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Synthesis, crystal structure and magnetic properties of an oxalato-bridged $\text{Re}^{\text{IV}}\text{Mo}^{\text{VI}}$ heterobimetallic complex†José Martínez-Lillo,^{*a,b} Donatella Armentano,^b Giovanni De Munno,^{*b} Francesc Lloret,^a Miguel Julve^a and Juan Faus^{*a}

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The $\text{Re}^{\text{IV}}\text{Mo}^{\text{VI}}$ compound of formula $(\text{PPh}_4)_2[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]$ (**1**) constitutes the first example of a heterodinuclear oxalato-bridged complex in the coordination chemistry of molybdenum.

The complex as ligand strategy is one of the best rational synthetic routes aimed at preparing nuclearity tailored heterometallic compounds. The success of this modular strategy is well illustrated by the impressive variety of multiproperty chemical architectures derived from the use of mononuclear species such as $[\text{M}(\text{ox})_3]^{6-2-}$ or $[\text{M}(\text{CN})_6]^{6-2-}$ (M = first-row transition metal ion and ox = oxalate dianion) as ligands toward fully solvated metal ions of preformed complexes whose coordination sphere is unsaturated.^{1,2} Most of this work concerns mixed 3d–3d systems and its extension to heavier elements (4d, 5d and 4f type metal ions) is of increasing interest in the context of molecular magnetism for both fundamental and practical reasons.^{3,4} In fact, the greater size of the local spins, larger anisotropy, more diffuse character of the magnetic orbitals and higher spin–orbit coupling values that the heavier metal ions can provide, are very important factors when thinking about hot topics in molecular magnetism such as the Single Molecule Magnets (SMMs) and Single Chain Magnets (SCMs).^{5,6} Among the heavy metal ions to be used as spin carriers in this building block approach, Re(IV) seems to be very appropriate because of: (i) its $S = 3/2$ spin ground state (in a six-coordinate environment); (ii) its large magnetic anisotropy arising from spin–orbit coupling (λ ca. 1000 cm^{-1} in the free ion) with values of the axial zero-field splitting as high as ca. 60 cm^{-1} in some mononuclear compounds;⁷ and (iii) the greater spin delocalization on its peripheral ligands which causes an enhancement of the magnetic coupling in comparison to the related compounds with chromium(III) (a 3d³ metal ion).⁸

The interest in the use of complexes of Re(IV) as building blocks can be illustrated by the recent reports concerning two series of complexes of the general formula $[\text{ReCl}_4(\mu\text{-CN})_2\text{M}(\text{dmf})_4]$ and $(\text{NBu}_4)_4[\{\text{ReCl}_4(\mu\text{-ox})\}_3\text{M}^{\text{II}}]$ (M = divalent first-row transition metal ion and NBu_4^+ = tetra-*n*-butylammonium cation).^{9,10} The former family is constituted by one-dimensional compounds which behave as SCMs, the Re(IV) precursor being the mononuclear *trans*- $[\text{ReCl}_4(\text{CN})_2]^{2-}$ unit. The second one deals with tetranuclear species where one of the members [$\text{M} = \text{Ni}(\text{II})$] exhibits slow relaxation of the magnetization, and is the first example of a heterometallic SMM with oxalate as the bridging ligand. In this latter family, the Re(IV) precursor is the mononuclear complex $[\text{ReCl}_4(\text{ox})]^{2-}$. The relatively easy preparation of the oxalate-containing rhenium(IV) precursor, and its stability, allowed us to explore its use as a ligand *versus* first-row transition metal ions, yielding oxalate-bridged di-,¹¹ tri-^{8b} and tetranuclear¹⁰ $\text{Re}^{\text{IV}}\text{M}^{\text{II}}$ compounds with intramolecular ferromagnetic interactions.

In an attempt to extend these studies to the unexplored 4d–5d(Re) mixed systems, we report here the preparation, crystal structure, and magnetic properties of a molybdenum(VI)–rhenium(IV) heterobimetallic compound of formula $(\text{PPh}_4)_2[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]$ (**1**) (Fig. 1) (PPh_4^+ = tetraphenylphosphonium cation). As far as we know, **1** is the first Re(IV) complex incorporating a 4d ion and the first example of a heterodinuclear oxalato-bridged complex in molybdenum chemistry. Attempts to obtain the magnetically more interesting Mo(V)–Re(IV) compound, indeed our initial goal, have so far failed.

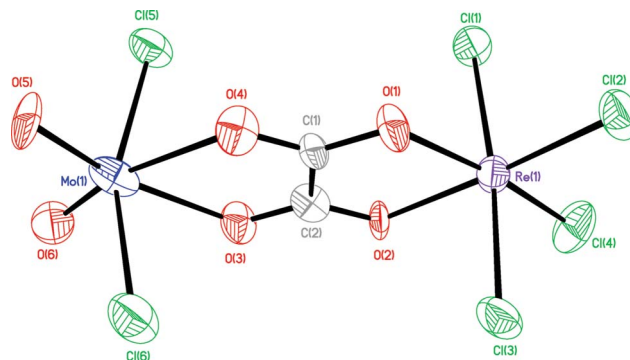


Fig. 1 ORTEP drawing of the $[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]^{2-}$ anion of **1** (the thermal ellipsoids are drawn at the 30% probability level).

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† Electronic supplementary information (ESI) available: Figures S1, S2 and preparation. CCDC reference number 795006. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01323d

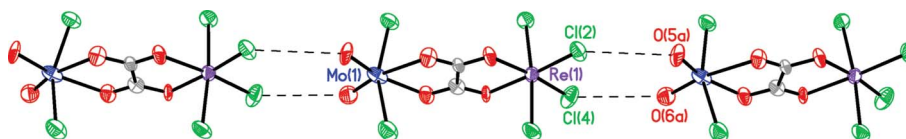


Fig. 2 Perspective view of the chain arrangement of $[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]^{2-}$ anions of **1** through intermolecular $\text{Cl}\cdots\text{O}$ contacts (dashed lines).

Compound **1** was prepared by reacting $(\text{PPh}_4)_2[\text{ReCl}_4(\text{ox})]$ (0.05 mmol) and MoCl_5 (0.05 mmol) dissolved in an acetonitrile : ethyl acetate (1 : 1, v/v) mixture. Slow evaporation at room temperature of the resulting orange–yellowish solution afforded orange parallelepipedic crystals of **1** which were suitable for X-ray diffraction studies. Yield: ca. 52% (See ESI†).

The crystal structure of **1**‡ is made up of $[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]^{2-}$ anions and PPh_4^+ cations which are held together by means of electrostatic forces and van der Waals interactions. A perspective drawing of the structure of the anionic unit along with the atom numbering is depicted in Fig. 1. Each $[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]^{2-}$ entity contains Re(IV) and Mo(VI) metal ions which are interconnected through a bis-bidentate oxalate ligand. Each rhenium atom is surrounded by two oxalate-oxygen and four chloro atoms, building a distorted octahedral environment. The short bite angle of the oxalate is the main cause of the distortion, the value of the angle subtended by this ligand at the rhenium atom being $80.1(4)^\circ$ [O(1)–Re(1)–O(2)]. No significant differences were found in the Re–Cl [values in the range 2.258(5)–2.343(5) Å] and Re–O [mean value 2.098(10) Å] bond lengths. Both Re–Cl and Re–O bond distances and angles within the $[\text{ReCl}_4(\text{ox})]$ fragment are in agreement with those found for this unit in previous reports.^{7a,8b,10} The best equatorial plane around the rhenium atom is defined by the O(1)O(2)Cl(2)Cl(4) set of atoms, the largest deviation from planarity being 0.010(7) Å at O(2). The Re atom lies 0.021(5) Å below this plane. The value of the dihedral angle between the mean equatorial plane and the oxalate group is $0.7(3)^\circ$.

Each molybdenum atom is also six-coordinated with two oxalate-oxygens, two oxo groups and two chloro atoms building a highly distorted octahedral environment around the metal atom. The best equatorial plane is defined by the O(3)O(4)O(5)O(6) set of atoms [largest deviation is 0.007(7) Å at O(3)], the Mo atom being 0.08(2) Å below this plane. The value of the dihedral angle between this mean plane and the oxalate group is $3.1(3)^\circ$. The Mo–Cl bond lengths [average value 2.358(6) Å] are in agreement with those reported for other species with a similar Mo(VI) environment.¹² The values of the Mo–O_{oxo} bond lengths [1.778(8) and 1.812(13) Å for **1**] are somewhat longer than those observed in the previously reported homodinuclear complex $(\text{NBu}_4)_2\{[\text{MoO}_2\text{Cl}_2]_2(\mu\text{-ox})\}$ (**2**) [1.685(1) and 1.688(1) Å for **2**], whereas no significant differences were found in the Mo–O_{ox} bond lengths in the two compounds [mean values 2.246(10) (1) and 2.242(1) Å (**2**)].¹² The lengthening of Mo–O_{oxo} bond lengths in **1** is most likely due to the electron-withdrawing effect induced by the rhenium(IV) ion.^{8b,10} The value of the Re \cdots Mo separation across the oxalate bridge is 5.609(9) Å.

Short $\text{Cl}\cdots\text{O}$ contacts of 3.52(1) and 3.57(1) Å among adjacent dinuclear units [Cl(2) \cdots O(5a) and Cl(4) \cdots O(6a) ($a = x, y-1, z$)] in **1** generate pseudo-chains developing along b axis (Fig. 2). These pseudo-chains are well separated from each other by PPh_4^+ cations (Fig. S1†) exhibiting the sextuple phenyl embrace (SPE)

supramolecular motif.¹³ The value of the shortest intermolecular Re \cdots Re distance is 9.647(1) Å [Re(1) \cdots Re(1b); ($a = x-1, y, z$)] while the shortest intermolecular Cl \cdots Cl separation is 5.609(7) Å [Cl(2) \cdots Cl(5a)]. Additional weak Cl \cdots H–C type interactions between cations and anions in **1** contribute to the stabilization of the crystal structure (Fig. S1†).

The magnetic properties of **1** under the form of $\chi_M T$ vs. T plot [χ_M being the magnetic susceptibility per dinuclear $\text{Re}^{\text{IV}}\text{Mo}^{\text{VI}}$ unit] are shown in Fig. 3. The $\chi_M T$ value at 300 K is $1.56 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, a value which is close to that observed for a magnetically isolated Re(IV) centre ($S_{\text{Re}} = 3/2$) and in line with supporting the diamagnetic character of the Mo(VI) ion. Upon cooling, $\chi_M T$ values decrease, first slowly and then faster, reaching a minimum value of ca. $0.85 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2.0 K. No maximum of χ_M is observed for **1** in the temperature range explored. The observed decrease of $\chi_M T$ is due to zero-field splitting effects of the six-coordinated Re(IV) ion, as discussed in previous reports.^{7,8b,10}

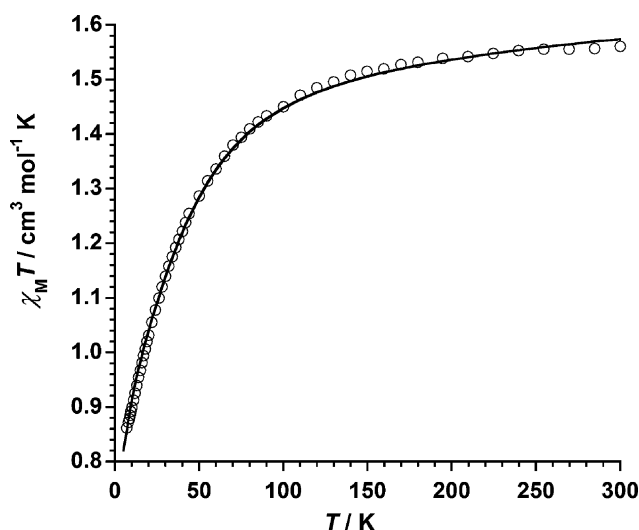


Fig. 3 Thermal dependence of $\chi_M T$ (O) for **1**. The solid line is the calculated best-fit curve (see text).

The field dependence of the magnetization (M) for **1** at 2.0 K exhibits a continuous increase with the applied magnetic field (Fig. S2†) and the maximum value of M per rhenium(IV) ion at the highest magnetic field available (5 T) is ca. $1.6 \mu_B$. This value agrees with that observed for the magnetically isolated $[\text{ReCl}_4(\text{ox})]^{2-}$ entity in its tetraphenylarsonium salt.^{7a}

The susceptibility data of **1** were analysed by means of the theoretical expression for the magnetic susceptibility derived from the Hamiltonian in eqn (1)

$$\hat{H} = D[\hat{S}_z^2 - S(S+1)/3] + g_{\parallel}\beta H_z \hat{S}_z + g_{\perp}\beta(H_x \hat{S}_x + H_y \hat{S}_y) \quad (1)$$

where the first term accounts for the zero-field splitting of the Re(IV) centre, and the last two terms correspond to the Zeeman effects. Best least-squares fit parameters for **1** are: $|D| = 48.6 \text{ cm}^{-1}$, $g = 1.80$ and $\theta = -1.0 \text{ K}$ with $R = 7.9 \times 10^{-5}$ [R being the agreement factor defined as $\sum i[(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum i[(\chi_M T)_{\text{obs}}(i)]^2$]. In order to avoid overparametrization, an average g factor was assumed. In addition, the possibility of weak intermolecular interactions was considered in the fit by introducing a θ parameter as $T - \theta$. As shown in Fig. 3, the calculated curve for **1** reproduces very well the magnetic data in the whole temperature range. The $|D|$ value is close to those values reported for other similar heterodinuclear complexes involving Re(IV) and first-row transition metal ions.¹¹

In summary, the crystal structure and magnetic study of a new molybdenum(VI)–rhenium(IV) (4d–5d) heterobimetallic compound, namely $(\text{PPh}_4)_2[\text{ReCl}_4(\mu\text{-ox})\text{MoO}_2\text{Cl}_2]$ (**1**), are reported. This compound is the first polynuclear Re(IV) complex incorporating a 4d ion and it opens a new route toward other mixed 4d–5d polynuclear species.

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Notes and references

‡ Crystal data for **1**: $\text{C}_{50}\text{H}_{40}\text{Cl}_6\text{P}_6\text{O}_6\text{MoRe}$, $M = 1293.6$, triclinic, space group $P1$, $a = 9.6472(4)$, $b = 11.7440(5)$, $c = 11.9908(5) \text{ \AA}$, $\alpha = 101.132(2)$, $\beta = 93.506(2)$, $\gamma = 106.257(1)^\circ$, $V = 1270.05(9) \text{ \AA}^3$, $T = 298(2) \text{ K}$, $Z = 1$, $\mu = 3.054 \text{ mm}^{-1}$, $D_c = 1.691 \text{ g cm}^{-3}$, 15176 reflections collected, 12010 unique ($R_{\text{int}} = 0.0130$), final $R1 = 0.0822$, $wR2 = 0.2128$, $\text{GOF} = 1.082$ for 10397 observed reflections, data/restraints/parameters = 12010/3/591. Single crystal X-ray diffraction data of **1** were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and processed through the SAINT (SAINT, Version 6.45, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003) reduction and SADABS (SADABS, Version 2.03, Bruker AXS Inc., Madison, WI, USA 2000) absorption software. The structure was solved by the Patterson method and subsequently completed by Fourier recycling using the SHELXTL (SHELXTL NT, Version 5.10, Bruker Analytical X-ray Inc., Madison, WI, USA, 1998. M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659) software packages and refined by the full-matrix least-squares refinements based on F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically except the oxygen atom O(6) that, if not considered to be approximately isotropic goes 'non-positive-definite'. All the hydrogen atoms were set in calculated positions and refined as riding atoms. The final geometrical calculations were carried out with the PARST97 program (M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659) whereas the graphical manipulations were performed with the DIAMOND program (DIAMOND 2.1d, Crystal Impact GbR, CRYSTAL IMPACT K; Brandenburg & H. Putz GBR, Bonn, Germany, 2000) and the XP utility of the SHELXTL system. CCDC reference number 795006.

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