

Pentachloro(pyrazine)rhenate(IV) complex as precursor of heterobimetallic pyrazine-containing $\text{Re}^{\text{IV}}_2\text{M}^{\text{II}}$ ($\text{M} = \text{Ni}, \text{Cu}$) species: synthesis, crystal structures and magnetic properties†

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Three novel Re(IV) mononuclear complexes of formulae $\text{NBu}_4[\text{ReCl}_5(\text{pyz})]$ (**1**), $\text{NH}_2\text{Me}_2[\text{ReCl}_5(\text{pyz})]$ (**2**) and $\text{NH}_4[\text{ReCl}_5(\text{pyz})] \cdot 0.75\text{H}_2\text{O}$ (**3**), (pyz being pyrazine; NBu_4^+ = tetra-*n*-butylammonium cation, NH_2Me_2^+ = dimethylammonium cation and NH_4^+ = ammonium cation), were synthesized by ligand substitution reaction from $[\text{ReCl}_6]^{2-}$ anion and pyrazine in *N,N*-dimethylformamide (DMF). In addition, two new heterobimetallic compounds, the salt namely $[\text{ReCl}_5(\text{pyz})]_2[\text{Ni}(\text{cyclam})]$ (**4**) (cyclam = 1,4,8,11-tetraazacyclotetradecane) and the heterotrinnuclear $\{[\text{ReCl}_5(\mu\text{-pyz})]_2\text{Cu}(\text{DMF})_4\}$ (**5**) complex, were prepared by using as precursor **1** and **3**, respectively. Compounds **1–5** were characterized by single-crystal X-ray diffraction. **1–3** are made up of discrete $[\text{ReCl}_5(\text{pyz})]^-$ anions and NBu_4^+ (**1**), NH_2Me_2^+ (**2**) and NH_4^+ (**3**) cations. $[\text{ReCl}_5(\text{pyz})]^-$ unit interacts toward Ni(II) (**4**) and Cu(II) (**5**) metal ions through different modes. In **4** two $[\text{ReCl}_5(\text{pyz})]^-$ anions weakly interact with a $[\text{Ni}(\text{cyclam})]^{2+}$ cation through chloro atoms, while compound **5** is a heterotrinnuclear pyrazine-bridged $\text{Re}^{\text{IV}}_2\text{Cu}^{\text{II}}$ complex made up of $[\text{ReCl}_5(\text{pyz})]^-$ anions and $[\text{Cu}(\text{DMF})_4]^{2+}$ cations. The magnetic properties of **1–5** were investigated in the temperature range 1.9–300 K. The magnetic behaviour of **1** is that of a magnetically diluted Re(IV) complex with a large value of zero-field splitting of the ground state ($|2D|$ is *ca.* 18.8(1) cm^{-1}), whereas those of **2** and **3** are typical of antiferromagnetically coupled systems exhibiting susceptibility maxima at 10 (**2**) and 12 K (**3**). Compound **4** shows antiferromagnetic interactions between Re(IV) metal ions, Ni(II) being diamagnetic (because of its square-planar geometry), while **5** exhibits a ferromagnetic coupling between Re(IV) and Cu(II) metal ions across the pyrazine bridges with a J_{ReCu} value of +11.8(1) cm^{-1} .

Introduction

An important amount of work has been devoted to study the magnetic properties of heteropolynuclear complexes containing transition metal ions, mainly from the first-row, these being connected by bridging ligands.¹ The nature and magnitude of the magnetic exchange coupling depend on several factors and have been explained in terms of the symmetry of the interacting magnetic orbitals.^{1–3} In contrast to the complexes obtained with first-row transition metal ions, those containing second- and third-row ones are less known and remain relatively unexplored. In

a series of previous papers, we have reported the study of the magnetic behaviour of heteropolynuclear complexes containing Re(IV) ($5d^3$ ion) and 3d transition metal ions (M^{II}) bridged by oxygen-donor oxalato (ox) and malonato (mal) ligands from the $[\text{ReCl}_4(\text{ox})]^{2-}$ and $[\text{ReCl}_4(\text{mal})]^{2-}$ precursor complexes.^{4–11} To date, the $[\text{ReCl}_4(\text{ox})]^{2-}$ complex has proven to be more fruitful affording, some selected results as for example, two series of heterometallic complexes, one formed by bimetallic dinuclear complexes of general formula $[\text{ReCl}_4(\mu\text{-ox})\text{M}^{\text{II}}(\text{dmphen})_2]$ where $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$ and Ni (dmphen = 2,9-dimethyl-1,10-phenanthroline),⁷ and the other by bimetallic trinnuclear complexes of general formula $(\text{NBu}_4)_2\{[\text{ReCl}_4(\mu\text{-ox})]_2\text{M}^{\text{II}}(\text{Him})_2\}$ with $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ and Cu (Him = imidazole).⁸ In both series were observed antiferro- ($\text{M} = \text{Mn}$) and ferromagnetic ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ and Cu) couplings. A heterotetranuclear $\text{Re}^{\text{IV}}_3\text{Ni}^{\text{II}}$ compound of formula $(\text{NBu}_4)_4\{[\text{ReCl}_4(\mu\text{-ox})]_3\text{Ni}\}$, which is the first Re(IV) complex showing single-molecule magnet (SMM) behaviour, was also obtained and studied.⁹

Recently, the synthesis of the $\text{NBu}_4[\text{ReBr}_5(\text{Hpyzc})]$ compound, obtained from a pyrazine-derived ligand (Hpyzc = 2-pyrazinecarboxylic acid), has provided the preparation of two new heterodinuclear $\text{Re}^{\text{IV}}\text{M}^{\text{II}}$ complexes of general formula $[\text{ReBr}_5(\mu\text{-pyzc})\text{M}^{\text{II}}(\text{dmphen})_2] \cdot 2\text{CH}_3\text{CN}$ ($\text{M} = \text{Co}, \text{Ni}$) that exhibit an intramolecular ferromagnetic coupling between Re(IV) and M(II) metal ions.¹²

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† Electronic supplementary information (ESI) available: Tables S1–S3 and Figs. S1–S6. CCDC reference numbers 677856–677860 (**1–5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b802112k

To develop this study and get deeper insights on these interesting 5d–3d systems we focus here on the pyrazine (pyz) ligand, which seems us of particular interest in order to synthesize new Re(IV) complexes that can act as ligands toward transition metal ions generating polynuclear compounds with interesting magnetic properties. This π -delocalised and N-donor ligand has been explored for the three last decades, due to its ability to act as a bridging ligand, affording from discrete bimetallic complexes to two- and three-dimensional compounds. In general, the pyrazine ligand provides an antiferromagnetic coupling between the paramagnetic metal ions that it connects.¹³

A survey of the literature shows that rhenium nitrosyl compounds,¹⁴ oxo- and dioxo-rhenium(v) species, which present one or more terminally coordinated pyrazine ligands, have been recently reported.^{15,16} Moreover, polymeric rhenium(III) compounds linked by pyrazine bridge have been described.¹⁷ A homodinuclear pyrazine-bridged Re(IV) complex, $(\text{NEt}_3)_2\{[\text{ReCl}_5]_2(\mu\text{-pyz})\}$, obtained by refluxing $[\text{ReCl}_5(\text{MeCN})]^-$ and $[\text{ReCl}_5(\text{pyz})]^-$ in CH_2Cl_2 , is also found in the literature.¹⁸ Although the $[\text{ReCl}_5(\text{pyz})]^-$ compound was prepared and isolated as its NEt_4^+ salt in 1971, to date its magnetism and X-ray studies have not been performed. More recently, another Re(IV) mononuclear complex with this ligand coordinated, $[\text{ReCl}_4(\text{pyz})(\text{PPh}_3)]$, has been also described.¹⁹ But up to now, as far as we know, no heteropolynuclear pyrazine-bridged $\text{Re}^{\text{IV}}\text{M}^{\text{II}}$ complex has been reported.

In this work, we present the results obtained from the synthesis of five novel Re(IV) compounds of formula $\text{NBu}_4[\text{ReCl}_5(\text{pyz})]$ (**1**), $\text{NH}_2\text{Me}_2[\text{ReCl}_5(\text{pyz})]$ (**2**), $\text{NH}_4[\text{ReCl}_5(\text{pyz})]\cdot 0.75\text{H}_2\text{O}$ (**3**), $[\text{ReCl}_5(\text{pyz})]_2[\text{Ni}(\text{cyclam})]$ (**4**) and $[\{\text{ReCl}_5(\mu\text{-pyz})\}_2\text{Cu}(\text{DMF})_4]$ (**5**), where NBu_4^+ = tetra-*n*-butylammonium cation, NH_2Me_2^+ = dimethylammonium cation, NH_4^+ = ammonium cation, pyz = pyrazine, cyclam = 1,4,8,11-tetraazacyclotetradecane and DMF = *N,N*-dimethylformamide, including the crystal structures and magnetic properties of all of them. **1–3** are paramagnetic mononuclear Re(IV)–pyrazine complexes, whereas **4** and **5** are heterobimetallic pyrazine-containing $\text{Re}^{\text{IV}}\text{M}^{\text{II}}$ compounds.

Results and discussion

Synthesis of the complexes

By heating a mixture of $(\text{NH}_4)_2[\text{ReCl}_6]$ and pyz in *N,N*-dimethylformamide (DMF) the monosubstituted complex $[\text{ReCl}_5(\text{pyz})]^-$ was obtained and further isolated as its NBu_4^+ (**1**), NH_2Me_2^+ (**2**) and NH_4^+ (**3**) salts. Ligand substitution reactions of the inert hexahalorhenates $[\text{ReX}_6]^{2-}$ ($\text{X} = \text{Cl}, \text{Br}$) in hot dry DMF have been reported in recent years as a convenient method for the preparation of a variety of Re(IV) complexes.^{20–26} Although $\text{NEt}_4[\text{ReCl}_5(\text{pyz})]$ has been reported in the literature it was synthesized starting from $[\text{ReCl}_5(\text{CH}_3\text{CN})]^-$ and its structure remains unknown up to now.^{18a} Compound **1** was isolated by precipitation after adding an aqueous solution of NBu_4Br , this being a general procedure used in other cases,^{22–24} whereas in **3** $[\text{ReCl}_5(\text{pyz})]^-$ crystallizes due to NH_4^+ ions present in the initial solution. On the other hand, **2** was an unexpected product that was obtained when intending the isolation of a complex with the pyrazine ligand protonated, $[\text{ReCl}_5(\text{Hpyz})]$, in an aqueous acid solution. Since dimethylammonium cation, NH_2Me_2^+ , has not been added, it arises from the hydrolysis of the solvent DMF. We

have not studied this reaction further, but the fact that a few crystals of **2** are also obtained in the synthesis of **3** indicates that the hydrolysis occurs during the formation of $[\text{ReCl}_5(\text{pyz})]^-$ upon heating at *ca.* 100 °C and/or when the solvent is evaporated in air at 60 °C (see Experimental section). There are several examples recently reported in where NH_2Me_2^+ cation, resulting from hydrolysis or decarbonylation of DMF, serves as counterion in the reaction product.^{27–32}

Given that pyz is a bridging ligand, $[\text{ReCl}_5(\text{pyz})]^-$ can be used as a ligand toward other metal ions. Indeed, the interaction between **3** and Cu(II) in a DMF–isopropanol solution allowed the synthesis of a novel trinuclear $\text{Re}^{\text{IV}}_2\text{Cu}^{\text{II}}$ complex $[\{\text{ReCl}_5(\mu\text{-pyz})\}_2\text{Cu}(\text{DMF})_4]$ (**5**). Nevertheless, $[\text{ReCl}_5(\text{pyz})]^-$ was not coordinated to the Ni(II) in $[\text{Ni}(\text{cyclam})]^{2+}$ complex and compound **4**, $[\text{ReCl}_5(\text{pyz})]_2[\text{Ni}(\text{cyclam})]$, resulted in a simple salt.

Description of the crystal structures of $\text{NBu}_4[\text{ReCl}_5(\text{pyz})]$ (1**), $\text{NH}_2\text{Me}_2[\text{ReCl}_5(\text{pyz})]$ (**2**) and $\text{NH}_4[\text{ReCl}_5(\text{pyz})]\cdot 0.75\text{H}_2\text{O}$ (**3**).** The crystal structure of compounds **1–3** is made up of $[\text{ReCl}_5(\text{pyz})]^-$ anions and NBu_4^+ (**1**), NH_2Me_2^+ (**2**) and NH_4^+ (**3**) cations held together by electrostatic and van der Waals forces (**1–3**), π – π stacking and hydrogen bonding interactions (**2** and **3**). A perspective drawing of the molecular structure of the $[\text{ReCl}_5(\text{pyz})]^-$ unit in compound **1**, showing the atom numbering, is depicted in Fig. 1, while selected bond lengths and angles are listed in Table S1 (ESI†).

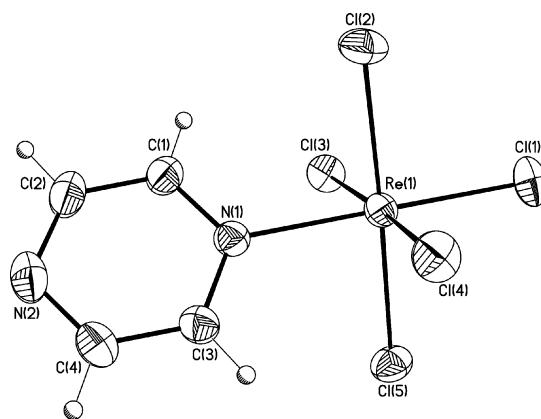


Fig. 1 Perspective view of the $[\text{ReCl}_5(\text{pyz})]^-$ anion of **1** showing the atom numbering. Thermal ellipsoids are drawn at the 30% probability level.

In the $[\text{ReCl}_5(\text{pyz})]^-$ unit of **1–3** the rhenium atom shows a distorted octahedral geometry, with the Re–Cl [average values of 2.338(1), 2.348(2) and 2.342(8) Å in **1–3**, respectively] and Re–N [2.173(2) (**1**), 2.154(4) (**2**) and 2.150(6) Å (**3**)] bond lengths in agreement with those found in the literature concerning similar Re(IV) compounds.^{4–12,21–26} The pyz ligand is planar and its C–C and C–N bond lengths are in agreement with those reported for the free pyrazine structure.³³ Its mean plane forms a dihedral angle of 87.7° (**1**) and 90.0° (**2** and **3**) with the main equatorial plane around the Re atom.

In **1**, $[\text{ReCl}_5(\text{pyz})]^-$ anions weakly interact each other through the pyrazine rings *via* a $\text{N}(2)\cdots\text{H}-\text{C}(1a)$ pathway [2.586(1) Å; (a) = +x, 0.5 – y, –0.5 + z], building a zigzag motif that extends along the crystallographic *c* axis (Fig. 2). However, they are well separated in the *a* and *b* directions by means of NBu_4^+ cations (Fig. S1, ESI†). The value of the shortest $\text{Cl}\cdots\text{Cl}$ [$\text{Cl}(5)\cdots\text{Cl}(1b)$] and interionic $\text{Re}\cdots\text{Re}$ [$\text{Re}(1)\cdots\text{Re}(1b)$] distances are 5.932(1)

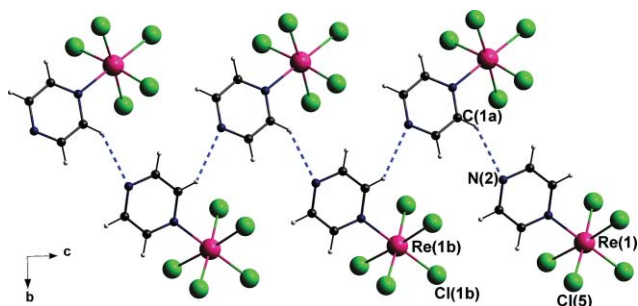


Fig. 2 A view along the *a* axis showing the N...H-C interactions between pyrazine rings of neighbouring $[\text{ReCl}_5(\text{pyz})]^-$ anions generating a zigzag motif in **1**.

and 8.683(1) Å, respectively [(b) = +*x*, +*y*, -1 + *z*]. Weak Cl...H-C contacts between $[\text{ReCl}_5(\text{pyz})]^-$ anions and NBu_4^+ cations help to stabilize the structure of **1** (Fig. S1, ESI†).

In compounds **2** and **3**, obviously due to the nature of the cations, hydrogen-bonding interactions involving cations and chloro atoms are observed [in **2**: 3.329(1) Å for N3...Cl(2) and N3...Cl(2d), (d) = -0.5 - *x*, +*y*, +*z*; in **3**: 3.442(1) Å for N5...Cl(3) and N5...Cl(3f), 3.415(1) Å for N6...Cl(5) and N6...Cl(5g), (f) = +*x*, 2 - *y*, +*z*, (g) = +*x*, 3 - *y*, +*z*] (Fig. 3; Fig. S2 and S3, ESI†). Moreover, adjacent $[\text{ReCl}_5(\text{pyz})]^-$ anions interact in a very similar way. In fact, relevant in-set π - π type interactions take place between pyz rings, which are stacked down the crystallographic *a* (**2**) and *b* (**3**) axis, with an interplanar distance of *ca.* 3.63 Å (**2**) and 3.55 Å (**3**) and, in both cases, an overlap efficiency of *ca.* 80% (Fig. 3 and 4).

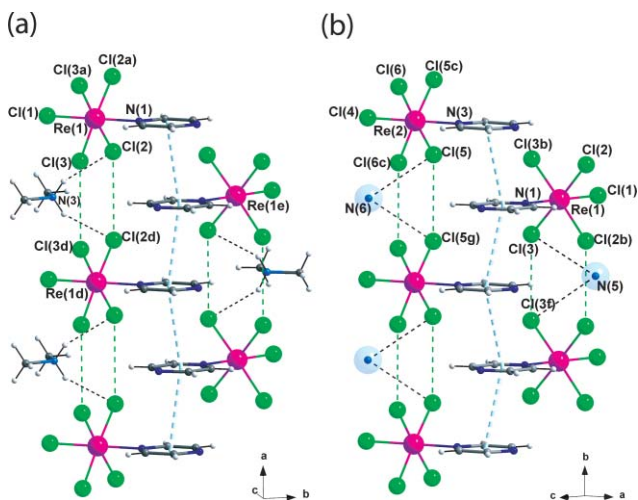


Fig. 3 A parallel view of the $[\text{ReCl}_5(\text{pyz})]^-$ anions arrangement in one direction in **2** (a) and **3** (b) showing the π - π overlap between pyz rings, the Cl...Cl contacts and the hydrogen bonds between cations and anions (dashed lines, see text) [(a) -*x* + 1/2, *y*, *z*; (b) *x*, -*y* + 1, *z*; (c) *x*, -*y*, *z*]. In **2** (a), the shortest Cl...Cl and interionic Re...Re distances are 3.918(1) [Cl(3)...Cl(3d), (d) = -0.5 - *x*, +*y*, +*z*] and 7.245(1) Å [Re(1)...Re(1e), (e) = -*x*, 1 - *y*, *z*], respectively.

However, due to the different steric hindrance of the respective counterion, the crystal packing of **2** and **3** shows important differences in the plane perpendicular to the stacking axis (*bc* in **2**, *ac* in **3**) (Fig. 4).

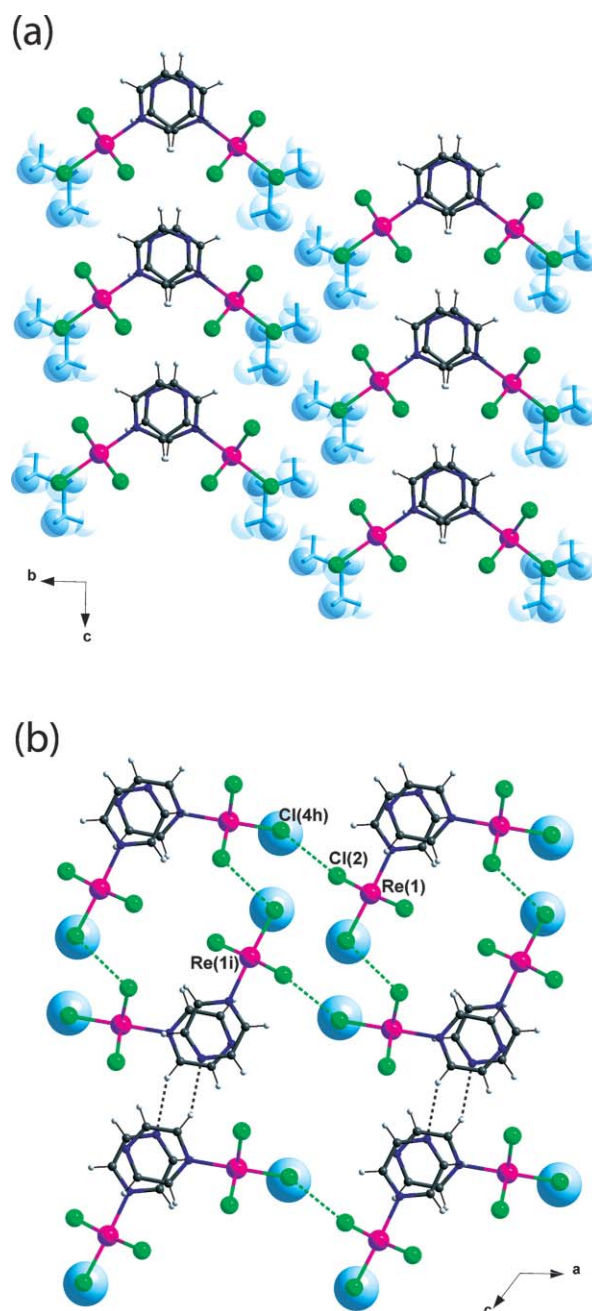


Fig. 4 A parallel view of the $[\text{ReCl}_5(\text{pyz})]^-$ anions arrangement in **2** (a) and **3** (b) in the plane perpendicular to the stacking axis: the position of cations are evidenced with a semitransparent space-filling model; ammonium cations in **3** are depicted with the biggest spheres. In **3** (b), the shortest Cl...Cl and interionic Re...Re distances are 3.596(1) [Cl(2)...Cl(4h), (h) = -0.5 + *x*, -0.5 + *y*, +*z*] and 6.892(1) Å [Re(1)...Re(1i), (i) = 1.5 - *x*, 0.5 - *y*, 1 - *z*], respectively.

In particular, as shown in Fig. 3(b), additional Cl...Cl and pyz...pyz interactions [2.552(1) Å *via* a N(2)...H-C(7l) pathway, (l) = 1.5 - *x*, 1.5 - *y*, -*z*] are present in compound **3** in the *ac* plane. Actually, the crystal structure of **3** can be described as a 3D supramolecular open-channel network made by $[\text{ReCl}_5(\text{pyz})]^-$ anions, with intercalated ammonium cations. Pseudo-rectangular channels, that extend along the *b* direction, are filled by crystallization water molecules, which occupy

crystallographic special positions and are involved in further hydrogen bonds [O1W...N(4m) 2.857(1) Å, O1W...N(6) 2.737(1) Å, O2W...Cl(4) 3.631(1) Å, O2W...Cl(6) 3.875(1) Å; (m) = 0.5 + x, 0.5 + y, +z] (Fig. S3 and S4, ESI†).

The shortest Cl...Cl and Re...Re distances are observed along the stacking direction (crystallographic *a* axis) in **2** (Fig. 3(a)) and in the *ac* plane in **3** (Fig. 4(b)).

Description of the crystal structures of [ReCl₅(pyz)]₂[Ni(cyclam)] (4) and [{ReCl₅(μ-pyz)]₂Cu(DMF)₄] (5). In compound **4**, two [ReCl₅(pyz)]⁻ and one [Ni(cyclam)]²⁺ units weakly interact through a chloro atom with a long distance of *ca.* 3.22 Å (Fig. 5). Selected bond lengths and angles are listed in Table S2 (ESI†).

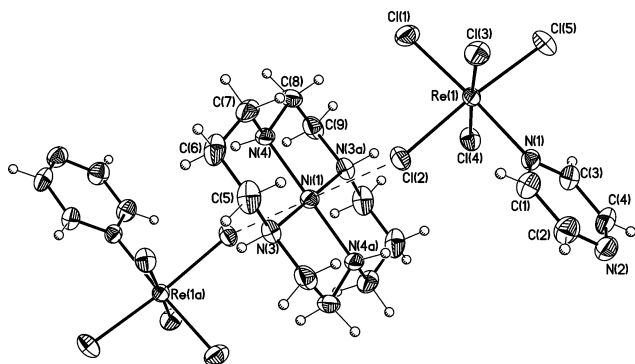


Fig. 5 Perspective view of the interacting [ReCl₅(pyz)]⁻ and [Ni(cyclam)]²⁺ units in **4** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code (a) = 1 - *x*, 2 - *y*, -*z*.

Each [ReCl₅(pyz)]⁻ unit exhibits in **4** the same coordination environment around the rhenium atom observed in the compounds described above (**1–3**). No significant differences were found in the Re–Cl and Re–N bond lengths, these being in agreement with those reported for other similar Re(IV) complexes.^{4–12,21–26}

In the [Ni(cyclam)]²⁺ units, the Ni atom exhibits a square-planar geometry (*D*_{4h}), with the metal atom exactly placed in the plane defined by the four nitrogen atoms from the cyclam molecule [average value of the Ni–N bond lengths is *ca.* 1.94 Å]. The pyrazine ligands are practically planar [mean deviation from plane of 0.0027(1)] and afford both π–π stacking [interplanar distance of *ca.* 3.60 Å] and Cl...π interactions [chloro atom distance from the pyz ring mean plane is *ca.* 3.65 Å] (Fig. 6).³⁴

Similarly to compound **3**, the resulting crystal structure of **4** can be described as an extended 3D supramolecular open-framework of interacting [ReCl₅(pyz)]⁻ anions. Many C–H...Cl type interactions among the cyclam molecule and chloro atoms of the surrounding [ReCl₅(pyz)]⁻ anions contribute to segregate the [Ni(cyclam)]²⁺ cations inside of the channels that extend in the *a* and *b* directions (Fig. S5 and S6, ESI†). The shortest Cl...Cl and Re...Re distances are 3.743(1) and 6.328(1) Å, respectively [Cl(1)...Cl(1b), (b) = 2 - *x*, 1 - *y*, -*z*; Re(1)...Re(1c), (c) = 2 - *x*, 1 - *y*, -1 - *z*]. The C–C and N–N bond lengths in pyz ligand are as expected.^{13,33}

The crystal structure of **5** is made up of neutral [{ReCl₅(μ-pyz)]₂Cu(DMF)₄] heterotrimeric units held together essentially by van der Waals interactions. A perspective drawing, showing the atom numbering, is depicted in Fig. 7. Selected bond

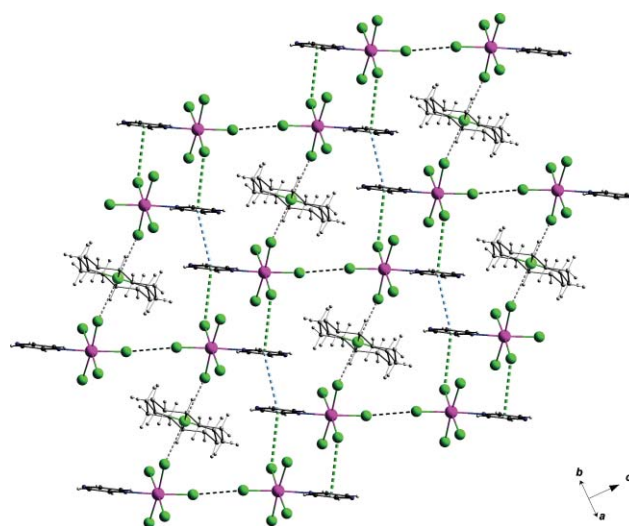


Fig. 6 A view along the [110] direction of a packing fragment showing the π–π stacking, the anion–π and the shortest Cl...Cl interactions that allow the occurrence of a supramolecular anionic open-framework including [Ni(cyclam)]²⁺ cations in **4** (see text).

lengths and angles are listed in Table S3 (ESI†). The [{ReCl₅(μ-pyz)]₂Cu(DMF)₄] unit contains two Re(IV) and one Cu(II) ions bridged by two pyz ligands. Each rhenium atom shows the same coordination environment found in the compounds described above (**1–4**). The average value of the Re–Cl bond lengths is 2.337(1) Å. The Re–N bond length value is 2.186(2) Å, in agreement with those reported for **1–4**.

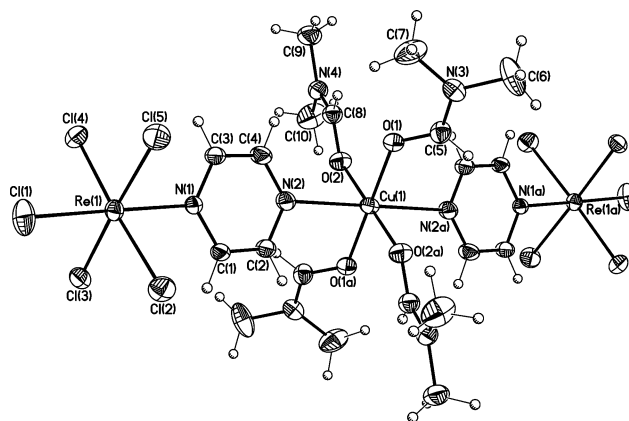


Fig. 7 Perspective view of the [{ReCl₅(μ-pyz)]₂Cu(DMF)₄] unit in **5** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Symmetry code (a) = 1 - *x*, 1 - *y*, 1 - *z*.

The copper atom exhibits a distorted octahedral geometry, equatorial positions being occupied by four oxygen atoms from four DMF molecules and the axial ones being filled by two nitrogen atoms from two pyrazine groups. The metal atom is practically placed in the equatorial plane defined by oxygen atoms. Cu–O bond lengths [average value of *ca.* 1.964 Å] are quite shorter than the Cu–N ones [2.477(2) Å]. The two pyrazine ligands are planar and form a dihedral angle of 76.3(1)° with the mean equatorial plane, exhibiting a dihedral angle of 2.5(1)° between them. The carbon–carbon and carbon–nitrogen bond lengths are in agreement with those reported for the coordinated pyrazine group.¹³

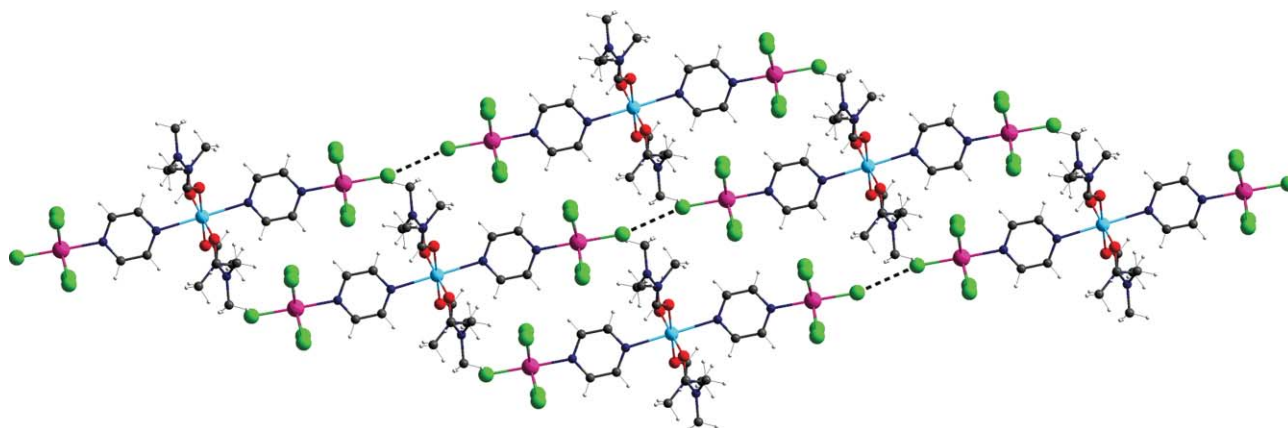


Fig. 8 A view along the $[1 -1 0]$ direction of adjacent pseudo-chains generated by short $\text{Cl}\cdots\text{Cl}$ contacts (broken lines) in **5**.

The $\text{Re}\cdots\text{Cu}$ distance across the bridging pyrazine–nitrogen atoms is $7.428(1)$ Å. In the packing of **5**, in spite of the presence of aromatic rings, no π – π interactions are observed. The value of the shortest intermolecular $\text{Re}\cdots\text{Re}$ distance is $6.827(1)$ Å [$\text{Re}(1)\cdots\text{Re}(1b)$; $(b) = -x, -y, -z$]. A short $\text{Cl}\cdots\text{Cl}$ contact of $3.440(1)$ Å among adjacent trinuclear units [$\text{Cl}(1)\cdots\text{Cl}(1c)$; $(c) = -1 + x, -1 + y, -z$] generates interdigitated pseudo-chains developing in the xy plane (Fig. 8). Additional $\text{Cl}\cdots\text{H-C}(\text{pyz})$ and $\text{Cl}\cdots\text{H-C}(\text{DMF})$ weak van der Waals interactions contribute to stabilize the crystal structure in **5**.

Magnetic properties. The magnetic properties of **1** in the form of $\chi_M T$ vs. T plot (χ_M being the molar magnetic susceptibility) are shown in Fig. 9. At room temperature, the value of $\chi_M T$ is $1.58 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. This value is practically that expected for a magnetically isolated mononuclear Re(IV) complex ($\chi_M T$ ca. $1.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $S_{\text{Re}} = 3/2$ and $g = 1.8$ – 1.9).⁴ $\chi_M T$ values remain practically constant upon cooling until 60 K and they decrease at lower temperatures tending to reach a value close to $1.00 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$. No maximum of susceptibility is observed for **1** in the temperature range explored.

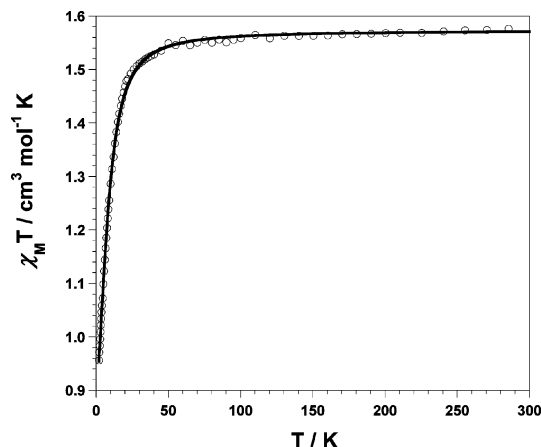


Fig. 9 Thermal variation of the $\chi_M T$ product for **1**. The solid line is the calculated curve.

In the light of previous magneto-structural studies on magnetically isolated rhenium(IV) mononuclear complexes,^{4,5} this

decrease of $\chi_M T$ can be attributed exclusively to the zero-field splitting, which is very large for Re(IV) in a distorted octahedral environment, because of the high value of the spin–orbit coupling constant (λ ca. 1000 cm^{-1} in the free $5d^3$ ion). In fact, for six-coordinated Re(IV) , the first excited term which arises from the 4F free-ion ground term is $^4T_{2g}$ and, under a tetragonal distortion, this excited state is split into 4B_2 and 4E terms. Under this pattern, the interaction of these two excited terms with the quartet ground spin state, leads to two Kramers doublets, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$, which are separated by an energy gap of $|2D|$ (zero-field splitting resulting from the combined action of second-order spin–orbit interaction and the tetragonal crystal field).⁴ The separation between the paramagnetic $[\text{ReCl}_5(\text{pyz})]^-$ anions in the lattice of **1** is ensured by the bulky tetrabutylammonium cations. The shortest interionic $\text{Cl}\cdots\text{Cl}$ separation in **1** (ca. 5.93 Å) seems to be too much large to cause any significant through space magnetic coupling. Having these considerations in mind, we have analyzed the experimental magnetic data of **1** through the theoretical expression for the magnetic susceptibility derived from the Hamiltonian of eqn (1):^{1a}

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

where the first term accounts for the zero-field splitting of the interacting Re(IV) metal ions, then Zeeman effects are included. The large axial anisotropy from Re(IV) accounts for a great value of D together with different values for g_{\parallel} 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_{\parallel} and g_{\perp} or the sign of D . The fit of 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 main value of g remain practically constant. Least-squares fit of the experimental magnetic data of **1** through eqn (1) leads to the set of parameters listed in Table 1. As one can see, the calculated curve for **1** reproduces very well the experimental magnetic data in the whole temperature range. The $|2D|$ value of **1** is quite lower than those observed for other mononuclear complexes containing a bidentate ligand^{4,5} as $[\text{ReCl}_4(\text{ox})]^{2-}$ and $[\text{ReCl}_4(\text{mal})]^{2-}$ but very similar to those values reported for other anions such as $[\text{ReCl}_6]^{2-}$ or $[\text{ReCl}_5(\text{DMF})]^-$ in its tetraphenylarsonium (AsPh_4^+) and tetra-*n*-butylammonium

Table 1 Magnetic parameters for complexes 1–6

Complex ^a	$ D /\text{cm}^{-1}$	g_{Re}	g_{Cu}	J/cm^{-1}	θ/K	R^b
1	9.4	1.83	—	—	—	1.4×10^{-5}
2	6.7	1.79	—	—	-11.0	2.6×10^{-4}
3	7.4	1.86	—	—	-43.0	8.8×10^{-5}
4	5.0	1.90	—	—	-14.0	5.2×10^{-5}
5	34.3	1.79	2.10	+11.8	—	1.3×10^{-5}
6	45.8	1.86	2.11	+7.7	-1.6	1.6×10^{-5}

^a Complexes 1–5 are reported in this work, 6 being previously reported (see ref. 8). The Hamiltonian of eqn (1) is used to fit the experimental data of 1–4 whereas that of eqn (2) is used for 5 and 6 (see text). ^b R is the agreement factor defined as $\sum i[(\chi_M T)_{\text{obs}}(i) - (\chi_M T)_{\text{calc}}(i)]^2 / \sum i[(\chi_M T)_{\text{obs}}(i)]^2$.

(NBU_4^+) salts, respectively.^{4,22} In these compounds, the presence of bulky cations precludes the contacts between the spin carriers and causes the magnetic dilution, because of the large halogen \cdots halogen separation generated.

The magnetic properties of complexes 2 and 3 in the form of both $\chi_M T$ and χ_M vs. T plots are shown in Figs. 10 and 11, respectively. At room temperature, the values of $\chi_M T$ are 1.30 (2) and $1.40 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ (3). These values are lower than that

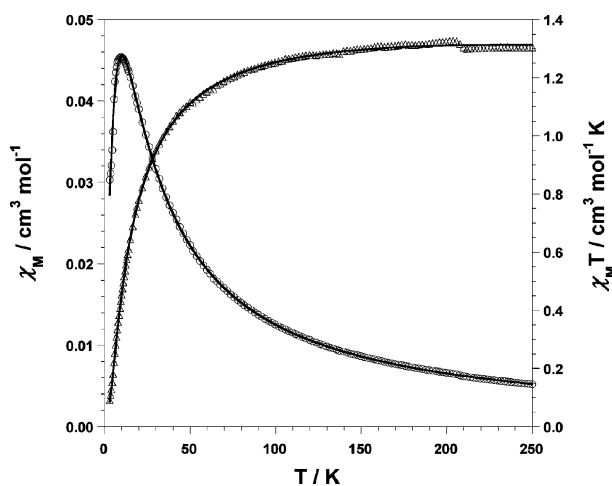


Fig. 10 Thermal variation of χ_M (○) and $\chi_M T$ (△) for 2: (—) best-fit curve (see text).

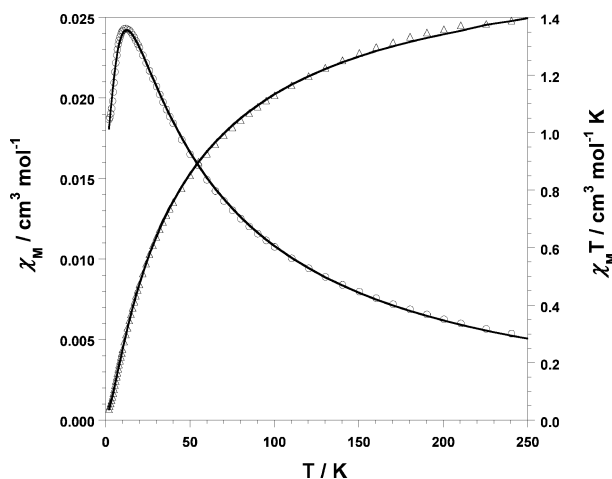


Fig. 11 Thermal variation of χ_M (○) and $\chi_M T$ (△) for 3: (—) best-fit curve (see text).

observed for 1, suggesting that a significant antiferromagnetic interaction occurs between Re(IV) metal ions. Upon cooling, $\chi_M T$ values for both compounds quickly decrease, and they vanish at very low temperatures. The susceptibility curves (χ_M vs. T) exhibit maxima at 10 (2) and 12 K (3). These last features observed for 2 and 3 are also characteristic of antiferromagnetically coupled systems. In comparison with NBU_4^+ in 1, the smaller size of NH_2Me_2^+ (2) and NH_4^+ (3) cations provides shorter $\text{Cl}\cdots\text{Cl}$ separations in 2 and 3. As a consequence, a θ parameter was included in the expression for the magnetic susceptibility derived from the Hamiltonian [eqn (1)] to fit the experimental data and to analyze the magnetic coupling between the $[\text{ReCl}_5(\text{pyz})]^-$ units. The best-fit parameters for 2 and 3 are given in Table 1. The calculated curves match quite well the experimental data in the whole temperature range. The negative θ values obtained show the occurrence of a significant antiferromagnetic coupling due to intermolecular interactions, θ being larger in compound 3. Hydrogen-bonding interactions involving crystallization water molecules in 3 together with shorter $\text{Cl}\cdots\text{Cl}$ contacts [*ca.* 3.9 (2) vs. *ca.* 3.6 Å (3)] would account for the larger θ value observed in 3 with respect to that of 2.

The magnetic properties of compound 4 are shown as $\chi_M T$ and χ_M vs. T plots in Fig. 12. At room temperature, a $\chi_M T$ value of *ca.* $4.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ is expected for one Ni(II) ($S_{\text{Ni}} = 1$) and two Re(IV) metal ions magnetically noninteracting.⁸ However, in 4 we observed that at room temperature $\chi_M T$ is *ca.* $2.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; $\chi_M T$ values upon cooling quickly decrease and they vanish at very low temperatures. The $\chi_M T$ value of *ca.* $2.6 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K indicates the occurrence of an antiferromagnetic coupling between Re(IV) metal ions, Ni(II) centre results to be diamagnetic with low spin state ($S_{\text{Ni}} = 0$) which is due to its square-planar geometry (D_{4h}). Therefore, Ni(II) metal ion acts here only as counteranion under the form of $[\text{Ni}(\text{cyclam})]^{2+}$ cation.

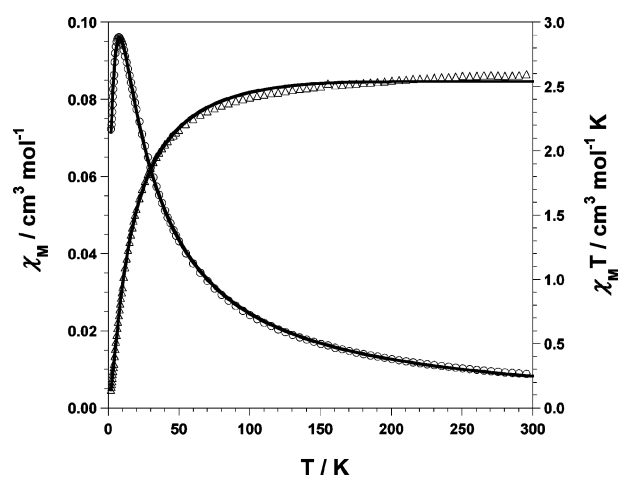


Fig. 12 Thermal variation of χ_M (○) and $\chi_M T$ (△) for 4: (—) best-fit curve (see text).

Several magnetic studies on cyclam-containing Ni(II) complexes are found in the literature.^{35–37} Studies on $[\text{Ni}(\text{cyclam})]^{2+}$ complex and halide showed variations in the magnetic properties, arguing that chloride and bromide complexes exhibit a high spin state while the iodide is diamagnetic.³⁵ More recently, the unusual magnetic behaviour of a Ni(II) –cyclam complex with iodide has been

reported.³⁷ In **4**, the long Ni...Cl distances lead to a D_{4h} geometry together with a low-spin state for Ni(II) metal ion. The χ_M vs. T curve exhibits a maximum at 7.5 K, which reveals an intermolecular antiferromagnetic coupling between Re(IV) metal ions due to short Re–Cl...Cl–Re contacts [shortest Cl...Cl separation being 3.743(1) Å] between adjacent $[\text{ReCl}_5(\text{pyz})]^-$ units (Fig. 6). As previously done for **2** and **3**, we have fitted the experimental data of **4** through the expression for the magnetic susceptibility derived from the same Hamiltonian [eqn (1)] including a θ parameter. The best-fit parameters for **4** are listed in Table 1. The computed curve reproduces very well the experimental magnetic data in the temperature range explored, the θ value showing the occurrence of a significant antiferromagnetic coupling between Re(IV) metal ions because of the intermolecular interactions indicated above.

The magnetic properties of the complex **5** in the form of a $\chi_M T$ vs. T plot (χ_M being the magnetic susceptibility per heterotrinary $\text{Re}^{\text{IV}}_2\text{Cu}^{\text{II}}$ unit) are shown in Fig. 13. At room temperature $\chi_M T$ is ca. $3.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, a value which is very close to that expected for one Cu(II) ($S_{\text{Cu}} = 1/2$) and magnetically isolated two Re(IV) ions.⁸ This value increases very slowly upon cooling, reaching a maximum ($\chi_M T_{\text{max}} = 3.71 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$) at 17 K, then it decreases steeply at lower temperatures. These features reveal an intramolecular ferromagnetic coupling between Re(IV) and Cu(II) metal ions through pyrazine bridges, the decrease of $\chi_M T$ in the low temperature range is most likely due to the rhenium(IV) zero-field splitting and/or intermolecular magnetic interactions. Taking into account the trinuclear structure of **5**, we have analyzed its experimental magnetic data by means of the Hamiltonian of eqn (2):

$$\hat{H} = -J(\hat{S}_{\text{Re1}} \cdot \hat{S}_{\text{Cu}} + \hat{S}_{\text{Re2}} \cdot \hat{S}_{\text{Cu}}) + D_{\text{Re1}}[(\hat{S}_{\text{Re1}}^z)^2 - 5/4] + D_{\text{Re2}}[(\hat{S}_{\text{Re2}}^z)^2 - 5/4] + \beta(\hat{S}_{\text{Re1}} g_{\text{Re1}} + \hat{S}_{\text{Re2}} g_{\text{Re2}} + \hat{S}_{\text{Cu}} g_{\text{Cu}}) \cdot H \quad (2)$$

in which J is the exchange coupling parameter between local spins from the central copper and rhenium atoms. The last term in eqn (2) accounts for the Zeeman effects of the three metal ions. Moreover, in order to avoid an overparametrization, we have assumed that $D_{\text{Re1}} = D_{\text{Re2}} = D_{\text{Re}}$ and $g_{\parallel} = g_{\perp} = g$ for Re(IV) and Cu(II) metal ions. Fit of the experimental magnetic data

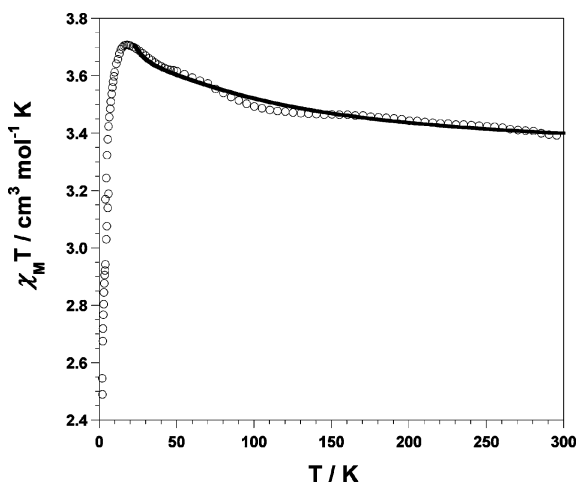


Fig. 13 Thermal variation of the $\chi_M T$ product for **5**. The solid line is the calculated curve.

of **5** has been only possible up to near the maximum, that is, ca. 20 K. The set of best-fit parameters are given in Table 1. As observed, the calculated curve matches reasonably well the experimental magnetic data until the maximum is reached. The nature of the magnetic coupling that takes place in **5** can be understood, qualitatively at least, on the basis of orbital symmetry considerations. If we assume an octahedral symmetry for the involved metal ions, Cu(II) ion ($t_{2g}^6 e_g^3$ electronic configuration) exhibits one unpaired electron in an e_g magnetic orbital that is orthogonal to the half filled t_{2g} magnetic orbitals from the Re(IV) metal ions (t_{2g}^3 electronic configuration). This orthogonality leads to a ferromagnetic coupling in the Re(IV)–Cu(II)–Re(IV) spin set, as the positive J_{ReCu} value from our fit indicates (Table 1).

As far as we know, the exchange coupling value (J_{ReCu}) that we have here reported for **5** is the first one which has been determined for the involved metal ions bridged through pyrazine ligand and, therefore, any comparison is precluded. Nevertheless, we may confront this value ($J_{\text{ReCu}} = +11.8 \text{ cm}^{-1}$ (**5**)) with that of recently reported heterotrinary $\text{Re}^{\text{IV}}_2\text{Cu}^{\text{II}}$ complex namely $(\text{NBu}_4)_2[\{\text{ReCl}_4(\mu\text{-ox})\}_2\text{Cu}^{\text{II}}(\text{Him})_2]$ (**6**), in which the bridging ligand is oxalate and J_{ReCu} value is $+7.7 \text{ cm}^{-1}$ (Table 1).⁸

In both cases the coupling between Re(IV) and Cu(II) metal ions is ferromagnetic but J_{ReCu} value is somewhat larger in **5**, in spite of the rhenium(IV)–copper(II) separation across the bridge unit being shorter in the case of the oxalate-containing compound [ca. 7.4 Å in **5** vs. ca. 5.5 Å in **6**]. The different donor atoms set or the different bridging modes of these ligands as well as other factors, such as the orientation of the Cu(II) magnetic orbitals in the direction of the bridges in **5** and **6**, may influence the magnetic orbitals overlap and consequently the J_{ReCu} parameter.

Conclusions

In this and also in previous work, we have reported the synthesis, crystal structure and magnetic properties of a variety of polynuclear Re(IV)–M(II) metal complexes, M being a 3d metal ion. We have observed the occurrence of antiferro- and ferromagnetic couplings between the different metal ions, which can be understood with the exchange model developed by Kahn. Up to now, most of these complexes are di-, tri- and tetranuclear species, only a few compounds could be described as an infinite chain. Our results suggest that extended structures should exhibit the most interesting magnetic properties. Thus, we are now trying to obtain, following the same work methodology, Re(IV)–M(II) coordination polymers with 2D and 3D structures.

We chose initially Re(IV), a paramagnetic 5d metal ion, with the hope that the larger radial extension of these orbitals should produce magnetic interactions more intense than those observed between transition metals of the first series. Indeed, our results confirm that 5d–3d couplings, antiferro- or ferromagnetic, have J values greater than those for similar 3d–3d interactions. Nonetheless, they range only between weak and moderate. It can be expected then that substituting a 4d or 5d ion for the 3d in heteropolynuclear Re(IV) complexes the magnetic interactions should be more intense. We are now turning our interest also in this direction and working on the synthesis and characterization of polynuclear metal complexes containing Re(IV) and other transition metal ions of the second or third series. This direction is not free of difficulties due to the scarcity of paramagnetic ions

of these elements and their tendency to form metal–metal bonds, but we think it is worthwhile.

Experimental

Materials

Reagents such as pyrazine, cyclam, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ and solvents employed in the synthesis were purchased from commercial sources and used as received. Ammonium hexachlororhenate(IV), $(\text{NH}_4)_2[\text{ReCl}_6]$, was prepared from the corresponding perrhenate salt following a literature procedure.³⁸

Preparation of the compounds

$\text{NBu}_4[\text{ReCl}_5(\text{pyz})]$ (1). A mixture of $(\text{NH}_4)_2[\text{ReCl}_6]$ (0.30 g, 0.69 mmol) and an excess of pyrazine (0.30 g, 3.75 mmol) in 4 mL of DMF (max. 0.03% water) was stirred and heated at 100–105 °C for 5 h leading to a dark brown–orange solution. After cooling at room temperature, any solid present was removed by filtration and discarded. **1** was separated as a pale pink solid after the addition to the filtrate of NBu_4Br (~1 g) dissolved in 15 mL of H_2O . This solid was filtered off, washed with cold isopropanol, ether and dried in air. Yield: ca. 75%. Polyhedral green–pink crystals suitable to X-ray studies were grown in a few days from a solution of **1** in an isopropanol– CH_3CN (2 : 1, v/v) mixture by slow evaporation at room temperature. Found: C, 35.08; H, 5.89; N, 6.01. Calc. for $\text{C}_{20}\text{H}_{40}\text{N}_5\text{Cl}_5\text{Re}$: C, 35.02; H, 5.88; N, 6.13%. IR: bands associated to pyrazine ligand appear at 3036m, 1514m, 1415vs, 810s and 471s cm^{-1} .

$\text{NH}_2\text{Me}_2[\text{ReCl}_5(\text{pyz})]$ (2). Compound **2** was prepared by using the same procedure described for **1** but only up to obtaining the dark brown–orange solution as filtrate. Then, the solvent was eliminated completely by heating at 60 °C and a brown residue was obtained. 50 mL of a 0.5 M HCl solution were added to the brown solid stirring for 10 min finally obtaining a green–yellow solution. Polyhedral green crystals, suitable for crystallographic studies, were formed from this solution after one month by slow evaporation at room temperature. Yield: ca. 50%. Found: C, 14.64; H, 2.50; N, 8.53. Calc. for $\text{C}_6\text{H}_{12}\text{N}_3\text{Cl}_5\text{Re}$: C, 14.72; H, 2.47; N, 8.58%. IR: bands assigned to pyrazine appear at 3030m, 1575m, 1512w, 1412vs, 799s and 466s cm^{-1} .

$\text{NH}_4[\text{ReCl}_5(\text{pyz}) \cdot 0.75\text{H}_2\text{O}]$ (3). The preparation of the complex **3** is analogous to that of **2** up to formation of the brown residue. 50 mL of CH_2Cl_2 – CH_3NO_2 (1 : 1, v/v) was then added to this solid stirring during 30–40 min. The resulting yellow solution was filtered and the insoluble part of the residue was discarded. In 2–3 weeks, orange parallelepipeds of **3** suitable to X-ray studies were grown from the yellow solution by slow evaporation at room temperature. Yield: ca. 40%. Found: C, 10.33; H, 1.74; N, 8.90. Calc. for $\text{C}_4\text{H}_{9.50}\text{N}_3\text{O}_{0.75}\text{Cl}_5\text{Re}$: C, 10.11; H, 2.01; N, 8.84%. IR: bands associated with the pyrazine ligand appear at 3037m, 1592w, 1511w, 1415vs, 810s and 471s cm^{-1} . A few green crystals of **2** were also obtained in this synthesis.

$[\text{ReCl}_5(\text{pyz})_2][\text{Ni}(\text{cyclam})]$ (4). 18.0 mg (0.05 mmol) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 10 mL of methanol were added to a solution of 70.0 mg (0.10 mmol) of **1** dissolved in 5 mL of methanol together with 4–5 drops of acetone (to dissolve **1**

fully). Then, 10.0 mg (0.05 mmol) of cyclam dissolved in 10 mL of methanol were added, affording an orange solution. After 2 h, a golden solid of **4** appeared which was filtered off and washed with methanol. Yield: ca. 40%. X-Ray quality crystals were obtained by redissolving the material obtained in acetonitrile and evaporating slowly at room temperature. Found: C, 19.10; H, 2.80; N, 9.80. Calc. for $\text{C}_{18}\text{H}_{32}\text{N}_8\text{Cl}_{10}\text{NiRe}_2$: C, 18.90; H, 2.81; N, 9.78%. IR: bands associated to pyrazine ligand appear at 1415s, 1060w, 1026w, 796m and 469m cm^{-1} .

$[\{\text{ReCl}_5(\mu\text{-pyz})\}_2\text{Cu}(\text{DMF})_4]$ (5). Compound **5** was prepared by means of slow diffusion in an H-shaped tube. In one arm were added 46.2 mg (0.10 mmol) of **3** dissolved in DMF (1 mL), and 18.1 mg (0.05 mmol) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ dissolved in 1 mL of an isopropanol–DMF (1 : 1, v/v) mixture in the other arm. The tube was filled by adding isopropanol in both arms and left to diffuse. In 3–4 weeks, polyhedral green crystals of X-ray quality appeared in the bridge of the tube. Yield: ca. 70–75%. Found: C, 19.46; H, 2.96; N, 8.87. Calc. for $\text{C}_{20}\text{H}_{36}\text{N}_8\text{Cl}_{10}\text{O}_4\text{CuRe}_2$: C, 19.33; H, 2.92; N, 9.01%. IR: bands associated to pyrazine ligand appear at 1409s, 805m, 478m cm^{-1} and those assigned to DMF at 1648vs, 1361s and 705m cm^{-1} .

Physical techniques

Infrared spectra of **1–5** were recorded with a Nicolet 320 FTIR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. Magnetic susceptibility measurements of **1–5** were carried out with a Quantum Design SQUID magnetometer in the temperature range 1.9–300 K and under an applied magnetic field of 1 T in the high-temperature range and 250 G at low temperatures ($T < 50$ K) to avoid any problem of magnetic saturation. The device was calibrated with $(\text{NH}_4)_2\text{Mn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and the diamagnetic contribution of the constituent atoms of **1–5** was estimated from Pascal constants.³⁹

X-Ray data collection and structure refinement

X-Ray diffraction data on single crystals of **1–5** were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer with graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). Crystal parameters and refinement results for **1–5** are summarized in Table 2. All data were processed through the SAINT⁴⁰ reduction and SADABS⁴¹ absorption software. The structures of **1–5** were solved by direct method and subsequently completed by Fourier recycling using the SHELXTL⁴² software packages. All non-hydrogen atoms were refined anisotropically, except for O1w and O2w in **3**. The hydrogen atoms of pyz, as those of the dimethylammonium cation in **2**, were placed in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. In compound **3** the hydrogen atoms on ammonium cations and water molecules were not defined. The final full-matrix least-squares refinements on F^2 , minimising the function $\sum w(|F_o| - |F_c|)^2$, reached convergence with the values of the discrepancy indices given in Table 2. The final geometrical calculations were carried out with the PARST97⁴³ program whereas the graphical manipulations were performed with the DIAMOND⁴⁴ program and the XP utility of the SHELXTL system. Main interatomic bond lengths and angles are listed in Tables S1 (**1–3**), S2 (**4**) and S3 (**5**).

Table 2 Summary of the crystal data for NBu₄[ReCl₅(pyz)] (1), NH₂Me₂[ReCl₅(pyz)] (2), NH₄[ReCl₅(pyz)]·0.75H₂O (3), [ReCl₅(pyz)]₂[Ni(cyclam)] (4) and [ReCl₅(μ-pyz)]₂Cu(DMF)₄ (5)

	1	2	3	4	5
Formula	C ₂₀ H ₄₀ Cl ₅ N ₃ Re	C ₃ H ₆ Cl _{2.50} N _{1.50} Re _{0.50}	C ₄ H _{9.50} Cl ₅ N ₃ O _{0.75} Re	C ₉ H ₁₆ Cl ₅ N ₄ Ni _{0.50} Re	C ₁₀ H ₁₈ Cl ₅ N ₄ O ₂ Cu _{0.50} Re
<i>M_r</i>	686.00	244.82	475.10	573.06	621.50
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Ama</i> 2	<i>C</i> 2/ <i>m</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	10.8300(6)	7.2660(2)	23.8479(19)	8.4084(7)	9.4579(3)
<i>b</i> /Å	33.1170(19)	26.3894(6)	7.0953(5)	8.5093(7)	10.2914(3)
<i>c</i> /Å	8.6825(5)	7.3267(2)	19.0101(14)	12.2145(12)	11.8237(4)
<i>a</i> /°	90.0	90.0	90.0	83.765(3)	109.361(1)
<i>β</i> /°	111.901(1)	90.0	126.475(6)	83.256(3)	99.969(1)
<i>γ</i> /°	90.0	90.0	90.0	72.767(3)	102.096(1)
<i>U</i> /Å ³	2889.3(3)	1404.86(6)	2586.6(3)	826.42(13)	1024.31(6)
<i>Z</i>	4	8	8	2	2
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)
<i>D_c</i> /g cm ⁻³	1.577	2.315	2.440	2.303	2.015
<i>F</i> (000)	1364	916	1764	544	593
<i>μ</i> (Mo-Kα)/mm ⁻¹	4.680	9.574	10.400	8.704	7.097
Refl. collected.	40388	15363	15067	21013	15185
Refl. indep. (<i>R</i> _{int})	10969 (0.0270)	2689 (0.0195)	4230 (0.0215)	3557 (0.0237)	6234 (0.0141)
Refl. obs. [<i>I</i> > 2σ(<i>I</i>)]	8388	2598	4020	3382	5840
No. param.	262	85	149	178	205
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)] (all)	0.0261 (0.0401)	0.0143 (0.0152)	0.0271 (0.0286)	0.0217 (0.0233)	0.0187 (0.0207)
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)] (all)	0.0597 (0.0621)	0.0353 (0.0553)	0.0844 (0.0851)	0.0535 (0.0542)	0.0448 (0.0458)
Goodness-of-fit on <i>F</i> ²	1.042	1.232	1.185	1.086	1.052
Abs. struct. param.		0.025(8)			
Δρ _{max, min} /e Å ⁻³	0.794 and -0.815	0.358 and -1.088	2.425 and -1.602	1.374 and -1.442	0.750 and -1.053

^a *R*₁ = Σ(|*F*_o| - |*F*_c|)/Σ|*F*_o|. ^b *wR*₂ = {Σ[w(*F*_o² - *F*_c²)²]/Σ[w(*F*_o²)²]}^{1/2} and *w* = 1/[σ²(*F*_o²) + (*mP*)² + *nP*] with *P* = [*F*_o² + 2*F*_c²]/3, *m* = 0.0292 (1), 0.0311 (2), 0.0347 (3), 0.0215 (4) and 0.0228 (5) and *n* = 0.21 (1), 0.00 (2), 23.27 (3), 1.77 (4) and 0.34 (5).

CCDC reference numbers 677856–677860 (1–5).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b802112k

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