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Magneto-structural correlations in dirhenium(IV) complexes possessing magnetic pathways with even or odd numbers of atoms.

Anders H. Pedersen, a Miguel Julve, b José Martínez-Lillo, *b Joan Cano, *b and Euan K. Brechin*a

Abstract

Employment of pyrazine (pyz), pyrimidine (pym) and s-triazine (triz) ligands in ReIV chemistry leads to the isolation of a family of complexes of general formula (NBu4)2[(ReX5)2(μ-L)] (L = pyz, X = Cl (1) or Br (2); L = pym, X = Br (3); L = triz, X = Br (4)). 1-4 are dinuclear compounds where two pentahalorhenium(IV) fragments are connected by bidentate pyz, pym and triz ligands. Variable-temperature magnetic measurements, in combination with detailed theoretical studies, uncover the underlying magneto-structural correlation whereby the nature of the exchange between the metal ions is dictated by the number of intervening atoms. That is, the spin-polarization mechanism present dictates that odd and even number of atoms favour ferromagnetic (F) and antiferromagnetic (AF) exchange interactions, respectively. Hence, while the pyz ligand in 1 and 2 mediates AF coupling, the pym and triz ligands in 3 and 4 promote F interactions.

Introduction

In 1963 McConnell proposed a mechanism to describe the magnetic exchange between radicals in aromatic organic molecules.1 Antiferromagnetic and ferromagnetic interactions, with singlet and triplet ground spin states, were favoured when the magnetic pathway was made up of even or odd numbers of atoms, respectively. Such a mechanism therefore dictated that the more stable spin configuration described an alternation of spin densities on adjacent atoms on the π-pathway through dynamic spin polarization, i.e. an ‘up-down-up-down’ arrangement. This proposal created new research avenues in the field of molecular magnetism that aroused great interest over several decades.2-7 However, doubts existed about its application to inorganic systems where the spin carriers were metal ions. For example, a dinuclear TiIII complex synthesized in the 1970s unexpectedly displayed moderate ferromagnetic exchange as a consequence of a spin polarisation mechanism of exchange. Although this was the very first example of an inorganic system exhibiting such behaviour, the result was largely ignored and remained unexploited for some time.8,9 Two decades later, the first magnetic systems with an operative McConnell mechanism containing paramagnetic metal ions were reported; these were “dinuclear” systems where one paramagnetic centre was a metal ion and the other an organic radical.10-12 In the early 1990s the first purely inorganic examples based on MoIII and CoII ions were reported.13-20 In the latter case, the nature of the magnetic coupling was nicely tuned
(ferromagnetic vs. antiferromagnetic) using diazine type ligands that provided π-exchange pathways with even or odd number of atoms. To this point all known inorganic systems were based on metal ions possessing magnetic t_{2g} orbitals interacting with a π-pathway. Metal complexes with magnetic e_{g} orbitals were not considered good candidates as they were assumed to promote spin delocalization. However, in 2001, this position was challenged when strong spin polarization between d\(^9\) Cu\(^{II}\) ions was observed,\(^{21}\) opening the door toward further research focusing on the study of magnetic communication across long intermetallic distances, and the application of these concepts in, for example, spintronics.\(^{22-26}\) In this paper, we have adapted this approach by employing pyrazine (pyz), pyrimidine (pym) and s-triazine (triz) ligands to examine the nature and magnitude of magnetic exchange between Re\(^{IV}\) ions (5d\(^3\) electronic configuration), leading to the first magneto-structural correlation of dinuclear [Re\(^{IV}\)\(_2\)] molecules of general formula (NBu\(_4\))\(_2\) [(Re\(_X\))\(_2\) (μ-L)] (L = pyz, X = Cl (1) or Br (2); L = pym, X = Br (3); L = s-triz, X = Br (4)).

**Experimental Section**

**Materials and methods**

All chemicals were used as received. Syntheses were carried out under aerobic conditions. (NBu\(_4\))\(_2\) [ReCl\(_6\)] and (NBu\(_4\))\(_2\) [ReBr\(_6\)] (NBu\(_4^+\) = tetra-n-butylammonium cation) were prepared as described previously.\(^{27,28}\) Crystals of 1-4 were collected and left open to air for use in further analysis. Elemental analyses (C, H, N) were performed by MEDAC Ltd. Direct current (dc) magnetic susceptibility measurements were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet in the temperature range 300-2.0 K. Diamagnetic corrections were applied using Pascal’s constants.\(^{29}\)

**Synthesis of (NBu\(_4\))\(_2\) [ReCl\(_5\)] (μ-pyz)] (1)**

(NBu\(_4\))\(_2\) [ReCl\(_5\)] (0.10 mmol, 88.0 mg) and pyrazine (0.20 mmol, 16.0 mg) in 4.5 cm\(^3\) of glacial acetic acid were stirred at 100 °C for 8 hours, after which the dark red solid which separated was collected by filtration. The solid was dissolved in dichloromethane (DCM) and layered with glacial acetic acid. Red crystals of 1 suitable for X-ray diffraction were collected after 3 days (yield ca. 17%). Elemental analysis (%) calculated (found) for C\(_{36}\)H\(_{76}\)Cl\(_{10}\)N\(_4\)Re\(_2\) (1): C, 33.5 (33.5); H, 5.9 (5.9); N, 4.3 (4.2).

**Synthesis of (NBu\(_4\))\(_2\) [ReBr\(_5\)] (μ-pyz)] (2)**

(NBu\(_4\))\(_2\) [ReBr\(_5\)] (0.10 mmol, 115.0 mg) and pyrazine (0.20 mmol, 16.0 mg) in 4.5 cm\(^3\) of glacial acetic acid were heated at 80 °C for 4 hours with stirring, and the resulting red solid was collected.
by filtration. It was dissolved in DCM and diffused with diethyl ether vapour. Brown single crystals of 2 were grown after 2 days (yield ca. 31%). Elemental analysis (%) calculated (found) for C_{36}H_{76}Br_{10}N_{4}Re_{2} (2): C, 24.9 (25.0); H, 4.4 (4.3); N, 3.2 (3.0).

*Synthesis of (NBu4)_2[(ReBr5)_2(μ-pym)] (3)*

(NBu4)_2[ReBr4] (0.10 mmol, 115.0 mg) and pyrimidine (0.20 mmol, 16 µl) were mixed in 4.5 cm³ of glacial acetic acid. The solution was stirred at 80 °C for 2 hours and the resulting precipitate was collected by filtration. It was dissolved in DCM and layered with isopropanol. X-ray quality crystals of 3 were collected after 3 days (yield ca. 13%). Elemental analysis (%) calculated (found) for C_{36}H_{76}Br_{10}N_{4}Re_{2} (3): C, 24.9 (25.0); H, 4.4 (4.3); N, 3.2 (3.1).

*Synthesis of (NBu4)_2[(ReBr5)_2(μ-triz)] (4)*

(NBu4)_2[ReBr6] (0.10 mmol, 115.0 mg) and s-triazine (0.20 mmol, 16.2 mg) in 4.5 cm³ of glacial acetic acid were stirred at 75 °C for 4 hours. The orange precipitate was collected by filtration. It was dissolved in DCM and layered with glacial acetic acid. After 2 days well shaped orange crystals suitable for X-ray diffraction were grown (yield ca. 19%). Elemental analysis (%) calculated (found) for C_{35}H_{75}Br_{10}N_{5}Re_{2} (4): C, 24.2 (24.3); H, 4.4 (4.3); N, 4 (3.8).

*Crystallography*

Data were measured on Rigaku Oxford Diffraction SuperNova (1, 2, 4) and Rigaku Oxford Diffraction XCalibur (3) X-ray diffractometers using Mo-Kα radiation. Structures were solved with olex2.solve (2, 3)³⁰ or ShelXS (1, 4)³¹ and refined by full-matrix least-squares on F-squared using ShelXL, interfaced through Olex2.³² All non-hydrogen atoms were refined anisotropically. Hydrogen atom parameters were constrained. For full details see Table S1. CCDC 1557650-1557653.

*Computational Details*

In order to estimate the nature and magnitude of the intramolecular magnetic exchange interactions in 1-4, calculations were performed with the Gaussian09 package using the CAM-B3LYP functional (a long range corrected version of B3LYP) and the quadratic convergence approach.³³-³⁷ Double-ζ and Los Alamos effective core potentials, as proposed by Hay and Wadt, were used for the Re⁵⁺, Cl⁻ and Br⁻ ions.³⁸-⁴⁰ Ahlrichs double-ζ basis set was used for the remaining atoms.⁴¹ Two-electron integrals and their derivatives were computed from Douglas-Kroll-Hess (DKH) 2nd order scalar relativistic calculations.⁴²,⁴³ An approach based on the use of broken-symmetry (BS) functions built from localized orbitals was used to evaluate the energies of
several spin states. The BS functions, which provide positive or negative spin densities on the paramagnetic centres, were obtained from the guess functions generated with the fragment tool implemented in Gaussian09. Intermolecular magnetic couplings for the shortest contacts were calculated from the experimental structures. Parameters corresponding to the acetonitrile solvent were included to simulate the electronic effects of the surrounding molecules. Calculations of the zero-field splitting (zfs) parameters were performed with version 3.0 of the ORCA program. The TZVP basis set proposed by Ahlrichs, and tight SCF criteria were used in all cases. Relativistic effects for the ReIV ions were introduced from a zero-order regular approximation (ZORA). For complete active space (CAS) calculations, this auxiliary basis set was replaced by TZV/C. Experimental geometries of 1 and 2 were used in the theoretical calculations. The zfs parameters were evaluated from Complete Active Space (CAS) and N-Electron Valence State Perturbation Theory (NEVPT2) calculations and an approach based on an 2nd order Hamiltonian for the spin-orbit coupling. This zfs calculation included contributions from ten quartet and twenty doublet states generated from electron promotion between d orbitals, which corresponds to the full active space built from only the five d orbitals of the ReIV ion.

Results and discussion

Description of the crystal structures of 1-4

Complex 1 crystallises in the monoclinic space group $P2_1\overline{1}c$ and its structure consists of tetrabutylammonium cations and the dinuclear $[(\text{ReCl}_5)(\mu-\text{pyz})]^2$ complex anion (Figure 1a). Each ReIV ion is six-coordinate with five chloride ions and a nitrogen atom from the pyrazine ligand building a slightly distorted octahedral surrounding. The Re–Cl bond lengths vary in the range 2.3006(8)–2.3552(8) Å, and the Re(1)–N(1) and Re(2)–N(2) bond lengths are 2.180(2) and 2.175(2) Å, respectively (Table S2). The intramolecular Re···Re separation is 7.1354(3) Å, with the pyrazine ligand twisted out of the Re$_2$Cl$_6$ plane by approximately 45°. The ReIV ions are positioned out of the equatorial Cl$_4$ plane away from the pyrazine ligand by 0.1186(4) Å for Re(1) and 0.1207(4) Å for Re(2). The structural parameters of the ReIV ions are similar to those published for the $[\text{ReCl}_5(\text{pyz})]^+$ monomer, and the C–C and C–N bond lengths of the pyrazine ligand agree with previously published results. Each $[(\text{ReCl}_5)(\mu-\text{pyz})]^2$ unit is well isolated from adjacent anions by the bulky NBu$_4^+$ cations as shown in the crystal packing (Figure S1). The organic cations pack around the complex anions through numerous C–H···Cl type interactions, with the shortest intermolecular Cl···Cl and Re···Re distances being 4.6976(11) and 8.3503(3) Å, respectively (Table S3).
Figure 1. The structures of 1-4 (a-d). Colour code: Re, cyan; Br, brown; Cl, green; C, grey; N, blue; H, white.

Compound 2 crystallises in the monoclinic space group $P2_1/n$ (Table S1). The asymmetric unit contains half the $\{[\text{ReBr}_5]\mu-$pyz$\}_2^\text{2-}$ complex anion and one NBu$_4^+$ cation, due to the presence of an inversion centre which is positioned at the centroid of the pyrazine ligand (Figure 1b). Each Re$^{\text{IV}}$ ion is coordinated to five bromide ions and a nitrogen atom from the pyrazine ligand. The Re–Br bond lengths range from 2.4489(6) to 2.4953(6) Å, with the Re–N bond being 2.196(4) Å (Table S2). The pyrazine moiety is disordered over two positions with the plane of the ligand twisted with respect to the Re$_2$Br$_6$ plane at inter-plane angles of 40 and 44°. The Re$^{\text{IV}}$ ion is displaced out of the equatorial Br$_4$ plane away from the pyrazine ligand by 0.1148(4) Å. The geometrical parameters for the Re$^{\text{IV}}$ ion agree with those in the previously published species NBu$_4[\text{ReBr}_5(\text{Hpyzc})]$ (Hpyzc = 2-pyrazinecarboxylic acid)$^{57}$ The intradimer Re···Re separation is 7.1723(4) Å. The NBu$_4^+$ cations in the crystal lattice pack around the complex anions, connected via numerous C-H···Br type interactions. Short Br···Br contacts occur between the complex anions, the shortest distance being 3.5202(9) Å [Br(2)···Br(2)'] creating a 1D network of complex anions interacting in an end-to-end fashion along the crystallographic $\alpha$-axis (Figure S2). This causes the shortest intermolecular Re···Re distance to be 8.4862(5) Å.

Complex 3 crystallises in the monoclinic space group $P2_1$ with the asymmetric unit containing two (NBu$_4$)$_2\{[\text{ReBr}_5]_2(\mu-$pym$)\}$ complexes. The two $\{[\text{ReBr}_5]_2(\mu-$pym$)\}_2^\text{2-}$ anions display near identical coordination geometries, with the first coordination sphere of the Re$^{\text{IV}}$ ions similar to that described for 2 (Figure 1c and Table S2). The values of the C–C and C–N bond lengths of the bridging pyrimidine ligand agree with those of previously published structures containing this
ligand. The two Re IV ions are disposed at an angle of approximately 118° with respect to the centre of the pyrimidine moiety, with the organic ligand positioned equidistant between the two perpendicular [ReCl₄] planes. The intradimer Re···Re distance is ca. 6.1 Å, with the shortest intramolecular Br···Br contact being 4.006(2) Å (Br(12)···Br(18)) (Table S3). Numerous C-H···Br type interactions are present between the complex anions and organic cations in the crystal lattice, causing each [[ReBr₅]₂(µ-pym)]²⁻ moiety to be well isolated from the neighbouring ones - the shortest intermolecular Br···Br contact being 4.707(2) Å (Figure S3).

Complex 4 crystallises in the monoclinic space group I2/a. The asymmetric unit contains one NBu₄⁺ cation and half a [[ReBr₅]₂(µ-triz)]²⁻ anion, due to a two-fold rotation axis intersecting the C(2) and N(2) atoms on the s-triazine ligand. The Re IV ion sits in a coordination sphere similar to the one described for complex 2 (Figure 1d and Table S2). The triazine molecule contains C–C and C–N bond lengths which correlate well to previously published results describing this ligand bridging two metal ions. In the [[ReBr₅]₂(µ-triz)]²⁻ unit the two Re IV ions are placed at angle of 121.91(4)° with respect to the triazine centroid, at a distance of 6.2390(4) Å. The shortest intramolecular Br···Br contact is 4.5249(4) Å [Br(2)···Br(3)'] (Table S3). The organic ligand is again positioned equidistant between the two approximately perpendicular [ReBr₄] planes. The complex anions in the crystal packing interact through short Br···Br interactions [Br(5)···Br(5)’ = 3.4304(4) Å] between neighbouring [[ReBr₅]₂(µ-triz)]²⁻ units (Figure S4). The shortest intermolecular Re···Re distance is 8.4090(3) Å.

Magnetic behaviour of 1-4

The magnetic behaviour of complexes 1-4 in the form of χM vs. T plots are shown in Figures 2-5 (χM being the molar magnetic susceptibility per two Re IV ions). The χM values at room temperature (2.68-3.36 cm³ mol⁻¹ K) are close to that expected for two S = 3/2 spin centres with g = 1.7-1.9. On cooling, the value of χM continuously decreases for 1 and 2, approaching zero at the lowest temperatures measured, accompanied by the appearance of a maximum in χM at ~45 K. This is suggestive of the presence of antiferromagnetic exchange between the metal ions, in concert with the large zero-field splitting [defined by the axial (D) and rhombic (E) components] expected for a Re IV ion (Figures 2 and 3). In contrast, the χM values for complexes 3 and 4 (Figures 4 and 5) increase slowly with decreasing temperature until approximately 30 K, before collapsing at lower temperatures. The behaviour in the high temperature region is indicative of ferromagnetic exchange between the Re IV ions and that at lower temperatures is potentially ascribed to zfs effects and/or antiferromagnetic intermolecular exchange interactions.
Figure 2. Thermal dependence of $\chi_M T$ (○) and $\chi_M$ (●) under an applied dc field of 0.1 T for 1. The solid line is the best-fit curve (see text).

Figure 3. Thermal dependence of $\chi_M T$ (○) and $\chi_M$ (●) under an applied dc field of 0.1 T for 2. The solid line is the best-fit curve (see text).

Figure 4. Thermal dependence of $\chi_M T$ (○) under an applied dc field of 0.1 T for 3. The solid line is the best-fit curve (see text).
Simulations based on a simple model can be used to help in the deconvolution of all the potential contributions to the magnetic data, providing a qualitative initial view of how different physical phenomenon contribute. These simulations, through spin-Hamiltonian (1) and shown in Figure 6, are based on two $S = 3/2$ ions and include both exchange ($J$) and axial zfs ($D$) parameters possessing a variety of signs and magnitudes. The local zfs tensors have been considered collinear in all cases. In this model the sign of $D$ has no effect on the thermal dependence of the magnetic susceptibility in the lack of magnetic exchange, and it is almost negligible in the case of antiferromagnetic exchange. When $J$ is positive and $D$ is non-zero a decrease in the $\chi_m T$ product is observed at low temperatures for both positive and negative values of $D$. Given the large intermolecular distances observed in the extended structures of 3 and 4, the decrease in $\chi_m T$ below 30 K for both is initially attributed to zfs effects (vide infra), but the simulations cannot distinguish between local positive and negative $D$ values (for $T > 5$ K).

$$H = \sum_{i=1}^{2} \gamma Re B \beta S_i + D[(S_i^x)^2 - S_i (S_i + 1)/3] + E \left[\left(S_i^x\right)^2 - \left(S_i^y\right)^2\right] - J S_i S_2 \quad (1)$$
In certain Re\textsuperscript{IV} complexes non-zero/non-negligible intermolecular magnetic exchange interactions can be observed, because of the presence of large spin densities on the coordinated ligands, originating from $\pi$-spin delocalization from the $t_{2g}$ magnetic orbitals. This is particularly evident when there are chloride or bromide anions as ligands.\textsuperscript{60} These interactions can be avoided by isolating the metal complexes from each other through the use of bulky counter ions, as done here. In order to check that intermolecular interactions do not play a prominent role in the low temperature magnetic behaviour of complexes 1-4, we performed DFT calculations to estimate their magnitude through the shortest X···X contacts ($X = \text{Cl or Br}$). A summary of these results is given in Table 1. It is clear from this Table that the intermolecular exchange interactions are very small for 2 and 4 and negligible for 1 and 3.
Table 1. Shortest $X\cdots X$ intermolecular contacts between neighbouring complex dianions in 1-4 together with their corresponding calculated magnetic coupling constants ($J$).

| Compound | $d(X\cdots X)$ / Å | $J$ / cm$^{-1}$ |
|----------|---------------------|-----------------|
| 1        | 4.695               | -0.04           |
| 2        | 3.520               | -0.23           |
| 3        | 4.705               | -0.007          |
| 4        | 3.430               | -0.55           |

In a spin-polarization mechanism the number of intervening atoms should dictate the nature of the magnetic exchange. Thus odd and even numbers of atoms favour ferromagnetic (F) and antiferromagnetic (AF) interactions, respectively. Hence, while the pyrazine ligand in 1 and 2 should mediate AF coupling, the pyrimidine and triazine ligands in 3 and 4 should promote F interactions. DFT calculations, summarised in Table 2, support this hypothesis. The spin density maps obtained for the broken-symmetry function corresponding to the spin ground states of 1-4 are shown in Figure 7. The alternation between the spin densities on contiguous atoms onto the $\pi$-pathway is clear, and is suggestive of the presence of an operative McConnell mechanism.

However, the position of the two adjacent bromide ions in 3 and 4 (Figure 1c, 1d; Figure 7, middle and bottom) result in a short intramolecular Br···Br contact (~4 Å) that could potentially offer an alternative (dipolar) pathway for magnetic exchange. In order to check this, two models were built to estimate the contribution through bonds and space, aimed at determining unambiguously the mechanism that governs the magnetic coupling in 3 and 4 (Table 2). The bromide ions mediating the alternative pathway in Model A were removed, and the diazine ligands in Model B were removed. Such a semi-quantitative/quantitative approach, based on a change in the coordination sphere, is valid here because the electronic configuration of three unpaired electrons in the $t_{2g}$ orbitals for the Re$^{IV}$ ions is maintained. The results show that only the diazine ligand is able to mediate ferromagnetic exchange.
Table 2. Magnetic coupling constants ($J$) in the Re$^{IV}_2$ moieties calculated for 1-4 and for the simplified models described in the text, each containing just one of the possible exchange pathways (diazone, Model A; Br, Model B). Two results are supplied for 3 because of the presence of two crystallographically independent Re$^{IV}_2$ molecules in the structure.

| System | $J$ / cm$^{-1}$ | $J$, Model A / cm$^{-1}$ | $J$, Model B / cm$^{-1}$ |
|--------|----------------|--------------------------|--------------------------|
| 1      | -10.1          |                          |                          |
| 2      | -8.9           |                          |                          |
| 3a     | +2.7           | +5.4                     | -0.4                     |
| 3b     | +1.9           | +4.6                     | -0.6                     |
| 4      | +3.0           | +4.4                     | -0.1                     |

Figure 7. Spin density plots for the ground spin states in (representative) 1, 3 and 4a. The isodensity surfaces correspond to a cut-off value of 0.002 e bohr$^{-3}$. Blue and magenta isosurfaces represent positive and negative regions of spin density, respectively.
Re$^{IV}$ ions present large zero-field splitting (zfs), which results in the separation of the $M_z$ states of the $S = 3/2$ spin state. The magnitude of the parameters defining this physical phenomenon ($D$ and $E$, the axial and rhombic components) directly depend on the molecular geometry and on the nature of the ligands that make up the coordination sphere of the metal ion. This can lead to additional complications in the interpretation of experimental and theoretical data. Fortunately, theoretical post-Hartree-Fock methods based on a Complete Active Space (CAS), that are more advanced than N-Electron Valence State Perturbation Theory (NEVPT2), have been previously used to a satisfactory level for the evaluation of the parameters that govern the zfs in Re$^{IV}$ complexes. Theoretical results calculated on the mononuclear models are given in Table 3. These models were built by (a) removing one of the Re$^{IV}$ ions together with its ligands, or (b) by replacing the Re$^{IV}$ ion with a Pb$^{IV}$ ion. In general, the sign and magnitude of the calculated values of $D$ fall within a small range of values, and only small discrepancies in the $E$ values are observed. Most cases point towards negative $D$ values, i.e. states with higher $|M_z|$ values are stabilised, and they are in the range -5 to -15 cm$^{-1}$, the majority being placed around -10 cm$^{-1}$. This variation highlights the strong dependence of $D$ on small changes in geometry.

Replacing the chloride ligands in 1 by bromide ions in 2-4 also has an effect on $|D|$. The impact is even observed in 3, where the same compound exists in two non-equivalent dinuclear units (3a and 3b), and where there is no inversion symmetry (1 and 3). Calculations were also performed on models where one of the Re$^{IV}$ ions has been replaced by a Pb$^{IV}$ ion, in order to minimize other electronic effects. The results show that both Re$^{IV}$ and Re$^{IV}$-Pb$^{IV}$ models provide the same (or very close), $D$ values in all cases (Table 3).

With the theoretical study in mind, we modelled the experimental magnetic data with spin-Hamiltonian (1) in which the only variable parameters were the $g$-factor, $J$ and $D$. Least-squares best-fit parameters obtained for 1-4 are shown as solid lines in Figures 2-5, and are summarized in Table 4. The results agree well with those proposed in the theoretical study, although the magnitude of the experimental magnetic coupling is somewhat greater than those calculated from theory. Despite a negative $D$ value being expected for 4, the sharp drop in $\chi_M T$ at low temperature can be reproduced only with positive values. This discrepancy is related to the simplistic nature of our model. In a model that considers collinear local zfs tensors, a positive $D$ value for the ferromagnetic $S = 3$ ground state can only be achieved from positive local $D$ values. This approach causes no problem in 1 and 2 because their local zfs tensors are parallel or near parallel (Figure 8). However, this is not the case in 3 and 4 where the $z$-axes of the local zfs tensors are almost perpendicular (Figure 8). In the ferromagnetic state, they therefore conform to an easy-magnetization plane, i.e., the $D$ parameter takes a positive value (Figure 9). A more
detailed/rigorous analysis of the magnetic data would demand the inclusion of the relative orientation of the local zfs tensors, but it would likely over-parameterize our model.

**Table 3.** Axial ($D$) and rhombic (as $E/D$ ratio) zfs parameters calculated on the models described in the text. The Re(i) notation is used to describe the mononuclear models and the i index indicates the number of Re centre. RePb and PbRe labels are used to describe the dinuclear model equivalent to Re(1) and Re(2), respectively. The identifications $a$ and $b$ are used to differentiate between the Re$_2$ units that coexist in 3.

| Compound | Model | CAS | NEVPT2 |
|----------|-------|-----|--------|
|          |       | $D$ / cm$^{-1}$ | $E/D$ | $D$ / cm$^{-1}$ | $E/D$ |
| 1        | Re(1) | -10.0 | 0.173 | -10.0 | 0.215 |
|          | RePb  | -10.3 | 0.176 | -10.2 | 0.208 |
|          | Re(2) | -5.1  | 0.082 | -4.1  | 0.205 |
|          | PbRe  | -5.6  | 0.066 | -4.5  | 0.181 |
| 2        | Re(1) | -6.6  | 0.247 | -6.3  | 0.292 |
|          | RePb  | -7.7  | 0.207 | -7.3  | 0.260 |
| 3        | Re(1)$_a$ | -7.5 | 0.183 | -9.4  | 0.110 |
|          | RePb$_a$ | -7.7 | 0.311 | -9.3  | 0.243 |
|          | Re(2)$_a$ | -15.7 | 0.201 | -17.4 | 0.184 |
|          | PbRe$_a$ | -18.0 | 0.148 | -19.9 | 0.135 |
|          | Re(1)$_b$ | -11.4 | 0.192 | -13.1 | 0.164 |
|          | RePb$_b$ | -11.0 | 0.280 | -12.7 | 0.247 |
|          | Re(2)$_b$ | -8.7  | 0.138 | -9.6  | 0.165 |
|          | PbRe$_b$ | -11.5 | 0.170 | -12.6 | 0.191 |
| 4        | Re(1) | -10.6 | 0.184 | -11.6 | 0.193 |
|          | RePb  | -12.6 | 0.184 | -13.8 | 0.199 |
Table 4. Best-fit parameters obtained with spin Hamiltonian (1) and the thermal dependence of $\chi_M T$ for 1-4. $F$ is the agreement factor defined as $F = \frac{\sum[(\chi_M T)_{exp}^2 - (\chi_M T)_{calc}^2]}{\sum(\chi_M T)_{exp}^2}$. Compound 4 required the inclusion of a small intermolecular interaction, $\theta$.

| Compound | g(Re)        | D(Re) / cm$^{-1}$ | J / cm$^{-1}$ | $\theta$ / K | $F \times 10^5$ |
|----------|--------------|-------------------|---------------|--------------|----------------|
| 1        | 1.819 ± 0.007 | -8.9 ± 0.6        | -20.22 ± 0.15 | ---          | 6.8            |
| 2        | 1.883 ± 0.004 | -7.4 ± 0.3        | -19.08 ± 0.08 | ---          | 3.0            |
| 3        | 1.855 ± 0.003 | +10.90 ± 0.16     | 0.77 ± 0.03   | ---          | 0.4            |
| 4        | 1.87 ± 0.04   | +21 ± 3           | +6.7 ± 1.2    | -0.14 ± 0.08 | 10             |
**Figure 8.** Relative orientation of the z-axes (magenta sticks) of the local zfs tensors of Re$^{\text{V}}$ ions in 1 (a), 2 (b), 3a (c) and 4 (d) obtained by CAS calculations. Hydrogen atoms are omitted for clarity. Colour code: purple (rhenium), blue (nitrogen), green (chlorine), brown (bromine) and grey (carbon).
Conclusions

A family of dirhenium(IV) complexes has been prepared by reaction between $[\text{ReX}_6]^2-$ ($X = \text{Cl}$ and $\text{Br}$) building blocks and the bidentate N-donors pyz (1 and 2), pym (3) and s-triz (4). Coupled variable-temperature magnetic measurements and theoretical calculations on the structurally characterised compounds established that a spin polarization mechanism governs the intramolecular magnetic exchange interactions in all four complexes. These are antiferromagnetic for an even number of intervening atoms in the exchange pathway, i.e. for the bridging pyz molecule in 1 and 2, and ferromagnetic for an odd number of intervening atoms in the exchange pathway, i.e. the bridging pym (3) and triz ligands (4).

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