (**2**) out of this plane. The values of the dihedral angle between the equatorial plane and that of the oxalate are 18.5(2) (**1**) and 12.1(4)° (**2**). The values of the angles around the rhenium atom are close to the ideal ones but are subtended by the oxalate [78.9(2)° for O(1)−Re(1)-O(2) in **1** and **2**] due to the short bite of this ligand.

The copper atom shows a cis-elongated distorted octahedral geometry,[10] being bonded to four nitrogen atoms from two phen molecules and to two oxalato oxygen atoms. The Cu−O bonds are longer than the Cu−N ones. In both compounds the oxalate anion is coordinated as an asymmetric bidentate ligand, with Cu−O distances 2.355(6) and 2.465(8) Å in **1**, and 2.32(2) and 2.41(2) Å in **2**. Assuming that the oxalate oxygens lie in the equatorial plane, a compression along the N(1)- - -N(3) axis is observed; the axial Cu−N distances average 1.994(8) (**1**) and 1.99(2) Å (**2**), whereas the equatorial ones are somewhat longer [2.089(6) (**1**) and 2.11(2) Å (**2**)]. The largest deviation from planarity in the O(3)O(4)N(2)N(4) mean plane is 0.085(7) (**1**) and 0.07(2) Å (**2**) for O(3). The values of the dihedral angle

Table 4. Selected Bond Distances (Å) and Bond Angles (Deg) for Compound **3**

Distances			
Re(1)−O(1)	2.07(1)	Re(1)−O(2)	2.05(1)
Re(1)−Cl(1)	2.316(5)	Re(1)−Cl(2)	2.322(5)
Re(1)−Cl(3)	2.341(5)	Re(1)−Cl(4)	2.335(5)
Cu(1)−N(1)	2.03(1)	Cu(1)−N(2)	1.94(1)
Cu(1)−N(3)	2.04(1)	Cu(1)−O(4)	2.05(1)
Cu(1)−O(3)	2.48(1)	Cu(1)−O(5)	2.22(1)
Re(2)−O(6)	2.05(1)	Re(2)−O(7)	2.05(1)
Re(2)−Cl(5)	2.334(5)	Re(2)−Cl(6)	2.325(6)
Re(2)−Cl(7)	2.341(5)	Re(2)−Cl(8)	2.354(5)
Cu(2)−N(4)	2.03(1)	Cu(2)−N(5)	1.92(1)
Cu(2)−N(6)	2.04(1)	Cu(2)−N(7)	1.98(2)
Cu(2)−O(9)	2.40(1)	Cu(2)−Cl(1)	3.077(6)
Angles			
O(1)−Re(1)−O(2)	79.7(5)	O(1)−Re(1)−Cl(2)	172.2(4)
O(1)−Re(1)−Cl(1)	92.1(4)	O(1)−Re(1)−Cl(3)	85.8(4)
O(1)−Re(1)−Cl(4)	88.3(4)	O(2)−Re(1)−Cl(2)	92.5(4)
O(2)−Re(1)−Cl(1)	171.7(4)	O(2)−Re(1)−Cl(3)	86.0(4)
O(2)−Re(1)−Cl(4)	88.8(4)	Cl(2)−Re(1)−Cl(1)	95.6(2)
Cl(2)−Re(1)−Cl(3)	92.8(2)	Cl(2)−Re(1)−Cl(4)	92.5(2)
Cl(1)−Re(1)−Cl(3)	92.0(2)	Cl(1)−Re(1)−Cl(4)	92.4(2)
Cl(3)−Re(1)−Cl(4)	172.8(2)	N(1)−Cu(1)−N(2)	78.8(6)
N(1)−Cu(1)−N(3)	160.0(6)	N(1)−Cu(1)−O(4)	98.4(6)
N(1)−Cu(1)−O(3)	86.5(5)	N(1)−Cu(1)−O(5)	94.9(5)
N(2)−Cu(1)−N(3)	81.1(6)	N(2)−Cu(1)−O(4)	164.3(5)
N(2)−Cu(1)−O(3)	89.4(5)	N(2)−Cu(1)−O(5)	107.5(5)
N(3)−Cu(1)−O(3)	93.1(5)	N(3)−Cu(1)−O(5)	91.2(5)
N(3)−Cu(1)−O(4)	100.9(6)	O(4)−Cu(1)−O(3)	75.0(4)
O(4)−Cu(1)−O(5)	88.1(5)	O(3)−Cu(1)−O(5)	163.0(4)
O(6)−Re(2)−O(7)	80.3(5)	O(6)−Re(2)−Cl(6)	173.8(4)
O(6)−Re(2)−Cl(5)	93.1(4)	O(6)−Re(2)−Cl(8)	86.9(4)
O(6)−Re(2)−Cl(8)	88.1(4)	O(7)−Re(2)−Cl(6)	93.5(4)
O(7)−Re(2)−Cl(8)	88.5(4)	O(7)−Re(2)−Cl(7)	88.3(4)
O(7)−Re(2)−Cl(8)	88.5(4)	Cl(6)−Re(2)−Cl(5)	93.1(2)
Cl(6)−Re(2)−Cl(7)	93.4(2)	Cl(6)−Re(2)−Cl(8)	91.4(2)
Cl(5)−Re(2)−Cl(7)	89.6(2)	Cl(5)−Re(2)−Cl(8)	93.0(2)
Cl(7)−Re(2)−Cl(8)	174.5(2)	N(4)−Cu(2)−N(5)	79.8(6)
N(4)−Cu(2)−N(6)	160.3(6)	N(4)−Cu(2)−N(7)	99.3(6)
N(4)−Cu(2)−O(9)	91.4(5)	N(4)−Cu(2)−Cl(1)	91.6(4)
N(5)−Cu(2)−N(6)	80.6(6)	N(5)−Cu(2)−N(7)	176.3(6)
N(5)−Cu(2)−O(9)	98.3(5)	N(5)−Cu(2)−Cl(1)	99.8(4)
N(6)−Cu(2)−O(9)	92.9(5)	N(6)−Cu(2)−Cl(1)	90.3(4)
N(6)−Cu(2)−N(7)	100.2(6)	N(7)−Cu(2)−O(9)	85.2(6)
N(7)−Cu(2)−Cl(1)	76.6(4)	O(9)−Cu(2)−Cl(1)	161.9(4)

between this mean plane and that of the oxalate are 20.1(2) (**1**) and 16.3(4)° (**2**). The two phen ligands are planar [the maximum deviations from the mean plane being 0.05(1) Å at C(10) atom in **1** and 0.07(2) Å at C(22) in **2**] and the values of dihedral angle between them are 52.8(1) (**1**) and 70.2(1)° (**2**). The values of the Re···Cu separation across the bridging oxalato are 5.628(2) (**1**) and 5.649(3) Å (**2**).

The presence of an acetonitrile molecule of crystallization in **2** causes a slightly greater separation between the dinuclear molecules, the shortest interdimer Re···Cu and Cl···Cl distances are 6.57 and 5.84 Å, respectively, in **2** and 6.19 and 4.81 Å, respectively, in **1**, with a different packing of these units in the crystal structure (Figures S2 and S3). A comparison of **1** and **2** with the recently reported molecular structure of [ReCl$_4$(μ-ox)-Cu(bipy)$_2$] shows that the phen substitution for bipy in the coordination sphere of Cu(II) changes the binding of the oxalato ligand from monodentate to bidentate, also decreasing the Cu−O(ox) bond lengths from 2.65 to 2.3−2.4 Å.

[ReCl$_4$(μ-ox)Cu(terpy)(H$_2$O)][ReCl$_4$(μ-ox)Cu(terpy)-(CH$_3$CN)] (3). The crystal structure of this compound is made up of two different and neutral bimetallic units, [ReCl$_4$(μ-ox)-Cu(terpy)(H$_2$O)] and [ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)], in a 1:1 ratio. Perspective drawings of their molecular structures showing the atom numbering are shown in Figures 2 a [Re(1)−Cu(1)
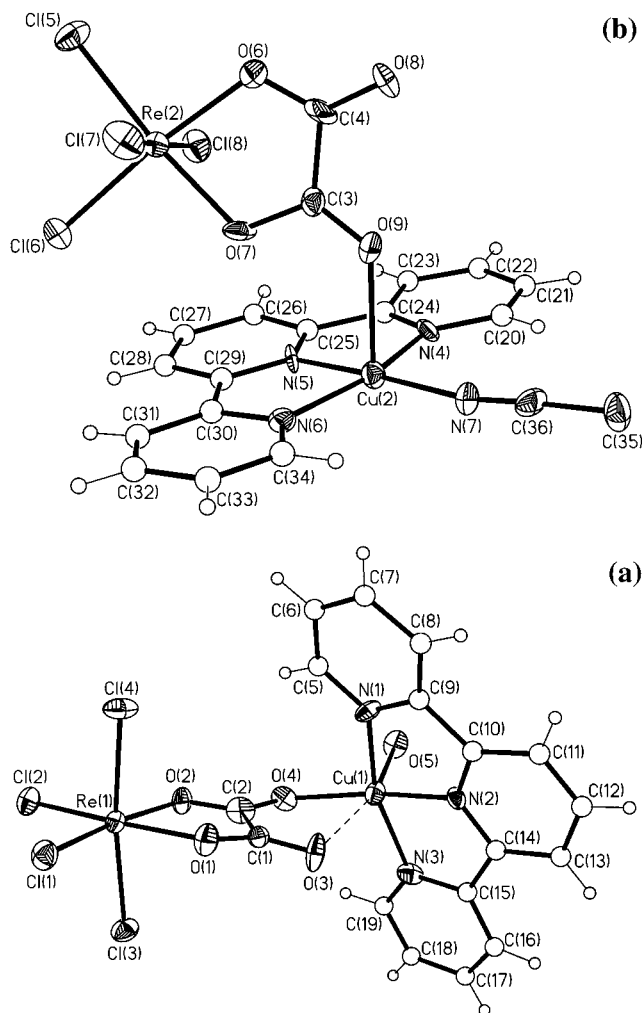
Figure 2. Perspective drawings of the [ReCl₄(μ-ox)Cu(terpy)(H₂O)] (a) and [ReCl₄(μ-ox)Cu(terpy)(CH₃CN)] (b) dinuclear units in **3** showing the atom numbering. Thermal ellipsoids, except for the carbon atoms of terpyridine, are plotted at 30% probability level.

Figure 3. Perspective drawing of the tetranuclear entity occurring in **3** which is formed through a weak interdimer chloro−copper interaction.

pair] and 2b [Re(2)−Cu(2) pair]. Both molecules contain the [ReCl₄(ox)] moiety which acts as a ligand toward a Cu(II) ion through the oxalato group. Each [ReCl₄(ox)] fragment contains a Re(IV) atom in a distorted octahedral geometry, being bonded to an oxalate and four chloride anions. No significant differences were found in the Re(1)−Cl and Re(2)−Cl [mean values 2.328(5) and 2.338(5) Å, respectively)] and in the Re(1)−O and Re(2)−O [average values 2.06(1) and 2.05(1) Å] bond distances. The values of both Re−Cl and Re−O bond lengths are in agreement with those found in **1** and **2**. Bonding angles around the Re atoms are close to the ideal values except for those subtended by the oxalato ligand [79.7(5) and 80.3(5)° for O(1)−Re(1)−O(2) and O(6)−Re(2)−O(7)]. The O(1)O(2)-Cl(1)Cl(2) set of atoms constitutes the equatorial plane around Re(1), the largest deviation from planarity being 0.01(1) Å for O(2). The Re(1) atom is only 0.024(2) Å out of this plane. The dihedral angle between the equatorial plane and that of the oxalate ligand is 5.4(4)°. The O(5)O(6)Cl(5)Cl(6) set of atoms constitutes the equatorial plane around Re(2) [the largest deviation from planarity being 0.03(1) Å for O(6)], and the value of the dihedral angle between this plane and that of the oxalate ligand is 2.3(3)°. The Re(2) atom practically lies within the equatorial plane [it is only shifted by 0.013(1) Å out of this plane].
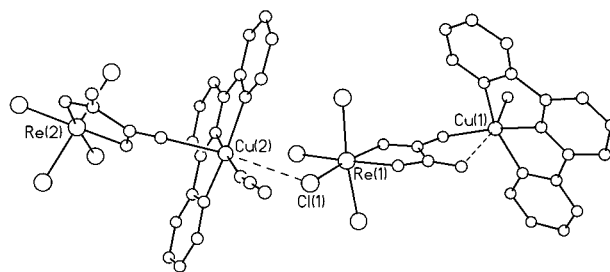
Both dinuclear units also have a very similar [Cu(terpy)] fragment, with Cu−N bond distances averaging 2.00(1) Å. The pyridyl rings of the terpy ligands are planar, as expected, the maximum deviation from the mean planes being 0.02(2) Å at C(9) atom and 0.03(2) Å at C(25). The dihedral angles between the three pyridyl rings are 5.6(6) and 3.5(6)° in the Re(1)−Cu(1) unit and 1.5(5) and 4.2(5)° in the Re(2)−Cu(2) one. The main differences between the two dinuclear units are the coordination number and geometry of the copper atoms and hence the coordination mode of the oxalato ligand. The Cu(1) atom is six-coordinated with an elongated octahedral geometry, and oxalate is bound to it in an asymmetric didentate way, occupying one equatorial [short Cu(1)−O(4) bond of 2.05(1) Å] and one axial [long Cu(1)−O(3) bond of 2.48(1) Å] position. The bite angle of the oxalato ligand is 75.0(4)°. The three terpy nitrogen atoms complete the equatorial plane, and the second axial position is occupied by a water molecule with a Cu(1)−O(5) bond length of 2.22(1) Å. The planes of the octahedron around Cu(1) are highly distorted except those containing the O(3)O(4)N(2)O(5) set of atoms. The Cu(1) atom is 0.029(3) Å out of this plane, which forms a dihedral angle of 21.9(4)° with the oxalate plane. The Re(1)···Cu(1) separation across the bis-(didentate) oxalato bridge is 5.504(3) Å. It is worthy to note that in [ReCl₄(μ-ox)Cu(terpy)(H₂O)] unit, one of copper to oxalato bonds is as short as the Re(IV)−oxalate ones [2.05(1) Å for Cu(1)−O(4)], and so, the bridge between the metal ions is better here than in the complexes **1**, **2**, and [ReCl₄(μ-ox)-Cu(bipy)₂]. The Cu(2) atom is five coordinated with a square pyramidal geometry. Oxalate is bound to this copper atom in a monodentate way, occuping the axial position with a long Cu(2)−O(9) bond [2.40(1) Å]. The three terpy nitrogen atoms [N(4), N(5), and N(6)] and the nitrogen atom of an acetonitrile molecule [N(7)] [1.98(2) Å for Cu(2)−N(7)] occupy the basal positions. The largest deviation from planarity of these four donor atoms is 0.01(1) Å. The Cu(2) atom is shifted by 0.049(3) Å out of this plane. The Re(2)···Cu(2) separation across the bidentate/monodentate oxalato bridge is 5.436(2) Å.

The two different molecules are oriented in the crystal structure in such a way that a chloro ligand of one of them [Cl(1)] points toward the copper atom of the other [Cu(2)] (Figure 3). The intermolecular Cu(2)···Cl(1) distance is 3.077(2) Å, a value which is greater than the sum of van der Waals radii, and for this reason it can be considered a nonbonding distance. Nevertheless, if one considers that it is a very weak bond, the Cu(2) environment may be alternatively described as a distorted octahedron. In this way, the two dinuclear units linked together would constitute a tetranuclear complex. In fact, the intermolecular Re(1)···Cu(2) separation through the chloro bridge, 4.763(2) Å, is shorter than the intramolecular Re(1)···Cu(1) and Re(2)···Cu(2) distances. Most likely, this interaction is the occurring one in the crystal structure of [ReCl₄(μ-ox)Cu(bipy)₂],[2] but because of the six coordination
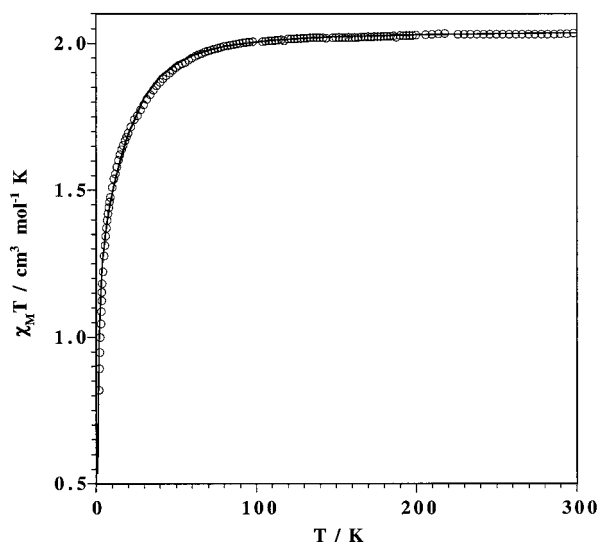
Figure 4. Thermal dependence of $\chi_M T$ for **2**: (o) experimental data; (−) best-fit curve (see text).

Scheme 2

of Cu(1) in the Re(1)−Cu(1) dinuclear unit, it affords a tetranuclear complex (**3**) and not a chain (bipy case). Moreover, the strict coplanarity of the equatorial donor atoms at Cu(2) accounts for the shorter axial bonds it has when compared to those of the copper atom in the [ReCl$_4$(μ-ox)Cu(bipy)$_2$] chain, where the four bipy nitrogen atoms exhibit a significant distortion toward the tetrahedron.

Magnetic Properties of 2 and 3. The magnetic properties of complex **2** under the form of a $\chi_M T$ versus T plot (χ_M being the magnetic susceptibility per Re(IV)Cu(II) heterobimetallic unit) are shown in Figure 4. The close similarity of the structures of **1** and **2** and the fact that only a very small amount of crystals of complex **1** were obtained induced us to investigate magnetically only the major product (that is compound **2**). The $\chi_M T$ for **2** at room temperature is 2.03 cm^3 mol^{-1} K, a value which is as expected for a uncoupled Re^{IV} (S$_{Re}$ = 3/2) − Cu^{II} (S$_{Cu}$ = 1/2) pair. It remains practically constant upon cooling and decreases fast at T < 100 K to reach a value of 0.82 cm^3 mol^{-1} K at 1.8 K. Taking into account the discrete dinuclear structure of **2**, the decrease of $\chi_M T$ in the lower temperature range could be only attributed to zero-field splitting effects of Re(IV) and intramolecular Re(IV)−Cu(II) magnetic interactions. Consequently, we have analyzed the magnetic behavior of **2** through the Hamiltonian of eq 1

$$H = -JS_{Re}S_{Cu} + DS^2_{zRe} + g_{Re}\beta HS_{zRe} + g_{Cu}\beta HS_{zCu} \quad (1)$$

where J is the exchange coupling parameter between the quartet Re(IV) and doublet Cu(II) local spins, $2D$ is the energy gap between the ±3/2 and ±1/2 Kramers doublets (the zero-field splitting of Re(IV)), and the last two terms account for the Zeeman effects of the two metal ions. Least-squares fit though eq 1 leads to the following set of parameters: $J = -0.90(2)$ cm^{-1}, $2D = 48(1)$ cm^{-1}, $g_{Re} = 1.88(1)$, $g_{Cu} = 2.02(1)$, and $R = 1.2 \times 10^{-5}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)_i^{obsd} - (\chi_M T)_i^{calc}]^2/[(\chi_M T)_i^{obsd}]^2$). The calculated curve matches very well the magnetic data.

Let us first analyze and discuss the values of these best-fit parameters concerning compound **2** prior to consider the magnetic behavior of complex **3**. As far as the large value of $2D$ is concerned, it is in agreement with the previously reported value of 60 cm^{-1} for the (AsPPh$_4$)$_2$[Re(Cl$_4$(ox)] mononuclear complex,[2] with the same ligands and the same site symmetry
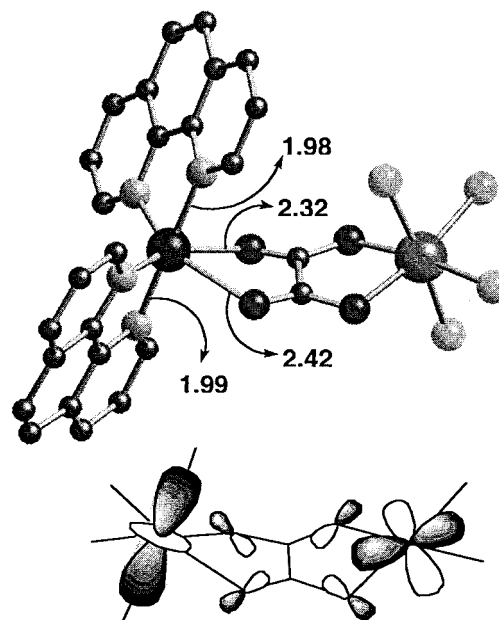
(C_{2v}). In fact, the great value of the spin−orbit coupling parameter of the third-row transition metal ions (λ ca. 1100 cm^{-1} for the Re(IV) single ion)[3] would account for this large value of $2D$. In addition, the positive value of λ also causes the g < 2 for the rhenium(IV) ion. Finally, the weak intradimer Cu(II)-Re(IV) antiferromagnetic coupling ($J = -0.90$ cm^{-1}) can be understood by considering the symmetry and poor overlap between the metal-centered magnetic orbitals through bridging oxalato (Scheme 2). We have chosen to visualize this interaction the symmetry adapted HOMO of the bridge ligand which overlaps (vía π) with the d$_{xy}$ orbital of Re(IV). So, both orbitals are coplanar and perpendicular to the magnetic orbital of Cu(II), defined roughly by a d$_{z^2}$ type orbital. Because of the asymmetry of the bridge and the distorted coordination geometry of Cu(II), the orthogonality between this orbital and the d$_{xy}$ one of the Re(IV) through oxalato is broken but the overlap is predicted to be very small, resulting in a weak antiferromagnetic coupling between the metal ions.

The magnetic properties of **3** under the form of $\chi_M T$ versus T plot (χ_M being the magnetic susceptibility per two Re(IV)-Cu(II) pairs) is shown in Figure 5. The $\chi_M T$ for **3** at room temperature is 3.93 cm^3 mol^{-1} K, a value which is as expected for a set of two Re(IV) and two Cu(II) ions which are magnetically isolated from each other. This value is kept constant upon cooling, and it quickly decreases at T < 100 K to attain a value of 2.72 cm^3 mol^{-1} K at 1.8 K. This decrease of $\chi_M T$ in the low temperaturte range may be due to zero-field splitting effects and/or magnetic interactions. Keeping in mind the tetranuclear nature of complex **3** (see Figure 3), we have analyzed its magnetic data through the Hamiltonian of eq 2

$$H = -J_{11}S_{Re(1)}S_{Cu(1)} - J_{22}S_{Re(2)}S_{Cu(2)} - J_{12}S_{Re(1)}S_{Cu(2)} +$$
$$D_1S^2_{zRe(1)} + D_2S^2_{zRe(2)} + g_{Re(1)}\beta HS_{zRe(1)} + g_{Re(2)}\beta HS_{zRe(2)} +$$
$$g_{Cu(1)}\beta HS_{zCu(1)} + g_{Cu(1)}\beta HS_{zCu(1)} \quad (2)$$

where J_{11}, J_{22}, and J_{12} are the exchange coupling constants for the Re(1)Cu(1), Re(2)Cu(2), and Re(1)Cu(2) units, respectively, $2D_1$ and $2D_2$ are the energy gaps between the ±3/2 and ±1/2 Kramers doublets for Re(1) and Re(2), and the last four terms account for the Zeeman effects associated at the Re(1), Re(2),
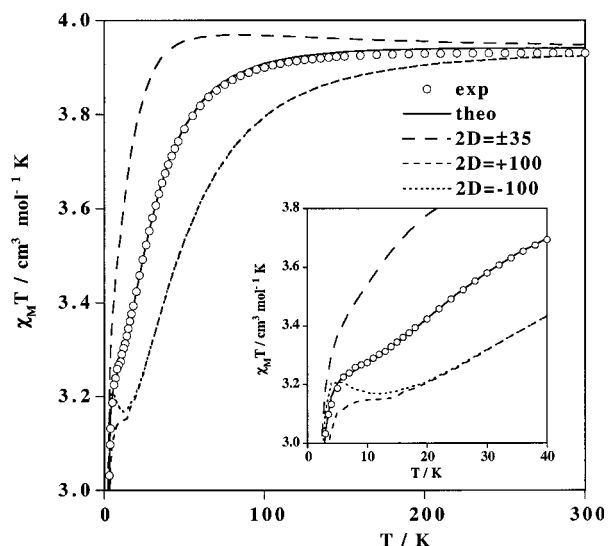
Figure 5. Thermal dependence of $\chi_M T$ for **3** illustrating the influence of $2D$ values on the fit: (o) experimental data; (−) best-fit curve (see text). The insets show the variation of the $\chi_M T$ curves in the low-temperature range for the set of $2D$ values indicated.

Cu(1), and Cu(2) metal ions. Least-squares fit through eq 2 leads to the following set of parameters: $J_{11} = -0.83(2)$, $J_{22} = +5.6(3)$, $J_{12} = +0.70(2)$ cm^{-1}, $2D_1 = 63(2)$, $2D_2 = 67(2)$ cm^{-1}, $g_{Re(1)} = 1.83(1)$, $g_{Re(2)} = 1.85(1)$, $g_{Cu(1)} = 2.00(1)$, $g_{Cu(2)} = 2.01(1)$, and $R = 1.8 \times 10^{-5}$. The fit is very good. However, the overparametrization cannot be excluded because of the large number of variable parameters considered. We have also analyzed the influence of D on the shape of the magnetic curve. The calculated curves using $2D$ as the only variable parameter (assuming the same value, either positive or negative, for the two rhenium atoms) are shown in Figure 5 for the whole temperature region. A detail of the different shapes of the theoretical curves in the low-temperature region is given in the inset.

Finally, the last point which requires our attention is the weak magnitude and different sign (ferromagnetic for J_{22} and J_{12} and antiferromagnetic for J_{11}) of the magnetic couplings within the tetranuclear unit. The three ReCu structural fragments of **3** and the corresponding pictures of the magnetic orbitals are shown in Scheme 3. Rhenium and oxalate orbitals in 3(a) and 3(b) are the same as in Scheme 2, and Scheme 3(c) shows the 3p orbital of the chloro bridge which overlaps via π with the d$_{xy}$ orbital of rhenium. Given the tetragonal elongated octahedral coordination of the Cu(1) and Cu(2), the magnetic orbital in both metal ions is the d$_{x^2-y^2}$ orbital (d$_{z^2-y^2}$ in the bimetallic fragment if we consider that the oxalate lies in the xy plane) and, therefore, perpendicular to the magnetic orbital of rhenium.

The asymmetric coordination and bite angle of the oxalato ligand within the Re(1)Cu(1) pair, Scheme 3(b), causes some overlap with the copper orbital, although very poor, resulting in a weak antiferromagnetic coupling ($J_{11} = -0.83$ cm^{-1}) as in **2**. On the other hand, the net overlap between the magnetic orbitals in the Re(2)Cu(2) (Scheme 3(a)) and Re(1)Cu(2) (Scheme 3(c)) pairs should be negligible, leading to a ferromagnetic coupling as observed. The J_{12} is smaller than J_{22} because of the very long Cu(2)···Cl(1) axial distance (ca. 3.08 Å). We would like to point out here that a significant antiferromagnetic coupling between Re(IV) and Cu(II) ions through these types of oxalato and chloro bridges was observed in the chain compound [Cu(bipy)$_2$(ox)ReCl$_4$]. The different sign for the magnetic interaction in the chain compound is due to the tetrahedral distortion of the copper environment, which causes a significant spin density of the magnetic orbital of the copper(II) ion in the axial position. This situation is precluded in the Cu(2) atom because the coplanarity of the four short equatorial bonds (N(4)N(5)N(6)N(7) set of atoms) ensures the localization of the magnetic orbital of the copper(II) within the equatorial plane.

Conclusions

Summarizing, the main conclusions from the present work are as follows: (i) we have demonstrated that it is possible to use the [Re(Cl$_4$(ox)]$^{2-}$ mononuclear complex as ligand toward first row transition metal ions, leading to the first bimetallic Re(IV)Cu(II) compounds, (ii) the coordination mode of the [Re(Cl$_4$(ox)]$^{2-}$ ligand changes with the nature of the other ligands in the coordination sphere of Cu(II), being monodentate in [ReCl$_4$(ox)Cu(bipy)$_2$] and in [ReCl$_4$(ox)Cu(terpy)(CH$_3$CN)], one of the two different dinuclear units in **3**, asymmetric

Scheme 3

(a)   **(b)**   **(c)**
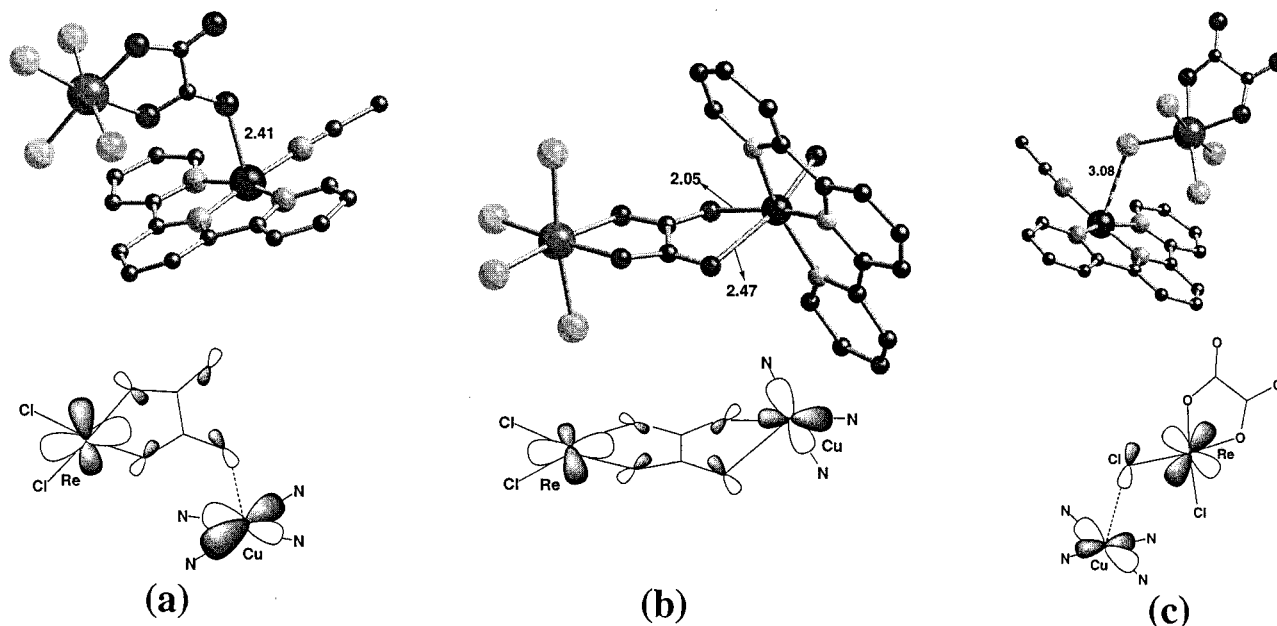
bidentate with two long Cu(II)−O bonds in [ReCl$_4$(ox)Cu-(phen)$_2$] (**2**) and asymmetric bidentate with one short and one long Cu(II)−O bonds in [ReCl$_4$(ox)Cu(terpy)(H$_2$O)], the other dinuclear unit of **3**, (iii) the coupling between Re(IV) and Cu(II) can be ferro- or antiferromagnetic but is very weak in all the cases, and (iv) the analysis of these results suggests that a quite strong ferromagnetic coupling should be obtained if the ligand is coordinated in a symmetric bidentate way with two short Cu(II)−O bonds. We are now trying the synthesis of such a complex.

Supporting Information Available: Perspective view of the structure of complex **2** (Figure S1), crystal packing of complexes **1** (Figure S2) and **2** (Figure S3), and X-ray crystallographic files for complexes **1**−**3** in CIF format. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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