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Rhenium(IV)–Copper(II) Heterobimetallic Complexes with a Bridge Malonato Ligand. Synthesis, Crystal Structure, and Magnetic Properties

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The Re(IV) complex $[ReCl_4(mal)]^{2-}$, in the form of two slightly different salts, $(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$ (**1a**) and $(AsPh_4)(HNEt_3)[ReCl_4(mal)]$ (**1b**), and the Re(IV)–Cu(II) bimetallic complexes $[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ (**2**), $[ReCl_4(\mu\text{-mal})Cu(bpy)_2]$ (**3**), and $[ReCl_4(\mu\text{-mal})Cu(terpy)]$ (**4**) (mal = malonate dianion, $AsPh_4$ = tetraphenylarsonium cation, $HNEt_3$ = triethylammonium cation, phen = 1,10-phenanthroline, bpy = 2,2′-bipyridine and terpy = 2,2′:6′,2″-terpyridine) have been synthesized and the structures of **1a**, **1b**, **2**, and **3** determined by single-crystal X-ray diffraction. The structures of **1a** and **1b** are made up of discrete $[ReCl_4(mal)]^{2-}$ anions and $AsPh_4^+$ and $HNEt_3^+$ cations, held together by electrostatic forces and hydrogen bonds. The Re(IV) atom is surrounded by four chloride anions and a bidentate malonate group, in a distorted octahedral environment. The structure of **2** consist of neutral dinuclear units $[ReCl_4(\mu\text{-mal})Cu(phen)_2]$, with the metal ions united through a bridge carboxilato. The environment of Re(IV) is nearly identical to that in the mononuclear complex, and Cu(II) is five coordinate, being surrounded by four nitrogen atoms of two bidentate phen ligands and one oxygen atom of the malonato ligand. In **3**, there are also dinuclear units, $[ReCl_4(\mu\text{-mal})Cu(bpy)_2]$, but the Cu(II) ions complete a distorted octahedral coordination by binding with the free malonato oxygen atom of a neighbor unit, resulting in an infinite chain. The magnetic properties of **1**–**4** were also investigated in the temperature range 2.0–300 K. The magnetic behavior of **1a** and **1b** is as expected for a Re(IV) complex with a large value of the zero-field splitting ($2D$ ca. 110 cm^{-1}). For the bimetallic complexes, the magnetic coupling between Re(IV) and Cu(II) is antiferromagnetic in **2** ($J = -0.39$ cm^{-1}), ferromagnetic in **4** ($J = +1.51$ cm^{-1}), and nearly negligible in **3** ($J = -0.09$ cm^{-1}).

Introduction

During the past 20 years, magneto-structural studies on polynuclear complexes have comprised a very active research field.[2] One of the crucial points in this area is the understanding of the structural and chemical factors that determine the exchange coupling between paramagnetic centers, either through space or through chemical bridges.

Along these lines, we have reported a detailed description of the magnetic behavior of heteropolynuclear complexes containing Re(IV) and an M(II) 3d metal ion (M = Cu, Ni, Mn, Fe) bridged by an oxalato ligand.[3] These compounds contain $[ReCl_4(ox)]^{2-}$ (ox = oxalate dianion) as building bloc, which exhibits different coordination modes depending on M and the auxiliary ligand used to complete its coordination sphere. Very different architectures can be found, ranging from isolated dinuclear units, for example, $[ReCl_4(\mu\text{-ox})Mn(dmphen)_2]\cdot CH_3CN$ (dmphen = 2,9-dimethyl-1,-10-phenanthroline),[3b,3c] to infinite chains with helicoidal conformation, as in the case of $[ReCl_4(\mu\text{-ox})Cu(bpy)_2]$ (bpy = 2,2′- bipyridine).[3a] The formation of such structures together with the particular characteristics of Re(IV) ($5d^3$ ion with a $^4A_2$ ground term and a significant zero-field splitting) result in interesting magnetic properties. Hence, we can find either ferromagnetic or antiferromagnetic

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coupling between Re(IV) and M(II) depending on the relative positions of the magnetic orbitals involved. This last fact is a consequence of the coordination mode of the oxalate ligand and the overall structure of the polynuclear complex.

Following with this idea, the malonate ion (dianion of the propanedioic acid, H_2mal) seems to be a good candidate for the preparation of Re(IV) complexes that can act as ligands toward M(II) 3d ions. As recently reviewed,[4] malonato ligand can adopt different bridging modes, with the carboxylate group in a syn−syn, anti−syn, or anti−anti conformation. These different spatial arrangements affect the magnitude of the magnetic interaction between spin centers (governed by the overlap density), resulting in ferro- or antiferromagnetic couplings. Even though this ligand has not been as extensively assayed as a bridging ligand as oxalate, several reports account for the versatility of malonate to build copper(II),[5,6] nickel(II),[7] cobalt(II),[6a,8] manganese(II),[6b,6c,6d,9] manganese(III),[10] molybdenum(II),[11] gadollinium(III),[12] praseodimium(III)[13] homometallic and copper(II)−manganese(II) [14] heterometallic polynuclear species.

With this in mind, this work reports the synthesis, crystal structure, and magnetic properties of two salts of $[ReCl_4(mal)]^{2-}$. This novel Re(IV) complex is used as a ligand to form new bimetallic Re(IV)−Cu(II) species: $[ReCl_4(\mu\text{-mal})Cu(phen)_2]$, $[ReCl_4(\mu\text{-mal})Cu(bpy)_2]$, and $[ReCl_4(\mu\text{-mal})Cu(terpy)]$ (phen = 1,10-phenanthroline, terpy = 2,2′:6′,2″-terpyridine). Their syntheses, crystal structures, and magnetic behavior over the temperature range 2−300 K are also reported herein.

Experimental Section

Materials. Copper(II) trifluoromethanesulfonate; copper(II) perchlorate hexahydrate; 1,10-phenanthroline monohydrate; 2,2′-bipyridine; 2,2′:6′,2″-terpyridine; malonic acid; tetraphenylarsonium chloride monohydrate ($AsPh_4Cl{\cdot}H_2O$); and the organic solvents acetonitrile, *N*,*N*-dimethylformamide, and 2-propanol were purchased from commercial sources and used as received. Triethylamine was distilled from CaH_2 before use.[15] The complex $(NBu_4)_2[ReCl_6]$ was prepared as previously reported.[3a,16]

Synthesis of the Complexes. $(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$ (1a). A mixture of 352 mg of $(NBu_4)_2[ReCl_6]$ (0.40 mmol), 250 mg of malonic acid (2.40 mmol), and 350 μL of triethylamine (2.50 mmol) in 20 mL of 2-propanol was refluxed under nitrogen atmosphere for 10 min. The light brown solution was filtered through paper, and a solution of 384 mg of $AsPh_4Cl{\cdot}H_2O$ (0.92 mmol) in 10 mL of 2-propanol was added. After 10−12 h, a green crystalline solid of the final product was obtained. The solid was filtered off and washed with 2-propanol (3 × 3 mL). Yield: 50−60%. Suitable crystals for X-ray diffraction studies were obtained by slow evaporation of a solution in acetonitrile at room temperature. Anal. Calcd for $C_{41}H_{40}As_{1.5}Cl_4O_4N_{0.5}Re$: C, 47.2; H, 3.9; N, 0.7; O, 6.1%. Found: C, 48.1; H, 4.3; N, 0.7; O, 6.3%. IR: bands associated to the malonate ligand appear at (cm^{-1}) 1649 (vs, broad), 1345 (vs), 958 (m), and 935 (m).

$(AsPh_4)(HNEt_3)[ReCl_4(mal)]$ (1b). This compound was prepared similarly to **1a** but with different amounts of malonic acid (500 mg, 4.80 mmol), triethylamine (700 μL, 5.0 mmol), and 2-propanol (30 mL) and a different refluxing time (30 min). The resulting solution was treated as above. Yield: 35−40%. Suitable crystals for X-ray diffraction studies were obtained directly from the mother liquor by slow evaporation at room temperature. Anal. Calcd for $C_{32}H_{38}AsCl_4O_4NRe$: C, 42.5; H, 4.2; N, 1.6%. Found: C, 43.7; H, 4.2; N, 1.6%. IR: bands associated to the malonate ligand appear at (cm^{-1}) 1665 (vs), 1613 (vs), 1355 (vs), 970 (m), and 936 (m).

$[ReCl_4(\mu\text{-mal})Cu(phen)_2]{\cdot}CH_3CN$ (2). A solution of 53 mg of **1a** (0.05 mmol) in 10 mL of acetonitrile was added to a solution of 18.1 mg of copper(II) trifluoromethanesulfonate (0.05 mmol) and 15.6 mg of $phen{\cdot}H_2O$ (0.10 mmol) in 15 mL of acetonitrile.

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Table 1. Summary of Crystal Data[a] for $(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$ (**1a**), $(AsPh_4)(HNEt_3)[ReCl_4(mal)]$ (**1b**), $[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ (**2**), and $[ReCl_4(\mu\text{-mal})Cu(bpy)_2]$ (**3**)

	1a	**1b**	**2**	**3**
chem formula	$C_{42}H_{40}As_{1.50}Cl_4N_{0.50}O_4Re$	$C_{33}H_{38}AsCl_4NO_4Re$	$C_{29}H_{21}Cl_4CuN_5O_4Re$	$C_{23}H_{18}Cl_4CuN_4O_4Re$
M	1056.13	915.56	895.05	805.95
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a, Å	10.703(1)	9.737(5)	10.120(1)	10.866(3)
b, Å	11.629(1)	20.344(2)	17.864(1)	15.559(5)
c, Å	38.132(5)	18.954(3)	9.558(1)	15.995(2)
α, deg	88.44(1)	90.00	98.56(1)	90.00
β, deg	84.25(1)	96.71(2)	115.97(1)	97.30(2)
γ, deg	63.19(1)	90.00	96.18(1)	90.00
V, Å^3	4213.76(80)	3728.6(19)	1506.72(30)	2682.3(12)
Z	4	4	2	4
D_c/kg m^{-3}	1665	1631	1973	1996
$F(000)$	2080	1804	868	1552
μ(Mo K), cm^{-1}	4.347	4.461	5.119	5.738
refln unique/obs	14918/9084	6925/3206	6900/5114	4708/2890
R^b	0.057	0.057	0.042	0.063
$R_w{}^c$	0.137	0.151	0.108	0.163
S^d	0.954	0.979	1.039	1.105

[a] Details in common: $T = 20$ °C, $I > 2\sigma(I)$. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [d] Goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

After 2 days, emerald green crystals were separated and washed with acetonitrile (3 × 2 mL). Yield: 70−80%. Anal. Calcd for $C_{29}H_{21}Cl_4O_4N_5CuRe$: C, 38.9; H, 2.4; N, 7.8%. Found: C, 38.5; H, 1.9; N, 7.1%. IR: bands associated to the malonate ligand appear at (cm^{-1}) 1662 (vs), 1384 (s), 970 (m), and 940 (m).

[ReCl$_4$(*μ*-mal)Cu(bpy)$_2$] (3). A solution of 53 mg of **1a** (0.05 mmol) in 50 mL of acetonitrile was added to a solution of 18.1 mg of copper(II) trifluoromethanesulfonate (0.05 mmol) and 15.6 mg of bpy (0.10 mmol) in 50 mL of acetonitrile. After 3−4 days, laminar blue-green crystals were separated and washed with acetonitrile (3 × 2 mL). Yield: 60−80%. Anal. Calcd for $C_{23}H_{18}Cl_4O_4N_4CuRe$: C, 34.3; H, 2.3; N, 7.0; O, 7.9%. Found: C, 34.3; H, 2.0; N, 7.0; O, 8.2%. IR: bands associated to the malonate ligand appear at (cm^{-1}) 1605 (vs), 1359 (s), 976 (m), and 930 (m).

[ReCl$_4$(*μ*-mal)Cu(terpy)] (4). A solution of 53 mg of **1a** (0.05 mmol) in 10 mL of acetonitrile/dimethylformamide (10:3) was added to a solution of 18.5 mg of copper(II) perchlorate hexahydrate (0.05 mmol) and 12 mg of terpy (0.05 mmol) in 10 mL of acetonitrile/dimethylformamide (10:3). After 1−2 days, blue-green crystals were separated and washed with acetonitrile (3 × 2 mL). Yield: 50−60%. Anal. Calcd for $C_{20}H_{18}Cl_4O_5N_4CuRe$: C, 30.6; H, 2.3; N, 7.1%. Found: C, 30.6; H, 2.3; N, 6.7%. IR: bands associated to the malonate appear at (cm^{-1}) 1666 (vs), 1365 (vs), and 937 (w).

Physical Techniques. The IR spectra (KBr pellets) were recorded on a Bomen MB FT-IR spectrophotometer. Elemental analysis was accomplished on a Carlo Erba model 1108 elemental analyzer. 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 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's constants.[17]

X-ray Data Collection and Structure Refinement. Crystals of dimensions 0.41 × 0.32 × 0.23 mm^3 (**1a**), 0.45 × 0.12 × 0.10 mm^3 (**1b**), 0.15 × 0.10 × 0.02 mm^3 (**2**), and 0.17 × 0.09 × 0.03 mm^3 (**3**) were mounted on a Bruker R3m/V (**1a**) and a Rigaku AFC-7S (**1b**, **2**, and **3**) automatic four-circle diffractometer and used for data collection. Diffraction data were collected at room temperature by using graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71069$ Å) with the $\omega-2\theta$ scan method. The unit cell parameters were determined from least-squares refinement of the setting angles of 25 (**1a**, **1b**, **2**) and 13 (**3**) reflections in the 2θ ranges of 15−30° (**1a**) and 10−20° (**1b**, **2**, and **3**). Information concerning crystallographic data collection and structure refinements is summarized in Table 1. Examination of two (**1a**) or three (**1b**, **2**, and **3**) standard reflections, monitored after every 50 (**1a**) or 150 (**1b**, **2**, and **3**) reflections, showed no sign of crystal deterioration. Lorentz-polarization and Ψ-scan absorption corrections[18,19a] were applied to the intensity data. The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The C2 atom in **3** show positional disorder and was refined split into two nonequivalent positions. The occupation of both positions was refined (constraining the sum of occupancies to 1) and converged to 0.5 within experimental uncertainty; thus the occupancy was fixed at 0.5 in the last refinement cycle. The hydrogen atoms were placed in geometrically suitable positions and were refined as riding atoms with $U_{iso} = 1.2U_{eq}$ of the parent atom except when the parent atom was a methyl group, where $U_{iso} = 1.2U_{eq}$ of the C atom. The refinement was performed on F^2 against 14918 (**1a**), 6925 (**1b**), 6900 (**2**), and 4708 (**3**) using 920 (**1a**), 96 (**1b**), and 82 (**3**) geometrical or thermal parameter constraints. The maximum and minimum found in the final Fourier difference maps were 0.90 and −0.67 for **1a**, 1.27 and −2.33 eA^{-3} for **1b**, 1.88 and −1.38 eA^{-3} for **2**, and 3.19 and −1.72 eA^{-3} for **3**. Maximum peaks were found, in the four cases, less than 1 Å from the Re atom. Solution and refinements were performed with the SHELXTL NT[20] (**1a**) and SHELX-97 (**1b**, **2**, and **3**) packages.[19b,c] The final geometrical calculations were performed using the PARST[21] and PLATON[19d] programs. The main interatomic bond distances and angles for **1a**, **1b**, **2**, and **3** are listed in Tables 2−4.

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for the $[ReCl_4(mal)]^{2-}$ Anion in Compounds **1a** and **1b**

	1a (α unit)	**1a** (β unit)[a]	**1b**
Distances			
Re(1)−O(1)	2.017(7)	2.014(7)	2.004(8)
Re(1)−O(2)	2.015(8)	1.963(8)	2.011(8)
Re(1)−Cl(1)	2.328(3)	2.336(3)	2.337(3)
Re(1)−Cl(2)	2.341(3)	2.306(4)	2.333(3)
Re(1)−Cl(3)	2.357(3)	2.302(4)	2.345(3)
Re(1)−Cl(4)	2.366(3)	2.320(4)	2.366(3)
Angles			
O(1)−Re(1)−O(2)	86.8(3)	86.6(3)	87.1(3)
O(1)−Re(1)−Cl(1)	175.4(2)	177.6(2)	178.2(2)
O(2)−Re(1)−Cl(1)	88.6(2)	91.0(2)	91.1(2)
O(1)−Re(1)−Cl(2)	91.6(2)	89.8(3)	87.7(2)
O(2)−Re(1)−Cl(2)	178.2(3)	176.3(3)	174.8(2)
O(1)−Re(1)−Cl(3)	87.2(3)	88.8(2)	89.9(2)
O(2)−Re(1)−Cl(3)	88.2(3)	89.0(4)	88.6(3)
O(1)−Re(1)−Cl(4)	88.6(3)	89.8(2)	90.7(2)
O(2)−Re(1)−Cl(4)	90.1(3)	90.3(4)	88.0(2)
Cl(1)−Re(1)−Cl(2)	93.1(1)	92.6(2)	94.0(1)
Cl(1)−Re(1)−Cl(3)	92.9(1)	91.6(1)	89.6(1)
Cl(1)−Re(1)−Cl(4)	91.2(1)	89.9(1)	89.6(1)
Cl(2)−Re(1)−Cl(3)	90.9(1)	90.3(3)	91.2(1)
Cl(2)−Re(1)−Cl(4)	90.6(1)	90.3(3)	92.3(1)
Cl(3)−Re(1)−Cl(4)	175.6(1)	178.4(2)	176.4(1)

[a] The numbering scheme for the $[ReCl_4(mal)]^{2-}$ β unit differs from that for the α unit and of **1b**. The chemically equivalent distances and angles are compared in this table.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ (**2**)

Distances			
Re(1)−O(1)	2.045(5)	Cu(1)−N(11)	2.029(5)
Re(1)−O(2)	2.000(4)	Cu(1)−N(12)	1.999(5)
Re(1)−Cl(1)	2.346(2)	Cu(1)−N(21)	2.072(5)
Re(1)−Cl(2)	2.347(2)	Cu(1)−N(22)	2.000(6)
Re(1)−Cl(3)	2.352(2)	Cu(1)−O(3)	2.273(5)
Re(1)−Cl(4)	2.363(2)		
Angles			
O(1)−Re(1)−O(2)	87.8(2)	Cl(2)−Re(1)−Cl(4)	91.2(1)
O(1)−Re(1)−Cl(1)	178.0(1)	Cl(3)−Re(1)−Cl(4)	175.3(1)
O(2)−Re(1)−Cl(1)	90.4(1)	N(11)−Cu(1)−N(12)	82.6(2)
O(1)−Re(1)−Cl(2)	88.7(1)	N(11)−Cu(1)−N(21)	142.1(2)
O(2)−Re(1)−Cl(2)	176.1(1)	N(11)−Cu(1)−N(22)	99.4(2)
O(1)−Re(1)−Cl(3)	87.6(2)	N(11)−Cu(1)−O(3)	134.8(2)
O(2)−Re(1)−Cl(3)	87.0(1)	N(12)−Cu(1)−N(21)	101.4(2)
O(1)−Re(1)−Cl(4)	88.4(2)	N(12)−Cu(1)−N(22)	171.9(2)
O(2)−Re(1)−Cl(4)	90.5(1)	N(12)−Cu(1)−O(3)	85.2(2)
Cl(1)−Re(1)−Cl(2)	93.1(1)	N(21)−Cu(1)−N(22)	82.0(2)
Cl(1)−Re(1)−Cl(3)	93.4(1)	N(21)−Cu(1)−O(3)	82.9(2)
Cl(1)−Re(1)−Cl(4)	90.6(1)	N(22)−Cu(1)−O(3)	87.9(2)
Cl(2)−Re(1)−Cl(3)	91.2(1)		

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[ReCl_4(\mu\text{-mal})Cu(bpy)_2]$ (**3**)

Distances			
Re(1)−O(1)	2.020(9)	Cu(1)−N(11)	1.987(10)
Re(1)−O(2)	2.027(9)	Cu(1)−N(12)	1.991(10)
Re(1)−Cl(1)	2.331(3)	Cu(1)−N(21)	2.005(11)
Re(1)−Cl(2)	2.318(4)	Cu(1)−N(22)	1.991(11)
Re(1)−Cl(3)	2.380(4)	Cu(1)−O(3)	2.546(9)
Re(1)−Cl(4)	2.337(4)	Cu(1)−O(4*)	2.851(14)
Angles			
O(1)−Re(1)−O(2)	88.2(4)	N(11)−Cu(1)−N(12)	82.4(4)
O(1)−Re(1)−Cl(1)	179.2(3)	N(11)−Cu(1)−N(21)	149.4(4)
O(2)−Re(1)−Cl(1)	91.1(3)	N(11)−Cu(1)−N(22)	100.6(5)
O(1)−Re(1)−Cl(2)	89.1(3)	N(11)−Cu(1)−O(3)	119.8(4)
O(2)−Re(1)−Cl(2)	176.6(3)	N(11)−Cu(1)−O(4*)	78.1(4)
O(1)−Re(1)−Cl(3)	87.7(3)	N(12)−Cu(1)−N(21)	105.1(4)
O(2)−Re(1)−Cl(3)	87.1(3)	N(12)−Cu(1)−N(22)	160.7(4)
O(1)−Re(1)−Cl(4)	88.8(3)	N(12)−Cu(1)−O(3)	75.9(4)
O(2)−Re(1)−Cl(4)	90.3(3)	N(12)−Cu(1)−O(4*)	81.4(4)
Cl(1)−Re(1)−Cl(2)	91.6(1)	N(21)−Cu(1)−N(22)	82.1(5)
Cl(1)−Re(1)−Cl(3)	91.9(1)	N(21)−Cu(1)−O(3)	90.8(4)
Cl(1)−Re(1)−Cl(4)	91.6(1)	N(21)−Cu(1)−O(4*)	73.9(4)
Cl(2)−Re(1)−Cl(3)	90.7(2)	N(22)−Cu(1)−O(3)	86.3(4)
Cl(2)−Re(1)−Cl(4)	91.8(2)	N(22)−Cu(1)−O(4*)	117.9(4)
Cl(3)−Re(1)−Cl(4)	175.7(2)	O(3)−Cu(1)−O(4*)	148.2(3)

*$-0.5 + x$, $0.5 - y$, $-0.5 + z$.

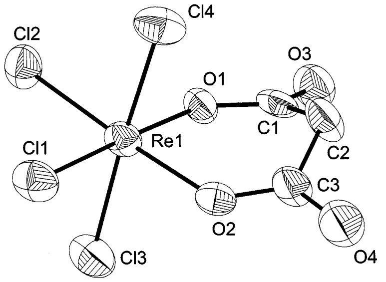

Figure 1. View of the $[ReCl_4(mal)]^{2-}$ anion in **1b** showing the atom numbering. Thermal ellipsoids are plotted at the 30% probability level, and hydrogen atoms were omitted for clarity.

Density Functional Theory (DFT) Calculations. All calculations were performed with the Gaussian 94 program[22] and using the double-ζ pseudopotential basis set (LanL2DZ).[23] The adiabatic connection method with three parameters (B3LYP)[24] was used, mixing the Hartree−Fock contribution for the exchange with generalized gradient approximation functionals.[25] Atomic spin densities were calculated through the natural bond orbital analysis.[26]

Results and Discussion

Crystal Structures of $(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$ (1a) and $(AsPh_4)(HNEt_3)$ $[ReCl_4(mal)]$ (1b). Compounds **1a** and **1b** contain the $[ReCl_4(mal)]^{2-}$ dianionic unit, packed with tetraphenylarsonium and triethylammonium cations in 2:3:1 and 1:1:1 ratios, respectively. This leads to different crystal structures for the two salts. However and despite the presence of two crystallographically nonequivalent $[ReCl_4(mal)]^{2-}$ units in **1a**, the anions are structurally quite similar in the two salts, as is shown in Table 2. With this in mind, only the anion complex in **1b** will be fully described, a drawing of which showing the atom numbering is provided in Figure 1. The Re(IV) atom is in a distorted octahedral environment, surrounded by four chloride anions and a

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bidentate malonate group. The Re−O bond distances are 2.005(9) and 2.011(12) Å, and the Re−Cl bond distances fall within the range 2.333(13)−2.366(21) Å. These values agree well with those found in the literature for other rhenium(IV) compounds[27] and especially for the analogous oxalato complexes with the $[ReCl_4(ox)]^{2-}$ unit.[3,28] Bonding angles are close to the ideal values, even the O(1)−Re−O(2) angle of 87.1(3)°, which corresponds to the bite angle of the malonato ligand. This point and the fact that little distortion is introduced in the dicarboxylate by the coordination represent a remarkable difference from the $[ReCl_4(ox)]^{2-}$ analogue.[3a] Cl(1), Cl(2), O(1), and O(2) atoms constitute an almost perfect equatorial plane around Re, the largest deviation from planarity being 0.003(3) Å for O(1). The Re atom is only 0.006(3) Å out of this plane toward Cl(4). Also O(3), O(4), and the malonate carbon atoms are clearly shifted from this plane toward Cl(4). The six-membered chelate ring exhibits a boat conformation in which C(1), O(1), O(2), and C(3) are nearly planar, and this ring planar section forms a dihedral angle of 16.1(5)° with the mean equatorial plane. C(1)O(1)O(3) and C(3)O(2)O(4) carboxylate groups form dihedral angles of 23.5(2) and 19.8(1)°, respectively, with the mean equatorial plane. Hydrogen bonding [O(3)···H(1A)−N(1) in **1a** and O(4)···H(1)−N(1) in **1b**] and short contacts between hydrogen atoms from the organic substituents in cations and several chloro atoms in anions contribute to stabilize of the tridimensional ionic lattices of both compounds. The anions are well separated from each other. The shortest rhenium−rhenium distances are 10.204(44) Å [Re(1)···Re(1′)] and 9.737(5) Å [Re(1)···Re(1a), a = 1 + *x*, *y*, *z*] in **1a** and **1b**, respectively. These distances are shorter than those reported for $(AsPh_4)_2[ReCl_4(ox)]$.[3a] Both the partial substitution of $(AsPh_4)^+$ by the smaller $(HNEt_3)^+$ and the presence of hydrogen bonding contribute to this result. Nevertheless, the large separation precludes any significant contact between ligand atoms of different anions. The closest atoms, O(3) and Cl(3′) in **1a** and O(4) and O(3b) (b = −*x*, −*y*, 1 − *z*) in **1b** are at 5.404(25) and 4.291(33) Å, respectively. The shortest Cl···Cl distances are 6.891(30) Å for Cl(2)···Cl(2′a) in **1a** and 5.514(47) Å for Cl(4)···Cl(3c) in **1b** (c = −0.5 + *x*, 0.5 − *y*, −0.5 + *z*). $[As(C_6H_5)_4]^+$ and $[HN(C_2H_5)_3]^+$ cations show the expected geometry, and we do not discuss them further.

Crystal Structure of $[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ (2). The structure of **2** is made up of neutral dinuclear units of $[ReCl_4(\mu\text{-mal})Cu(phen)_2]$ and one acetonitrile molecule of crystallization. A perspective drawing of the heterodinuclear unit in **2** is provided in Figure 2a. The atom numbering scheme for the $[ReCl_4(mal)]$ fragment in this compound and the next is the same as in **1b**. The malonato ligand is bidentate toward rhenium and monodentate toward copper. In this way, each unit contains Re(IV) and Cu(II) centers bridged by one carboxylate group exhibiting the anti−syn conformation. The $[ReCl_4(mal)]$ fragment is almost undistorted compared to the mononuclear anion in **1b**. As an example, the Re−Cl distances range from 2.345(10) to 2.363(10) Å, whereas the Re−O bond distances are 2.000(6) and 2.045(10) Å. The Re atom is 0.006(2) Å out of the Cl(1)Cl(2)O(1)O(2) mean equatorial plane toward Cl(4). The chelate ring adopts a boat conformation. The C(1)O(1)O(3) and C(3)O(2)O(4) carboxylate groups form dihedral angles with the equatorial plane of 25.3(3) and 31.8(8)°, respectively.

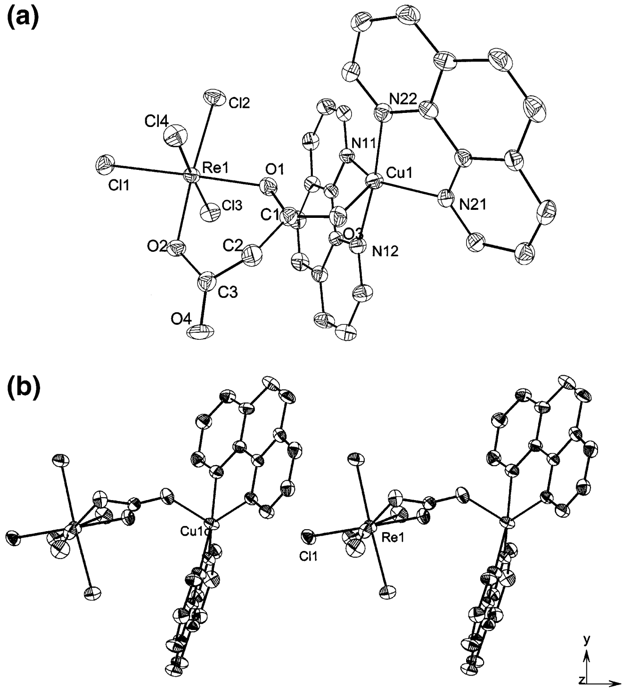

Figure 2. (a) View of dinuclear complex **2**. Thermal ellipsoids are plotted at the 30% probability level. Noncoordinated acetonitrile molecule and hydrogen atoms were omitted for clarity. (b) View of adjacent dinuclear units of **2** down *z* axis. Thermal ellipsoids are plotted at the 30% probability level.

The copper atom is bound to one malonate oxygen atom and four nitrogen atoms from two phen ligands (Figure S1). The coordination around the metal is intermediate between square pyramidal and trigonal bipyramidal, the geometric τ factor being 0.50 (the τ values for square pyramidal and trigonal bipyramidal metal environments are 0 and 1, respectively).[29] The almost linear N(12)−Cu−N(22) moiety [171.9(2)°] appears as the axis in a rough trigonal bipyramid, with equatorial positions occupied by N(11), N(21), and O(3), the metal atom being 0.037(3) Å out of this plane toward N(22). In this case, Cu−N(eq) distances [average 2.050(16) Å] are longer than Cu−N(axial) ones [average 2.000(8) Å], and the Cu−O(3) distance is 2.273(10) Å. Distortion of the geometry also becomes evident in other bonding angles, such as N(11)−Cu−N(21) [142.2(2)°] or O(3)−Cu−N(21)

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[82.9(2)°] in the basal plane. The phen ligands as a whole are quite planar, the dihedral angle between them being 36.6(1)°. The values of the angle subtended at the metal atom by the chelating phen [average 82.3(2)°] are reduced with respect to the ideal value but in agreement with those reported in similar copper complexes.[3b] The bond angle at the bridging O(3) atom is 110.1(5)°. The dihedral angle between the O(3)N(11)N(21) plane and the C(1)O(1)O(3) carboxylate group is 33.7(3)°.

The Re···Cu distance in the [$ReCl_4$(μ-mal)Cu(phen)$_2$] unit is 4.800(8) Å. These units are arranged along the *a* direction, giving an intermolecular Re(1)···Cu(1d) distance of 5.475(7) Å, (d = $-1 + x, y, z$). Figure 2b shows a drawing of two adjacent units viewed down the *z* axis. In this representation, one can see that the Cl(1) atom of the unit at the right is 3.714(11) Å from the Cu(1d) atom in the unit at the left. The shortest Cl···Cl and Cl···O contacts between units are 4.357(15) Å for Cl(3)···Cl(3e) (e = $-x, 1 - y, 2 - z$) and 3.745(12) Å for Cl(2)···O(4f) (f = $x, y, -1 + z$).

A comparison with the structure of the analogous [$ReCl_4$(μ-ox)Cu(phen)$_2$]·CH_3CN[3b] allows the influence of the bridge on the overall structure to be studied. In this latter compound, Re(IV) and Cu(II) are bridged by an asymmetric bis(bidentate) oxalate ligand, resulting in a six-coordinated copper ion. The Cu−O distances are 2.32 and 2.41 Å, larger than the 2.273 Å in **2**. As a consequence and even when malonate is monodentate toward Cu(II), the resulting Re···Cu intramolecular distance is shorter (4.800 Å in **2** compared to 5.649 Å in the analogous oxalate). Intermolecular Re···Cu and Cl···Cl distances are also shorter in compound **2**, at 5.475 and 4.357 Å, respectively, compared to 6.57 and 5.84 Å in [$ReCl_4$(μ-ox)Cu(phen)$_2$]·CH_3CN. The structure is more compact in the case of [$ReCl_4$(μ-mal)Cu(phen)$_2$]·CH_3CN.

Crystal Structure of [$ReCl_4$(μ-mal)Cu(bpy)$_2$] (3). Compound **3** can be described as being built of [$ReCl_4$(mal)]$^{2-}$ anions acting as bis(monodentate) ligands toward two adjacent [Cu(bpy)$_2$]$^{2+}$ cations, with the OCO carboxylate bridges exhibiting the anti−syn conformation. Despite the thermal disorder of the C(2) atom in the malonate ligand, bond distances and angles within the [$ReCl_4$(mal)]$^{2-}$ anion are comparable to those previously mentioned for **1b** and **2**. Re−Cl distances range from 2.317(12) to 2.381(4) Å, and the Re−O bond distances are 2.021(10) and 2.027(12) Å. The Re atom is 0.024(4) Å out of the Cl(1)Cl(2)O(1)O(2) mean equatorial plane. This equatorial plane forms dihedral angles of 16.2(10) and 20.5(9)° with the C(1)O(1)O(3) and C(3)O(2)O(4) carboxylate groups, respectively.

The copper atom is bonded to four nitrogen atoms from two bpy ligands and two oxygen atoms from two [$ReCl_4$(mal)]$^{2-}$ anions, showing a distorted six-coordinated geometry (Figure 3). Nitrogen atoms can be considered to occupy equatorial positions, defining a flattened tetrahedron. The Cu−N distances average 1.994(12) Å, and the dihedral angle between the N(11)N(12)Cu(1) and N(21)N(22)Cu(1) planes is 38.8(6)°, practically the same values as found in [$ReCl_4$(μ-ox)Cu(bpy)$_2$].[3a] That is also the case for the angle subtended at the copper atom by the bpy, which average 82.3(5)°. Oxygen atoms are at axial positions, Cu−O distances being 2.546(9) Å [Cu(1)···O(3)] and 2.851(14) Å [Cu(1)···O(4g), g = $-0.5 + x, 0.5 - y, -0.5 + z$], as expected for axial Cu(II)−O bonds.[30] However, the O(3)−Cu(1)−O(4 g) angle is only 148.2(3)°, significantly far from the ideal. The bond angles at the bridging O(3) and O(4) atoms are 112.5(9) and 109.1(8)°, respectively. Finally, the N(11)N(12)N(21)N(22) mean plane forms dihedral angles of 71.8(7) and 69.6(12)° with the C(1)O(1)O(3) and C(3g)O(2g)O(4g) carboxylate groups, respectively.

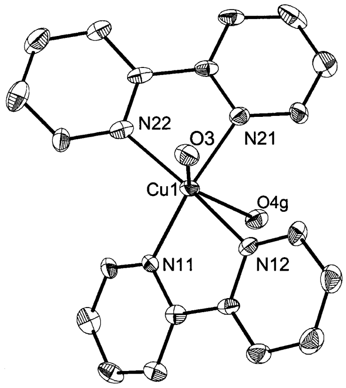

Figure 3. Perspective drawing of the local coordination environment of Cu(II) in compound **3**. Thermal ellipsoids are plotted at the 30% probability level, and hydrogen atoms were omitted for clarity.

As in the case of the analogous [$ReCl_4$(μ-ox)Cu(bpy)$_2$], well-defined chains are formed in the structure. Dinuclear units are connected by means of the sixth coordination position of the Cu(II) ion, now occupied by the oxygen atom O(4g) belonging to the malonate of an adjacent unit. Replacing oxalate by malonate in the polymeric structure results in the formation of Re−mal−Cu−mal−Re− chains instead of Re−ox−Cu−Cl−Re− ones. The chains run along the [101] direction, separated a *b*/2 distance in the (10−1) planes (Figure 4). Additional $\pi-\pi$ stacking interactions contribute to the stabilization of the crystal structure. The intrachain Re···Cu distances are 5.032(14) and 5.115(42) Å through O(3) and O(4), respectively, larger than those reported for [$ReCl_4$(μ-ox)Cu(bpy)$_2$], which are near 4.8 Å. Intrachain Cu···Cu separations through malonate are 9.083(76) Å. The shortest chloro−chloro contacts among chains, Cl(1)···Cl(3h) and Cl(3)···Cl(1h) (with h = $1 - x, -y, 2 - z$), are at 5.592(12) Å.

Magnetic Properties. Compounds **1a** and **1b** have nearly identical magnetic behaviors (Figure 5), as can be expected given that they both contain the same paramagnetic complex, [$ReCl_4$(mal)]$^{2-}$. The variation of $\chi_M T$ with the temperature can be attributed exclusively to the zero-field splitting, which is very large for Re(IV), a 5d^3 ion, in a distorted octahedral environment, because of the high value of its spin−orbit coupling constant (λ ca. 1000 cm^{-1} in the free ion). The separation between the anions in the lattice precludes any magnetic interaction. When smaller countercations are used,

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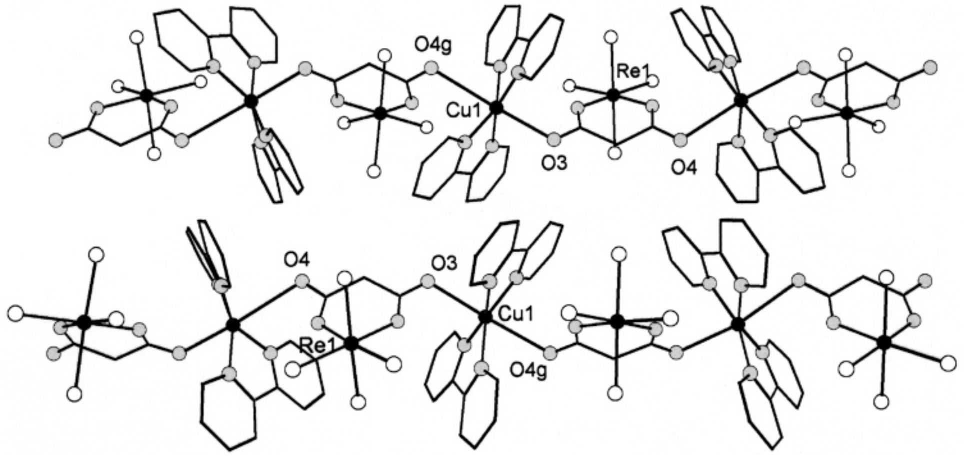

Figure 4. Ball-and-stick diagram of compound **3** showing the chain structure. Perspective view toward plane (10−1). Re and Cu atoms are represented as black balls, O and N atoms as gray balls, and Cl atoms as white balls.

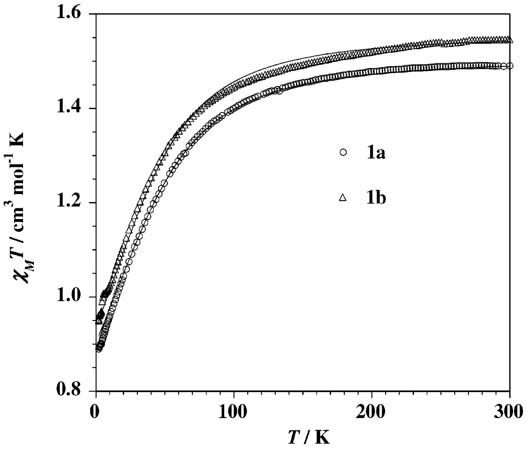

Figure 5. Thermal variation of the product $\chi_M T$ for compounds **1a** and **1b**. Continuous lines represent the best theoretical fit (see text).

Table 5. Best-Fit Magnetic Parameters for Complexes **1**−**4**

compound	g_{Re}	g_{Cu}	$\|2D\|^a$ cm^{-1}	J^b cm^{-1}	R^c $\times 10^{-5}$
$(AsPh_4)_{1.5}(HNEt_3)_{0.5}[ReCl_4(mal)]$ (**1a**)	1.79	−	114	−	5.4
$(AsPh_4)(HNEt_3)[ReCl_4(mal)]$ (**1b**)	1.82	−	107	−	6.3
$[ReCl_4(\mu\text{-mal})Cu(phen)_2]\cdot CH_3CN$ (**2**)	1.78	2.12	88	−0.39	1.6
$[ReCl_4(\mu\text{-mal})Cu(bipy)_2]$ (**3**)	1.79	2.13	119	−0.09	1.8
$[ReCl_4(\mu\text{-mal})Cu(terpy)]$ (**4**)	1.7	2.08	114	+1.51	1.0

[a] $2D$ is the energy gap between the $\pm^3/_2$ and $\pm^1/_2$ Kramers doublets [the zero-field splitting of Re(IV)]. [b] J is the exchange magnetic coupling parameter between Re(IV) and Cu(II) local spins. [c] R is the agreement factor, defined as $\sum_i[(\chi_M T)_{obsd} - (\chi_M T)_{calc}]^2/\sum_i[(\chi_M T)_{obsd}]^2$.

the direct anion−anion (Cl···Cl) contacts are not avoided, and significant magnetic interactions occur.[3a,31]

Least-squares fitting of the experimental data through the theoretical expression for the magnetic susceptibility[3a] derived from the Hamiltonian (eq 1) leads to the parameters reported in Table 5. These results are very similar to those obtained for the analogous oxalato complex, $[ReCl_4(ox)]^{2-}$, ($g = 1.85$, $2D = 120$ cm^{-1}).[3a]

$$\mathbf{H} = D[\mathbf{S}_z^{\,2} - S(S+1)/3] + g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) \quad (1)$$

Obviously, this large D value causes a significant axial anisotropy and, thus, different values for $g_{\|}$ and $g_{\perp}$. However, we have measured the magnetic susceptibility of microcrystalline powder samples, and from these measurements, it is not possible to define reliable and unique values for $g_{\|}$ and $g_{\perp}$ or the sign of D. The fit of the experimental data considering all of these parameters results in several (mathematically) possible solutions. However, in all of them the absolute value of D and the mean value of g remain practically constants. These are the values reported in Table 5.

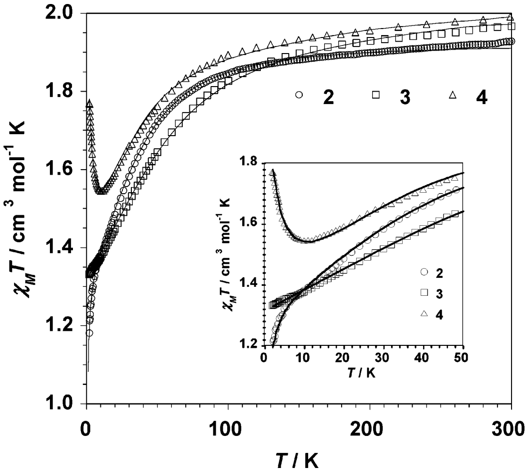

Figure 6. Thermal variation of the product $\chi_M T$ for compounds **2**−**4**. A detail of the low-temperature range is shown in the inset. Continuous lines represent the best theoretical fit (see text).

The magnetic properties of **2**−**4** in the form of $\chi_M T$ versus T plots (where χ_M is the magnetic susceptibility per $Re^{IV}Cu^{II}$ heterodinuclear unit) are shown in Figure 6. $\chi_M T$ values at room temperature for the three compounds are in the range of 1.90−1.95 cm^3 mol^{-1} K, within the expected range for an uncoupled $Re^{IV}Cu^{II}$ pair. These values decrease upon cooling, reaching a value of 1.17 (**2**) and 1.35 (**3**) cm^3 mol^{-1} K at 2 K. The behavior of **4** is different: $\chi_M T$ reaches a minimum at ca. 10 K, with a $\chi_M T$ value of 1.54 cm^3 mol^{-1} K, and then increases sharply at lower temperatures.

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(31) González, R.; Chiozzone, R.; Kremer, C.; De Munno, G.; Nicoló, F.; Lloret, F.; Julve, M.; Faus, J. *Inorg. Chem.* **2003**, *42*, 2512 and references therein.

To analyze the magnetic interaction between Re(IV) an Cu(II) in **2**−**4**, it is interesting to compare the $\chi_M T$ values at 2 K of **1a** and **1b** with those of **2**−**4**. As shown in Figure 5, the lowest $\chi_M T$ value for the mononuclear Re(IV) complexes (**1a** and **1b**) varies between 0.9 and 1.0 cm^3 mol^{-1} K, depending on the values of *g* and *D*. This limit is well-known for others mononuclear magnetically isolated Re(IV) complexes.[3] Given that one copper(II) is present in each **2**−**4**, in the absence of magnetic interactions, the value of this limit would increase by 0.4 ($S = {}^1/_2$ and $g = 2.08$), that is, the limit of $\chi_M T$ would be in the range 1.3−1.4 cm^3 mol^{-1} K.

Inspection of Figure 6 shows that the lowest value of $\chi_M T$ for **2** is 1.17 cm^3 mol^{-1} K, a value clearly below the above limit (1.3−1.4). This fact suggests the occurrence of an antiferromagnetic interaction between the metal ions. For **3**, the $\chi_M T$ value at 2 K is 1.35 cm^3 mol^{-1} K, a value that lies within the above range (1.3−1.4), suggesting the lack of any, or an extremely weak, magnetic interaction. Finally, in the case of **4**, the value of $\chi_M T$ at its minimum at 10 K is 1.54 cm^3 mol^{-1} K. This value is significantly greater than the calculated limit (1.3−1.4), indicating that a ferromagnetic coupling occurs between Re(IV) and Cu(II) in this compound.

Taking into account the discrete dinuclear structure of **2**, the decrease of $\chi_M T$ upon cooling could be attributed only to zero-field splitting of Re(IV) and intramolecular Re(IV)−Cu(II) magnetic interactions. Consequently, we analyzed the magnetic behavior of **2** through the Hamiltonian of eq 2. A least-squares fit leads to the parameters reported in Table 5. The calculated curve matches very well the magnetic data.

$$\mathbf{H} = -J\mathbf{S}_{\mathrm{Re}}\mathbf{S}_{\mathrm{Cu}} + D[\mathbf{S}_{z\mathrm{Re}}{}^2 - S(S+1)/3] + g\beta\mathbf{S}_{\mathrm{Re}}H + g\beta\mathbf{S}_{\mathrm{Cu}}H \quad (2)$$

The value of $J = -0.39$ cm^{-1} reveals a weak antiferromagnetic coupling between Re(IV) and Cu(II), a value somewhat lower than that of the analogous oxalato complex [ReCl$_4$(μ-ox)Cu(phen)$_2$] ($J = -0.90$ cm^{-1}),[3b] although the two complexes are not strictly comparable because of the different coordination modes of the bridge ligand, bidentate/monodentate in the malonato and bis(bidentate) in the oxalato. It is important to note that, although the shape of the magnetic plot for **2** is monitored basically by the zero-field splitting, the experimental data at low temperature cannot be reproduced theoretically without the presence of magnetic coupling.

As mentioned above, the magnetic properties of **3** suggested the lack of any, or an extremely weak, magnetic interaction between the metal ions. In fact, its magnetic properties can be reproduced theoretically using only the zero-field splitting (eq 1), that is, Cu(II) and Re(IV) magnetically isolated. However, a better fit is obtained when a magnetic interaction between these two ions through the Hamiltonian of eq 2 is considered. One can see in **3** that a regular alternation of two exchange pathway occurs: one through the Cu(1)−O(3) bond (2.54 Å) and the other through the Cu(1)−O(4) bond (2.84 Å). Given that the magnetic coupling so weak, the longer exchange pathway [Cu(1)−O(4)] has to be negligible, and thus, the chain **3** would behave magnetically as a Cu(II)−Re(IV) dinuclear complex through the Cu(1)−O(3) exchange pathway.

Table 6. DFT-Calculated Atomic Spin Densities on the ReCl$_4$(mal) Moiety for **2**[a]

atom	spin density	atom	spin density
Re(1)	2.4985 (2.25)[b]	Cl(1)	0.0981
O(1)	0.0327	Cl(2)	0.0727
O(2)	0.0553	Cl(3)	0.0727
O(3)	0.0227 (0.027)[b]	Cl(4)	0.0727
O(4)	0.0228 (0.027)[b]	C(1)	0.0006
		C(2)	0.0064
		C(3)	0.0025

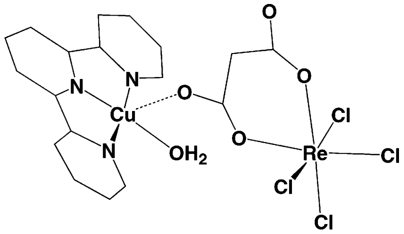
[a] Very similar spin densities were obtained for **3**. [b] The corresponding spin density for [ReCl$_4$(μ-ox)Cu(bpy)$_2$][3a] are given in parentheses.

It is interesting to note that the analogous oxalato-bridged Re(IV)−Cu(II) complex of formula [ReCl$_4$(μ-ox)Cu(bipy)$_2$] with Cu−O distances similar to those of **3** behaves as a ferrimagnetic chain, that is, the exchange pathways involved is more effective than those of **3**. The reason for this different magnetic behavior could be a decreased orbital overlapping associated with the large deviation of the O(3)CuO(4) angle from the ideal value as well as the different spin density values on the oxygen atoms: 0.023 in **3** versus 0.027 in [ReCl$_4$(μ-ox)Cu(bipy)$_2$]; see Table 6.

Discussion of the magnetic properties of **4** requires some considerations of its structure, which is unknown because it was not possible to obtain sutable crystals for the X-ray diffraction study. Taking into account the coordination modes of the malonato bridge, i.e., bidentate/monodentate as in **2** or bidentate/bis(monodentate) as in **3**, we can imagine the structure of **4** as a dinuclear complex (only one magnetic coupling parameter) or as an alternating chain (two magnetic coupling parameters). The magnetic properties of **4** can be reproduced satisfactorily with a simple dinuclear model (eq 2) with a ferromagnetic coupling of $J = +1.51$ cm^{-1} (see Table 5). This high-quality fit means that, if an alternating chain is involved, the additional coupling must be negligible.

Thus, **4** behaves as a dinuclear species (as do **2** and **3)**, but in this case, a weak but significant ferromagnetic coupling occurs. In this bimetallic species, because the terpy ligand fills only three equatorial positions around the Cu(II), the O atom of malonate could occupy an axial position or the remaining equatorial one. The ferromagnetic nature of the coupling strongly suggests that the O atom fills the axial position given that, in the related oxalato complexes, only this coordination mode, observed in the structure of [ReCl$_4$(μ-ox)Cu(terpy)(CH$_3$CN)],[3b] leads to a ferromagnetic coupling. The strict coplanarity of the three N equatorial atoms in **4**, in contrast to the flattened tetrahedron in **3**, produces the orthogonality between the magnetic orbitals of rhenium and copper. Then, the fourth equatorial position in **4** should be occupied by a solvent molecule. However, the presence of CH$_3$CN (the solvent used in the synthesis) can be ruled out by the IR spectrum and the elemental analysis, and thus, a water molecule is probably the lacking ligand, as occurs in [ReCl$_4$(μ-ox)Cu(terpy)(H$_2$O)],[3b] although in this case, it is located in an axial position. The proposed structure of **4** is shown in Chart 1. The dinuclear molecules can be united

Chart 1



forming chains similar to the observed ones in **3**, with relatively long Cu−O intermolecular distances.

DFT Calculations. Magnetic interactions between Re(IV) and Cu(II) through a malonato bridge can vary from weak antiferromagnetic to weak ferromagnetic depending on the molecular structure of the bimetallic species. These results are qualitatively similar to those observed in the analogous oxalato complexes, but quantitatively, the magnetic exchange is quite a bit smaller. With the aim of clarifying whether there are intrinsic differences between the two ligands as magnetic couplers, we performed DFT calculations on the $ReCl_4$(mal) fragment in **2** and **3** and compared the results with identical calculations performed previously on the $ReCl_4$(ox) fragment.[3a] The computed spin densities for the two compounds were basically the same, and they are included in Table 6. The spin density of the rhenium atom is somewhat delocalized onto the atoms of the ligands. The values are always positive in these atoms and vary in the order Cl > O > C, being higher in the atoms nearest to the metal ion. The calculation also reveals that the delocalization is less extensive in the malonato species than in the oxalato, although the differences are small. Thus, in the $ReCl_4$(ox) fragment, the spin densities on the metal ion and the O(3) and O(4) atoms are 2.248, 0.027, and 0.027, respectively.[3a]

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Supporting Information Available: Perspective drawing of the Cu(II) polyhedron in compound **2** (Figure S1). X-ray crystallographic files of compounds **1a**, **1b**, **2**, and **3** in CIF format. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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