Synthesis, Crystal Structure and Magnetic Properties of Heterodimetallic $Re^{IV}Cu^{II}$ Complexes

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The two rhenium(IV)-copper(II) heterometallic complexes $[CuL_β][ReCl_4(ox)]·DMF$ (**1**) and $[(CuL_α)_2Cl][ReCl_4(ox)]Cl$ (**2**) ($L_β$ = *N-dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and $L_α$ = *N-dl*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene) were synthesized, and the crystal structures of both compounds were determined at 173(2) K. Complex **1** crystallizes in a monoclinic space group $P2_1$, with a = 9.365(2) Å, b = 15.150(2) Å, c = 10.776(1) Å, $β$ = 110.01(1)°, Z = 2, whereas **2** crystallizes in an orthorhombic space group $Pca2_1$ with a = 16.660(5) Å, b = 16.017(5) Å, c = 17.066(5) Å, and Z = 4. The $CuL_β$ macrocycle cation is approximately planar and coordinated from above and below by $[ReCl_4(ox)]^{2–}$ units through the bis(bidentate) oxalato ligands. It features an oxalato-bridged heterometallic $Re^{IV}–Cu^{II}$ zigzag chain, the shortest intrachain metal–metal distances are Re···Cu = 5.568(2) and 5.870(2) Å in the direction of the b axis. The crystal structure of **2** consists of dinuclear complex cations $[(CuL_α)_2Cl]^{3+}$ with $[ReCl_4ox]^{2–}$ and isolated $Cl^–$ as counter anions. Cu atoms in $CuL_α$ are only fivefold coordinated in a square pyramidal surrounding, and the cations $(CuL_α)^{2+}$ are connected in pairs by chloride. The intramolecular Cu···Cu separation is 4.885(3) Å, the shortest Re···Cu distance is 7.612(3) Å. The magnetic behavior of **1** and **2** has been investigated over the temperature range 1.7–300 K. Compound **1** behaves like a ferrimagnetic Cu^{II}-Re^{IV} dimetallic, one–dimensional chain with intrachain antiferromagnetic coupling. Compound **2** shows weak antiferromagnetic interactions within the $Cu^{II}–Cu^{II}$ units.

Introduction

The design and synthesis of multidimensional magnetic materials is a major focus of molecular-based materials research.[1–2] The typical approach relies on the synthesis of materials with direct exchange coupling between metal ions and coordinated open shell ligands. In the last twenty years several compounds of that type containing metal ions of the first-transition-metal series have been characterized. The magnetic properties of related complexes containing second and third series transition elements, which induce larger spin-orbit coupling effects and a greater degree of covalence, are much less known. This is the case for the rhenium(IV) complexes, where the $5d^3$ ion usually forms octahedral compounds. Numerous types of hexachloro-, hexabromo- and hexaiodorhenate complexes have previously been investigated in full detail.[3–6] The study of magnetic properties of mononuclear hexahalogeno complexes revealed the occurrence of an intermolecular antiferromagnetic interaction whose magnitude depends on the size of the organic cation (bulk effect). The exchange of two chloride ions by an oxalato ligand in the rhenium coordination sphere allows for the synthesis of new heterodinuclear $Re^{IV}–Cu^{II}$ complexes. The oxalate dianion is a well-know ligand, which usually adopts a bidentate coordination mode when acting as a bridge between two metals. In fact, the coordination mode of the rhenium(IV) precursor $[ReCl_4ox]^{2–}$ changes with the nature of the other ligands in the coordination sphere of Cu^{II}, and is monodentate in $[Cu(bipy)_2$-$ReCl_4(ox)]$ (forming a long Cu–O axial bond of 2.65 Å) and a very asymmetric bidentate in $[Cu(terpy)_2ReCl_4(ox)(H_2O)]$ (forming one short and one long Cu–O bond, 2.05 and 2.47 Å, respectively).[7] The coupling between Re^{IV} and Cu^{II} can be ferro- or antiferromagnetic but is very weak in all cases because of the long Cu^{II}–O bonds and bite angle of the oxalate ligand. Distortions in the coordination geometry in reported complexes introduce very poor orbital overlap, which makes the interaction weak. Analysis of literature data suggest that a quite strong coupling should be obtained if the ligand is coordinated is a symmetric bidentate way with two short Cu^{II}–O bonds. For this reason, it seemed interesting to examine macrocyclic copper(II) complexes $CuL_α$ and $CuL_β$ (where $L_β$ = *N-dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene and $L_α$ = *N-dl*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene) (Scheme 1) in order to obtain heterometallic systems bridged by oxalato groups. The square planar macrocyclic complexes with two vacant coordination

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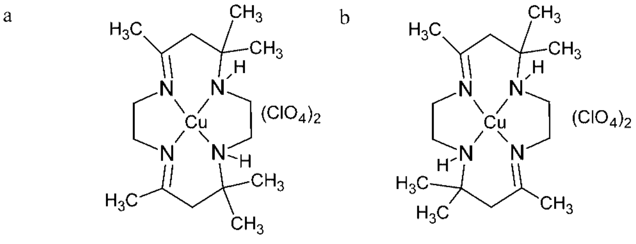
sites at the metal atom play the role of the so-called "building block".[8] In this paper, we present results of investigations of coordinatively unsaturated complexes of copper(II) as well as of simple $[ReCl_4ox]^{2-}$ ions. It is interesting to show how the configuration of the nitrogen donor ligands influences the crystalline structure as well as the magnetic properties.



Scheme 1. Schematic view of macrocyclic copper(II) complexes: a) $[CuL_\beta]$, b) $[CuL_\alpha]$.

Results and Discussion

Description of the Structures

[CuLβ][ReCl4(ox)]·DMF (1)

Complex **1** crystallizes in a monoclinic space group $P2_1$ (Table 1). Figure 1 shows an ORTEP plot of the asymmetric unit $[ReCl_4(\mu\text{-}ox)CuL_\beta]$ of this compound without the solvent molecule DMF.

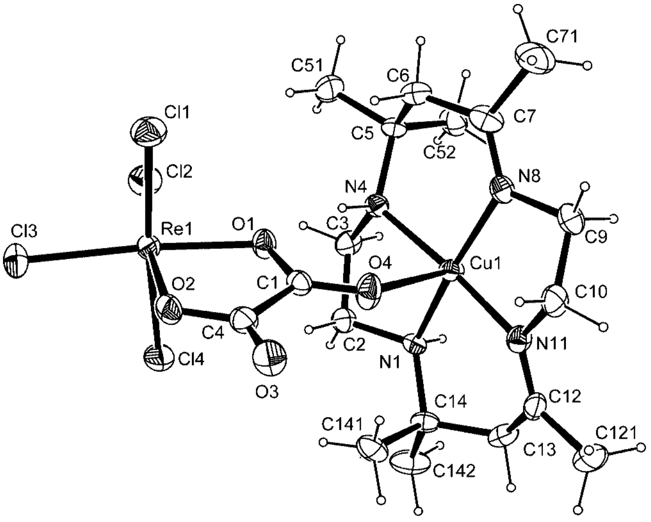


Figure 1. Asymmetric unit of compound **1** (ORTEP plot, 50% probability level).

In the crystal structure, the $[CuL_\beta]^{2+}$ cations and $[ReCl_4(ox)]^{2-}$ anions are arranged as polymeric chains running parallel to axis *b* (Figure 2). The rhenium atom is coordinated by four chloro and one chelating oxalato ligand.

The two remaining oxygen donor atoms of the tetradentate oxalato ligand are bound to two $[CuL_\beta]^{2+}$ units, widening the nearly planar coordination of Cu^{II} by the four N atoms of the L_β ligand to an elongated octahedron with the oxygen ligands in *trans* position. The bond lengths for Cu1–

Table 1. Crystal data and structure refinement.

Identification Code	$[(CuL\alpha)_2)Cl][ReCl_4(ox)]Cl$	$[CuL_\beta][ReCl_4(ox)]\cdot DMF$
Empirical formula	$C_{34}H_{60}Cl_6Cu_2N_8O_4Re$	$C_{19}H_{35}Cl_4CuN_5O_6Re$
Formula weight	1170.88	821.06
Temperature [K]	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$Pca2_1$	$P2_1$
a [Å]	16.660(4)	9.3647(14)
b [Å]	16.017(4)	15.1501(13)
c [Å]	17.066(5)	10.7762(9)
β [°]		110.015(8)
Volume [Å^3]	4554(2)	1436.5(3)
Z	4	2
Density$_{calcd.}$ [Mg/m^3]	1.708	1.898
Absorption coefficient [mm^{-1}]	3.974	5.364
Effective transmission min/max	0.689	0.607
F(000)	2348	808
Crystal size [mm]	0.2 × 0.15 × 0.1	0.3 × 0.1 × 0.06
θ range for data collection [°]	2.13–30.63	2.01–30.56
Index ranges	$-23 \le h \le 23$, $-20 \le k \le 22$, $-24 \le l \le 24$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-15 \le l \le 15$
Reflections collected	53678	17273
Independent reflections	13784 [*R*(int) = 0.0551]	8646 [*R*(int) = 0.0233]
Completeness to θ = 30.63° [%]	99.7	99.8
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2; inversion twin
Data/restraints/parameters	13784/1/517	8646/1/339
Goodness-of-fit on F^2	1.046	0.954
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0527$, $wR2 = 0.1183$	$R1 = 0.0251$, $wR2 = 0.0468$
R indices (all data)	$R1 = 0.0814$, $wR2 = 0.1310$	$R1 = 0.0309$, $wR2 = 0.0484$
Absolute structure parameter	0.016(8)	0.197(4)
Largest diff. peak and hole [e·Å^{-3}]	8.090 and –3.227	1.417 and –0.789

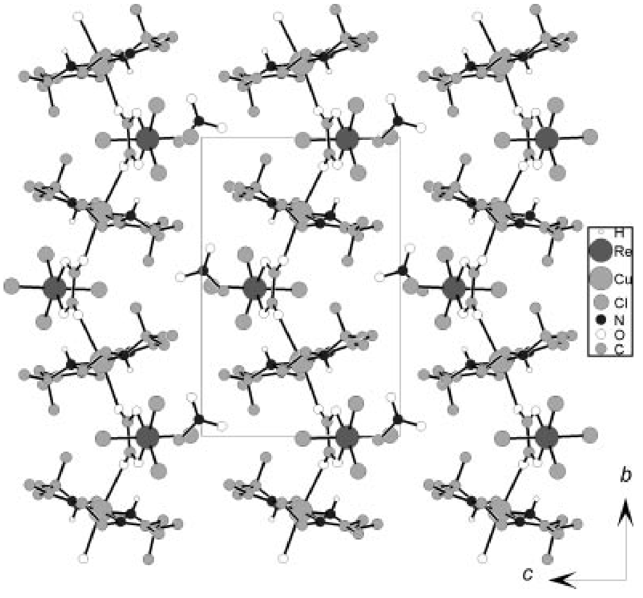


Figure 2. Crystal structure of **1** (view axis *a*; H atoms bound to C have been omitted for clarity).

O(3′) and Cu1–O4 are 2.655(4) and 2.58(4) Å, respectively, the O3′–Cu1–O4 angle is 168.1(1)° (Figure 3a). Re^{IV} and Cu^{II} complexes are linked through oxalato bridges resulting in Re···Cu distances of 5.568(2) and 5.870(2) Å and a Cu···Cu interspace distance of 7.550(3) Å within the chains. The shortest interchain Cu···Cu separations are 7.072(4) and 7.596(4) Å.

The ligand L_β in compound **1** is approximately planar with maximum deviations of ±0.48 Å from the least-squares plane defined by the 14 ring atoms and Cu. However, the axial methyl substituents C52 and C141 are placed in *anti* configuration 1.902(4) Å above and 1.711(4) Å below that plane. The Cu^{II} atom in the center of the ligand is thus open for additional coordination from two sides.

The ring members N8 and C7, and N11 and C12 are connected by double bonds; N1 and N4 are protonated.

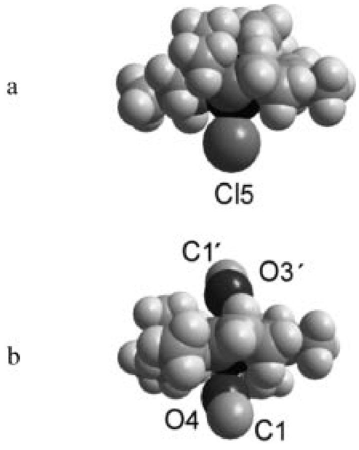


Figure 3. Space-filling model of the Cu surrounding in **2** (a) and **1** (b).

Apart from the C–O and C–C bond lengths of the oxalato ligand, the $[Re(IV)Cl_4ox]^{2-}$ part of the crystal structure shows no apparent structural deviations from those in **2** or in related compounds in the literature.

$[(CuL_\alpha)_2)Cl][ReCl_4(ox)]Cl$ (2)

Complex **2** crystallizes in an orthorhombic space group *Pca*2_1 (Table 1).

The crystal structure consists of dinuclear complex cations $[(CuL_\alpha)_2Cl]^{3+}$ and $[ReCl_4ox]^{2-}$, and isolated Cl^- as counter anions. An ORTEP plot of the asymmetric unit of the compound with the atom labelling is given in Figure 4.

The largest deviations of the 14 ring atoms and the central Cu^{II} from their least-square planes are +0.805(6)/ –0.528(6) Å in the first $(Cu^{II}L_\alpha)^+$ complex and +0.514(7)/ –0.794(6) Å in the second one with atom labels "a". The ring members N1–C2, N8–C9, N1a–C2a and N8a–C9a are connected by double bonds; N5, N12, N5a and N12a are protonated. The cationic complexes are linked in pairs by a chloride ligand with Cu–Cl bond lengths of 2.156 (2) Å and a Cu1–Cl–Cu1a angle of 152.2(1)°. The varying coordina-

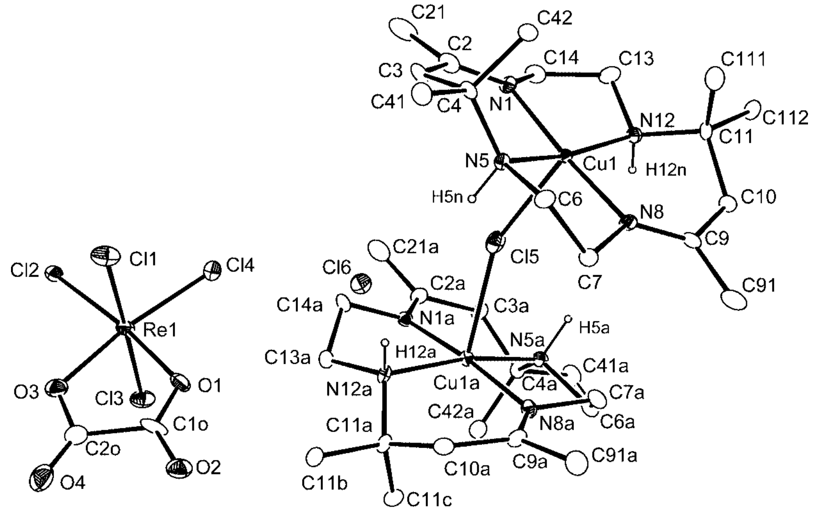


Figure 4. Asymmetric unit of compound **2** (ORTEP plot, 50% probability level; H atoms bound to C have been omitted for clarity).

tion behavior of Cu^{II} in the investigated compounds **1** and **2** results from the different configurations of the ligands L_α and L_β, respectively. The two axial methyl substituents of each ligand L_α (C42, C111 and C42a, C11c) are arranged in *syn* configuration 2.286(8)/2.353(9) Å above as well as 2.279(9)/2.320(9) Å below the appendant N_4 planes. The cap-shaped ligands enfold the copper atoms Cu1 and Cu1a, which are situated 0.153(3) and 0.143(3) Å out of their respective N_4 planes (Figure 3b). As there is no space for additional coordination on the outside of the cap (Figure 1), the Cu atoms are only fivefold coordinated in a square-pyramidal surrounding. The intramolecular Cu···Cu distance is 4.885(3) Å, and the shortest intermolecular Re···Cu and Re···Re distances are 7.612(3) and 8.581(2) Å, respectively. The $[ReCl_4ox]^{2-}$ anion with a chelating oxalato ligand shows no unusual structural features with respect to bond lengths or angles (Table 2).[9,10] A simplified view of the packing of the ions in the elementary cell is illustrated in Figure 5. The $[(CuL_\alpha)_2Cl]^{3+}$ cations are arranged in layers parallel to *ab* in $c = 0$ and $^1/_2$, the anions $[ReCl_4ox]^{2-}$ and Cl^- in $c = {}^1/_4$ and $^3/_4$, respectively.

Table 2. Selected bond lengths [Å] of **1** and **2**.

$[(CuL\alpha)_2Cl][ReCl_4(ox)]Cl^-$		$[CuL_\beta][ReCl_4(ox)]\cdot DMF$	
Re(1)–Cl(1)	2.344(2)	2.3568(9)	Re(1)–Cl(1)
Re(1)–Cl(4)	2.332(2)	2.322(2)	Re(1)–Cl(3)
Re(1)–Cl(2)	2.337(2)	2.328(2)	Re(1)–Cl(2)
Re(1)–Cl(3)	2.346(2)	2.3497(8)	Re(1)–Cl(4)
Re(1)–O(3)	2.036(6)	2.036(3)	Re(1)–O(2)
Re(1)–O(1)	2.044(5)	2.041(3)	Re(1)–O(1)
Cu(1)–Cl(5)	2.516(2)	2.665(4)	Cu(1)–O(3)
Cu(1A)-Cl(5)	2.517(2)	2.580(4)	Cu(1)–O(4)
Cu(1)–N(8)	1.984(6)	1.974(3)	Cu(1)–N(8)
Cu(1)–N(1)	1.994(6)	1.975(3)	Cu(1)–N(11)
Cu(1)–N(12)	2.015(6)	2.009(3)	Cu(1)–N(1)
Cu(1)–N(5)	2.033(5)	2.011(3)	Cu(1)–N(4)
Cu(1A)–N(8A)	2.517(2)	---	---
Cu(1A)–N(1A)	1.988(5)	---	---
Cu(1A)–N(5A)	1.991(5)	---	---
Cu(1A)-N(12A)	2.009(6)	---	---
O(1)–C(1O)	1.20(1)	1.299(6)	O(1)–C(1)
O(3)–C(2O)	1.32 (1)	1.303(6)	O(2)–C(4)
O(2)–C(1O)	1.24(1)	1.208(6)	O(3)–C(4)
O(4)–C(2O)	1.17(1)	1.212(6)	O(4)–C(1)
C(1O)–C(2O)	1.62(2)	1.550(4)	C(1)–C(4)

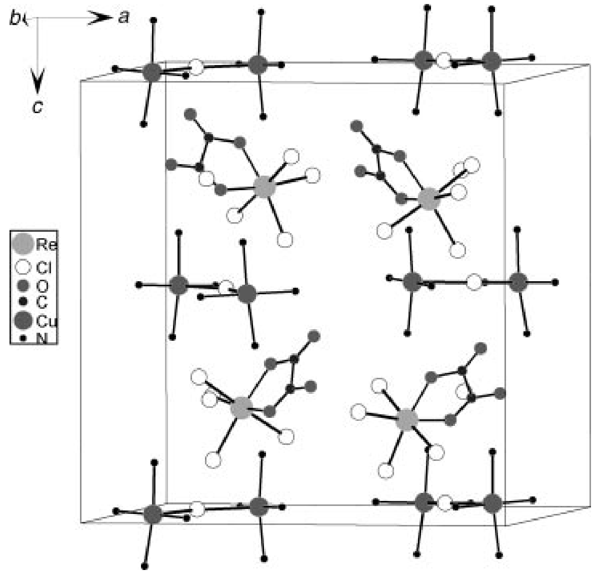


Figure 5. Unit cell of **2** (C and H atoms of the macrocycle have been omitted for clarity).

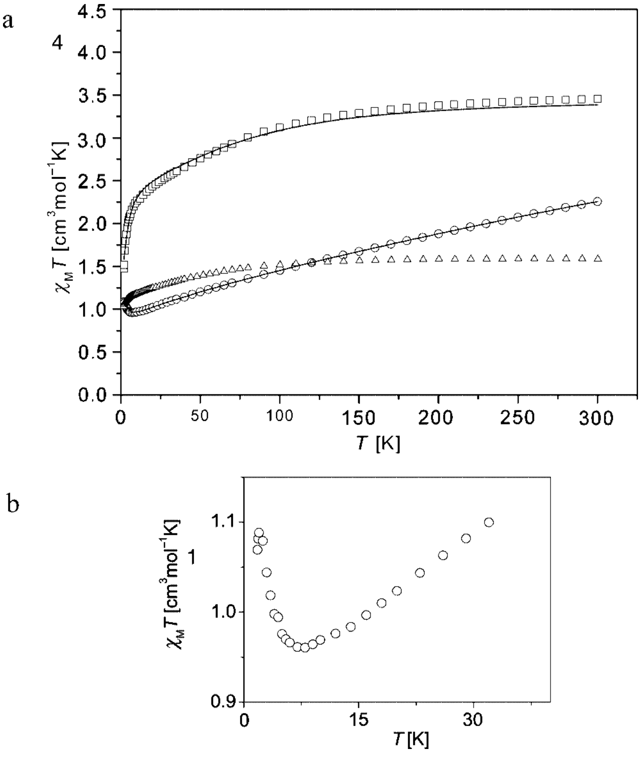


Figure 6. a) Thermal dependence of $\chi_M T$ for: (□) $[CuL_\beta][ReCl_4(ox)]\cdot DMF$ (**1**), (○) $[(Cu_2L_{\alpha 2})Cl][ReCl_4(ox)]Cl$ (**2**), (Δ) $[Bu_4N]_2[ReCl_4(ox)]$. The solid lines are the calculated curves. b) The low-temperature region of $\chi_M T(T)$ for compound **1**.

Magnetic Properties of 1 and 2

The magnetic susceptibility studies for the examined complexes have been performed within the temperature range of 1.7–300 K. The experimental data show the product $\chi_M T$ as a function of temperature (Figure 6a and Figure 6b). The $\chi_M T$ data of $[Bu_4N]_2[ReCl_4ox]$ is also included for comparison.

Complex **1** shows a typical 1D ferrimagnetic behavior. At room temperature, $\chi_M T$ is 2.26 cm^3 mol^{-1} K, a value that is expected for an uncoupled Re^{IV} ($S_{Re} = {}^3/_2$) and Cu^{II} ($S_{Cu} = {}^1/_2$) pair. With decreasing temperature, $\chi_M T$ continuously goes down in value and reaches its minimum (see inset) at 8 K with $\chi_M T = 0.96$ cm^3 mol^{-1} K. The presence of a minimum in the $\chi_M T$ data is consistent with the 1D model, assuming the occurrence of antiferromagnetic exchange interactions between Re^{IV} and Cu^{II} ions.[11] When the temperature is lowered below 8.0 K, $\chi_M T$ increases and reaches a maximum at 2.0 K before rapidly decreasing to between 2.0and 1.80 K. Due to additional exchange interactions between spins of the nearest neighboring chains at these low

$$H = \sum_i \left\{ \begin{array}{l} -JS^z_{2i-1}S^z_{2i} + g_{\parallel\mathrm{Cu}}\beta S^z_{2i-1}H_z + g_{\parallel\mathrm{Re}}\beta S^z_{2i}H_z + \\ g_{\perp\mathrm{Cu}}\beta\left(S^x_{2i-1}H_x + S^y_{2i-1}H_y\right) + g_{\perp\mathrm{Re}}\beta\left(S^x_{2i}H_x + S^y_{2i}H_y\right) + 2D\left[\left(S^z_{2i}\right)^2 - \frac{5}{4}\right] \end{array} \right\} \quad (1)$$

temperatures, the system undergoes a change to 3D antiferromagnetic ordering.[11]

To quantitatively interpret the susceptibility data, we used a one-dimensional model in which the magnetic susceptibility in the high-temperature region of **1** can be described by two contributions: the susceptibility of the $^4A_{2g}$ term of the Re(IV) ions (with zero-field splitting) and that of the $^2T_{2g}$ term of the $\mathrm{Cu^{II}}$ ions modified by a factor predicted from the Ising model of the magnetic exchange interactions and different local g values of g_{Cu} and g_{Re}.[1,13,14] The relevant spin Hamiltonian is defined by Equation (1),[12] where the total spins are $S_{2\mathrm{i}} = S_{\mathrm{Re}}$ and $S_{2\mathrm{i}-1} = \mathrm{S_{Cu}}$. J is the exchange coupling parameter between the quartet $\mathrm{Re^{IV}}$ and doublet $\mathrm{Cu^{II}}$ local spins and $2D$ is the energy gap between the ±3/2 and ±1/2 Kramers doublets.

The least-squares fit of the experimental data using this equation was limited to the 8.0–300 K range and leads to $2D = 99.1\ \mathrm{cm^{-1}}$, $g_{\mathrm{avRe}} = 1.91$, $g_{\mathrm{avCu}} = 2.27$ and $J = -3.36\ \mathrm{cm^{-1}}$ for **1**. The agreement factor R defined as $R = \Sigma(\chi_{\exp}T - \chi_{\mathrm{calc}}T)^2/\Sigma(\chi_{\exp}T)^2$ is $1.26{\cdot}10^{-4}$. The calculated curve agrees very well with the magnetic data and illustrates that the J parameter is clearly associated with the exchange pathway involving the oxalato bridge.

The variation of the magnetization M (in B.M. units) versus the magnetic field H at 1.8 K (Figure 7a and Figure 7b), i.e. below magnetic ordering, clearly supports the occurrence of spontaneous magnetic moments in complex **1**. As the magnetic field increases, the M versus H curve is linear up to 1000 G, and then shows a sinusoidal variation before reaching saturation at a value of $Ms = 1.51$ B.M. perrhenium-copper pair.[13] This value is smaller than that for the tetrabutylammonium compound $\mathrm{[Bu_4N]_2ReCl_4(ox)}$, ($Ms = 1.60$ B.M. per rhenium atom).

The magnetization versus temperature curves (Figure 8) measured at 50 Oe reveal the presence of spontaneous magnetization below the transition temperature $T_c = 3.50$ K. Spontaneous magnetization appears as the result of switching of the interchain exchange interactions at low temperatures that leads to 3D magnetic ordering of $\{\mathrm{[CuL_\beta]ReCl_4ox}\}_n$ ferrimagnetic chains.[13] The magnetic data show the predominance of one-dimensional exchange interactions at $T > 3.50$ K with a crossover to 3D ferrimagnetic ordering at $T \approx 3.50$ K.

Complex **2** exhibits different magnetic properties. The value of $\chi_M T$ at room temperature is $3.96\ \mathrm{cm^3\,mol^{-1}\,K}$, which is expected for uncoupled $\mathrm{Re^{IV}}$ and $\mathrm{Cu^{II}}$–$\mathrm{Cu^{II}}$ units. The $\chi_M T$ value smoothly decreases for a wide temperature range before it rapidly decreases at the lower temperatures [Figure 6]. The slight decrease in $\chi_M T$ can be due to the zero-field splitting effect of $\mathrm{Re^{IV}}$ ions and to intramolecular exchange interactions between $\mathrm{Cu^{II}}$–$\mathrm{Cu^{II}}$ ions. The crystal structure of **2** is built up by isolated paramagnetic ions $\mathrm{[(CuL_\alpha)_2Cl]^{3+}}$ and $\mathrm{[ReCl_4ox]^{2-}}$ and a diamagnetic $\mathrm{Cl^-}$ ion,

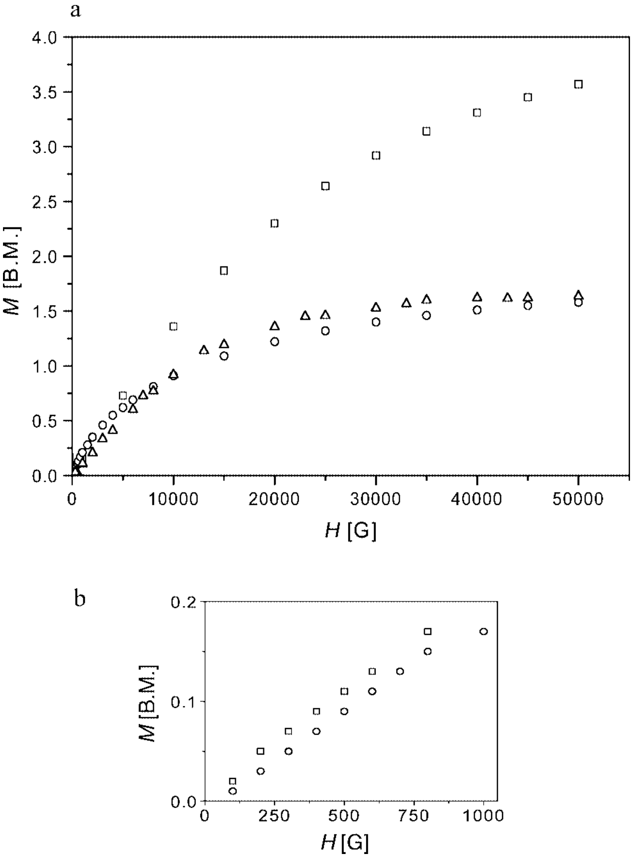


Figure 7. Field dependence of the magnetization for complexes for: (○) $\mathrm{[CuL_\beta][ReCl_4(ox)]{\cdot}DMF}$ (**1**), (□) $\mathrm{[(CuL\alpha)_2)Cl][ReCl_4(ox)]Cl}$ (**2**), (Δ) $\mathrm{[Bu_4N]_2[ReCl_4(ox)]}$.

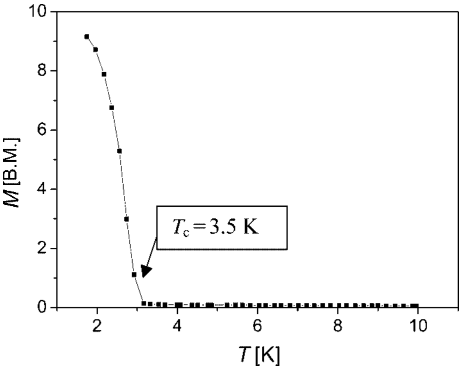


Figure 8. M vs T plots in the low-temperature range and a field of 50 Oe for $\mathrm{[CuL_\beta][ReCl_4(ox)]{\cdot}DMF}$ (**1**).

so that Wiedemann's equation can be used to interpret the magnetic data. Since the two magnetic ions exist at a ratio of 1:1, the equation [Equation (2)] for molar magnetic susceptibilities of complex **2** can be reduced to the simple form:

$$\chi_{\mathrm{sample}} = \chi_{\mathrm{av}[\mathrm{ReCl_4ox}]^{2-}} + \chi_{[(\mathrm{CuL}_\alpha)_2\mathrm{Cl}]^{3+}} + \chi_{\mathrm{Cl}^-} \qquad (2)$$

where the average magnetic susceptibility of $\mathrm{Re^{IV}}$ is equal to $\chi_{\mathrm{av}} = \frac{1}{3}\cdot\chi_{\mathrm{II}} + \frac{2}{3}\cdot\chi_{\perp}$

The parallel and perpendicular zero-field susceptibilities for $S = 3/2$ ($\mathrm{Re^{IV}}$) with an axial crystal field distortion were described in a previous paper.[9] The magnetic susceptibility of the dinuclear copper unit was specified by the Bleaney–Bowers expression.[14]

A least-squares fit leads to the following set of parameters: $g_{\mathrm{avRe}} = 2.30$, $g_{\mathrm{avCu}} = 2.21$, $J = -2.81$, $2D = 91.2$ and $R = 5.36\cdot10^{-4}$.

The macrocyclic complex cations $\mathrm{CuL_\alpha}^{2+}$ and $\mathrm{CuL_\beta}^{2+}$ used for the synthesis occur in the form of two isomers differing in the configuration of the donor nitrogen atoms. In complex **1** both methyl groups are found in an *anti* configuration, in which the central ion is accessible to the bridging oxalato ligands from both sides. The resulting oxalato bridges in the generated dimetallic zigzag chains are known to mediate magnetic interactions between metal centers. The possible mechanism for the one-dimensional ordering in **1** can be understood through orbital symmetry considerations. The magnitude of the interaction is due to the overlap of the magnetic orbital on either side of the bridge. Tetrahedral distortion of the copper environment is the apparent cause for the four short equatorial bonds to N(4), N(8), N(11), and N(15), which ensure the delocalization of the unpaired electron of the d_{z^2} magnetic orbital within the equatorial plane and disrupt the orthogonality between this orbital and the d_{xy} orbital of $\mathrm{Re^{IV}}$ through the oxalato ligand. The oxalato ligand between the Re(1)–Cu(1) pair causes poor overlap resulting in weak antiferromagnetic coupling $J = -3.36\ \mathrm{cm^{-1}}$. It deserves to be noted that the $2D$ value for complex **1** is greater than that for $[\mathrm{Bu_4N}]_2\mathrm{ReCl_4(ox)}$ ($53\ \mathrm{cm^{-1}}$).[9] These relatively large values of the $2D$ parameter for third-row transition-metal ions would account for the large value of the spin-orbit parameter ($\lambda \approx 1100\ \mathrm{cm^{-1}}$ for the $\mathrm{Re^{IV}}$ single ion).

The differences in the crystalline structure of complex **2** compared to complex **1** has a significant influence on its magnetic properties.The partial conversion of the macrocyclic ring conformation in **2** is accompanied by a change of the methyl groups from *anti*- to *syn* conformation. As a consequence the methyl groups block one of the axial sites at the $\mathrm{CuL_\alpha}^{2+}$ ion causing the availability of only one vacant site at the central copper(II) ion. This macrocycle ion with a $\mathrm{Cu^{II}}$ magnetic center is linked by a chloride bridge to another $\mathrm{Cu^{II}}$ unit. Halide bridges have been observed in other copper complexes, but most of these have at least two bridges with angular Cu–halogen–Cu bonds. The Cu–Cl bond distance in the present structure (2.156 Å) is shorter than the average of the bridging Cu–Cl bond distances: 2.514 Å in $[\mathrm{Co(en)_3}]_2[\mathrm{Cu_2Cl_8}]\mathrm{Cl_2}\cdot2\mathrm{H_2O}$,[15] 2.501 Å in $[\mathrm{Cu(tet\ b)Cl}]\mathrm{ClO_4}$, and 2.507 Å in $[\mathrm{Cu(L^1)Cl(CuCl_3)}]$ ($\mathrm{L^1}$ = 12-methyl-12-nitro-1,4,7,10-tetra-azacyclotridecane).[16] For dinuclear copper(II) compounds with bridging chloride ions, antiferromagnetic exchange interactions have been observed, and the singlet–triplet splitting ($2J$) varies linearly with φ, the bridging Cu–Cl–Cu angle. It should be noted that in the last reported compound $[\mathrm{Cu(L^1)Cl(CuCl_3)}]$, which has the same square-based pyramid coordination geometry as complex **2**, there is no antiferromagnetic spin coupling. The magnetic susceptibility from 4.25 to 301.6 K follows the Curie low, with a magnetic moment of 1.86 B.M. In complex **2**, because of the very long Cu(1)···Re(1) axial distance, the overlap between the magnetic orbitals in the $\mathrm{Re^{IV}}$ and $\mathrm{Cu^{II}}$ dimeric units can be neglected, leading to a nonexchange interaction as observed. On the other hand, observed antiferomagnetic interactions can be understood in terms of the nonzero overlap between the copper(II) magnetic $d_{x^2-y^2}$ orbitals.[17–19] Studies of chloride-bridged dimeric systems have shown that the bridging angle Cu–Cl–Cu of 152.2(1)° generates an antiferromagnetic coupling of copper(II) magnetic centers.[19]

Conclusions

Our results show that it is possible to synthesize new $\mathrm{Re^{IV}}$–$\mathrm{Cu^{II}}$ heterodimetallic complexes by using $[\mathrm{ReCl_4(ox)}]^{2-}$ anions as components that bridge macrocyclic $[\mathrm{Cu^{II}L}]^{2+}$ cations. The magnitude of magnetic coupling between $\mathrm{Re^{IV}}$ and $\mathrm{Cu^{II}}$ in the examined compounds can be tuned by changing the coordination geometry around the copper(II) ions. This coordination depends on the position of the methyl groups around the equatorial nitrogen atoms of the ligands. In the case of the nearly square-planar coordinated $[\mathrm{CuL_\beta}]^{2+}$, a 1D ferrimagnetic chain compound was obtained. Each $[\mathrm{ReCl_4(ox)}]^{2-}$ ion is bound by two long $\mathrm{Cu^{II}}$–O bonds to two macrocyclic fragments. The magnetic measurements indicate weak antiferromagnetic interactions between the $\mathrm{Re^{IV}}$ and $\mathrm{Cu^{II}}$ metal ions within the chains. The temperature dependency of magnetization has revealed a transition from a one-dimensional ferrimagnetic system to a three-dimensional magnetically ordered system. In the case of a non-planar coordination sphere around $\mathrm{Cu^{II}}$, the complex cation is open for coordination only on one side. This position is then occupied by a bridging chloro ligand, which connects two $\mathrm{Cu^{II}}$ macrocycle units, and the isolated anion $\mathrm{ReCl_4(ox)}^{2-}$ is responsible for the charge balance. Strong antiferromagnetic interaction is not expected in the dimetallic $\mathrm{Re^{IV}}$-$\mathrm{Cu^{II}}$ macrocyclic compounds **1** and **2** because of poor overlap of the magnetic orbitals. The analysis of these results suggest that a stronger magnetic interaction should be obtained if the rhenium(IV) ions were coordinated by other first-row transition-metal macrocycles.

Experimental Section

Physical Measurements: Magnetic measurements in the temperature range 1.7–300 K were performed using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The SQUID magnetometer was calibrated with the palladium rod sample (Materials Research Corporation, measured purity 99.9985%). The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Measurements were made at a magnetic field of 0.5 T. Corrections are based on subtracting the sample-holder signal and contribution χ_D estimated from the Pascal constants.

Materials: All materials used in this work were of reagent grade purity and were used as commercially obtained. The compounds $[Bu_4N]_2[ReCl_4(ox)]$, $[CuL_\alpha](ClO_4)_2$, and $[CuL_\beta](ClO_4)_2$ were prepared as previously reported.[8,9]

Synthesis of the Complexes – $[CuL_\beta]$ $[ReCl_4(ox)] \cdot DMF$ (1): A solution of $CuL_\beta(ClO_4)_2$ (2.5 mg, 0.075 mmol) in a MeC/eNO$_2$ (10 mL) (5:1) mixture was added, dropwise, to a solution of $[Bu_4N]_2ReCl_4(ox)$ (6.7 mg, 0.075 mmol) in 10 mL of the same solvent. The mixture was subsequently stirred. After a few days, by slow evaporation a dark-violet crystalline solid was formed from the violet solution. It was filtered and washed using methanol (2 × 20 mL) and diethyl ether. Yield: 5.86 mg (96%). Polyhedral violet single crystals suitable for X-ray diffraction studies were obtained by the slow mixing of solution of both reagents in DMF/MeCN (8:1) at room temperature. IR: bands associated to the oxalato ligand appear at 1718 (m), 1663 (s), 1375 (m), 800 (m) cm^{-1}. $C_{38}H_{70}N_{10}Cl_8O_{12}Cu_2Re_2$ (821.06): calcd. C 28.44, H 4.21, Cl 18.67, N 7.37; found: C 27.51, H 4.36, Cl 19.42, N 6.99. The rhenium and copper content was determined by ICP method: calcd. Cu 7.73, Re 24.51; found Cu 7.05, Re 24.32.

Synthesis of the Complexes – $[(CuL_\alpha)_2Cl][ReCl_4(ox)]Cl$ (2): A solution of $[CuL_\alpha](ClO_4)_2$ (5.0 mg, 0.15 mmol) in methanol (10 mL) was added dropwise to a solution of $[Bu_4N]_2[ReCl_4(ox)]$ (6.7 mg, 0.075 mmol) in 10 mL of the same solvent. The mixture was subsequently stirred. The resulting pink precipitate was filtered off, washed with diethyl ether and dried in air. Yield: 4.01 mg (46 %). Pink crystals of **2** suitable for X-ray diffraction studies were obtained by slow evaporation of a MeC/MF (5:1) solution of the previously prepared precipitate. IR: bands associated to the oxalato ligand appear at 1703 (m), 1666 (m), 1377 (s), 801 (m) cm^{-1}. $C_{136}H_{240}N_{32}Cl_{24}O_{16}Cu_8Re_4$ (1170.88): calcd. C 34.75, H 5.50, Cl 18.14, N 9.51; found: C 35.01, H 5.54, Cl 19.65, N 8.99. The rhenium and copper content were determined by ICP method: calcd. Cu 10.85, Re 15.86; found Cu 10.21, Re 15.12. Note: The chloride ligands on the copper(II) dimer are from the tetrachlorooxalato rhenium(IV) complex anions.

X-ray Crystallographic Study: Single crystal X-ray data was collected on a Bruker-XPS-diffractometer (CCD area detector, Mo-K_α radiation, $\lambda = 0.71073$ Å, graphite monochromator), empirical absorption correction using symmetry-equivalent reflections (SADABS),[20] structure solution and refinement by SHELXS-97[21] and SHELXL-97[22] in the WINGX system (Table 1) was performed.[23] Most of the hydrogen atoms were located by difference Fourier syntheses. CCDC-237149 and CCDC-237150 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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