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# Hexakis(diethylacetamide)iron(II) hexahalorhenate(IV) ionic salts: X-ray structures and magnetic properties

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## Abstract

Two novel Fe<sup>II</sup>-Re<sup>IV</sup> compounds of general formula [Fe<sup>II</sup>(DEA)<sub>6</sub>][Re<sup>IV</sup>X<sub>6</sub>] where DEA = diethylacetamide and X = Cl (**1**) and Br (**2**) have been prepared and magnetostructurally characterised. Complexes **1** and **2** are isomorphous ionic salts that crystallise in the trigonal crystal system with space group *R*(-3). The rhenium(IV) ion in **1** and **2** is six-coordinate with six chloro (**1**) or bromo (**2**) ligands building a regular octahedral chromophore. The Fe<sup>II</sup> ion is also six-coordinate, and bonded to six oxygen atoms from six DEA molecules. [Fe<sup>II</sup>(DEA)<sub>6</sub>]<sup>2+</sup> cations and [Re<sup>IV</sup>X<sub>6</sub>]<sup>2-</sup> anions alternate in the crystal lattice of **1** and **2** generating supramolecular structures whose magnetic properties are dominated by the high anisotropy of the six-coordinate iron(II) and rhenium(IV) ions. Variable-temperature magnetic susceptibility data of **1** and **2** are well reproduced by a model of isolated *S* = 2 (Fe<sup>II</sup>) and *S* = 3/2 (Re<sup>IV</sup>) centres with high values of the local zero-field splitting. **1** and **2** are the first examples of hexahalorhenate(IV) salts incorporating Fe<sup>II</sup> complex cations to have been magnetostructurally investigated.

*Keywords:* Rhenium(IV) complexes; Iron(II) complexes; X-ray diffraction; Magnetic properties

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## 1. Introduction

Magnetic systems based on hexahalorhenate(IV) salts, [ReX<sub>6</sub>]<sup>2-</sup> (X = F, Cl, Br and I), have been thoroughly investigated for decades in the field of molecule-based magnetism, the different magnetic properties they exhibit being at the origin of this interest [1-8]. In addition to their intrinsic value, they have been used as starting materials to prepare stable Re<sup>IV</sup>-based metalloligands containing potential bridging ligands such as oxalate or malonate which in turn have been employed to construct a wide family of tailor-made homometallic complexes [6]. Re<sup>IV</sup> is a 5d<sup>3</sup> ion with a ground electronic state <sup>4</sup>A<sub>2g</sub>, with three unpaired electrons (t<sub>2g</sub><sup>3</sup>

configuration), and its high value of the spin-orbit coupling constant ( $\lambda \sim 1000 \text{ cm}^{-1}$  for the free ion) accounts for the high magnetic anisotropy that  $\text{Re}^{\text{IV}}$  compounds exhibit [9].

Polarized neutron diffraction studies and density functional theory calculations performed on  $\text{Re}^{\text{IV}}$  systems have revealed a strong spin delocalization from the  $\text{Re}^{\text{IV}}$  centre onto the peripheral atoms of the ligands of its complexes [10-13]. This fact accounts for the significant intermolecular magnetic interactions existing between spin densities on neighbouring molecules, which are generally mediated through  $\text{Re-X}\cdots\text{X-Re}$  contacts ( $\text{X} =$  halogen atom) in the crystal lattice of these systems [6]. Hexahalorhenate(IV) salts of diamagnetic univalent cations, such as  $\text{Ag}^{\text{I}}$  and alkaline metal ions, show significant antiferromagnetic interactions, which are transmitted through these intermolecular  $\text{Re-X}\cdots\text{X-Re}$  pathways [14,15]. Remarkably, magnetic ordering due to spin canting was observed below 24 K in the case of the compound  $\text{K}_2[\text{ReI}_6]$  [15], demonstrating the efficiency and strength of these through-space exchange interactions.

These intermolecular contacts can be minimized or even avoided by using bulky organic cations such as tetraphenylarsonium ( $\text{AsPh}_4^+$ ) and tetra-*n*-butylammonium ( $\text{NBu}_4^+$ ), the magnetic behaviour observed in these circumstances being due to the local anisotropy of the magnetically isolated  $\text{Re}^{\text{IV}}$  compounds [6]. In contrast, the use of paramagnetic centres as countercations has provided new insights into the magnetic properties of this family of materials. Antiferromagnetic interactions have been observed in hexachlororhenate(IV) salts with organic radicals and the ruthenium(III) complexes  $[\text{RuCl}(\text{NH}_3)_5]^{2+}$  and  $[\text{RuCl}_2(\text{en})_2]^+$  as countercations [16,17], these last  $\text{Re}^{\text{IV}}\text{-Ru}^{\text{III}}$  mixed salts being examples of spin canted antiferromagnets [17]. Finally, a magneto-structural study of a family of hexahalorhenate(IV) salts with organometallic ferrocenium and decamethylferrocenium countercations of general formulae  $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{ReX}_6]$  and  $[\text{Fe}(\text{C}_5\text{Me}_5)_2]_2[\text{ReX}_6]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ) revealed the presence of antiferromagnetic interactions between the anions, whereas ferromagnetic coupling between cations and anions is the dominant interaction in the compound  $[\text{Fe}(\text{C}_5\text{H}_5)_2]_2[\text{ReI}_6]$  [18].

Having in mind the significant anisotropy of the six-coordinate iron(II) ion, we envisaged the possibility of preparing mixed  $\text{Fe}^{\text{II}}\text{-Re}^{\text{IV}}$  systems where high local anisotropy and significant magnetic exchange interactions would coexist. Our first attempts have produced heterobimetallic compounds of general formula  $[\text{Fe}^{\text{II}}(\text{DEA})_6][\text{Re}^{\text{IV}}\text{X}_6]$  where DEA

= diethylacetamide and X = Cl (**1**) and Br (**2**). **1** and **2** are the first examples of hexahalorhenate(IV) salts incorporating Fe<sup>II</sup>-based cations. The present work discusses their preparation, structures and magnetic behaviour.

## 2. Experimental

### 2.1. Materials

All manipulations were performed under aerobic conditions, using chemicals as received. The Re<sup>IV</sup> precursors, (NBu<sub>4</sub>)<sub>2</sub>[ReCl<sub>6</sub>] and (NBu<sub>4</sub>)<sub>2</sub>[ReBr<sub>6</sub>], were prepared following literature procedures [19].

### 2.2. Synthesis

#### 2.2.1. [Fe(DEA)<sub>6</sub>][ReCl<sub>6</sub>] (**1**)

Compound **1** was prepared by means of slow diffusion in an H-shaped tube. (NBu<sub>4</sub>)<sub>2</sub>[ReCl<sub>6</sub>] (50.0 mg, 0.06 mmol) dissolved in 2 mL diethylacetamide (DEA) was placed in one arm, and Fe(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (20.5 mg, 0.06 mmol) dissolved in the same solvent (1 mL) was introduced into the other arm. The tube was filled by adding DEA to both arms. Diffusion at room temperature lead to the isolation of X-ray quality pale green crystals of **1** in the bridge of the tube after two weeks. Yield: *ca.* 38%. Found: C, 38.0; H, 6.8; N, 7.7. Calc. for C<sub>36</sub>H<sub>78</sub>N<sub>6</sub>O<sub>6</sub>Cl<sub>6</sub>FeRe (**1**): C, 37.7; H, 6.9; N, 7.3%. IR (KBr pellets/cm<sup>-1</sup>): bands assigned to the DEA ligand appear at 2987 (m), 2964 (s), 2929 (m), 2872 (m), 1609 (vs), 1495 (s), 1453 (s), 1433 (m), 1361 (m), 1312 (m), 1287 (m), 1218 (m), 1168 (w), 1094 (m), 1075 (m), 1038 (m), 998 (w), 951 (m), 919 (w), 793 (w), 710 (w), 622 (m), 590 (m), 498 (w), 460 (m).

#### 2.2.1. [Fe(DEA)<sub>6</sub>][ReBr<sub>6</sub>] (**2**)

Compound **2** was prepared as for **1** but using (NBu<sub>4</sub>)<sub>2</sub>[ReBr<sub>6</sub>] (69.0 mg, 0.06 mmol) dissolved in 2 mL of an acetonitrile-DEA (1:1, v/v) mixture. Yield: *ca.* 53%. Found: C, 30.9; H, 5.8; N, 5.7. Calc. for C<sub>36</sub>H<sub>78</sub>N<sub>6</sub>O<sub>6</sub>Br<sub>6</sub>FeRe (**2**): C, 30.6; H, 5.6; N, 6.0%. IR (KBr pellets/cm<sup>-1</sup>): bands associated to the DEA ligand appear at 2988 (m), 2965 (s), 2930 (m), 2872 (m), 1608 (vs), 1494 (s), 1455 (s), 1432 (m), 1360 (m), 1310 (m), 1288 (m), 1218 (m),

1169 (w), 1095 (m), 1075 (m), 1037 (m), 1000 (w), 952 (m), 920 (w), 795 (w), 710 (w), 620 (m), 592 (m), 495 (w), 458 (m).

### 2.3. Physical measurements

Elemental analyses (C, H, N) were carried out on a CE Instruments EA 1110 CHNS analyzer, and a 1:1 Fe/Re molar ratio was determined for both compounds (**1** and **2**) through a Philips XL-30 scanning electron microscope equipped with an X-ray microanalysis system from the Central Service for the Support to Experimental Research of the University of Valencia. Infrared spectra of **1** and **2** were recorded on a PerkinElmer Spectrum 65 FT-IR spectrometer in the 4000-450 cm<sup>-1</sup> region. Variable-temperature, solid state direct current (dc) magnetic susceptibility data down to 1.9 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities by using Pascal's constants [20,21].

### 2.4. Crystallographic data collection and structure determination

X-ray diffraction data of single crystals of dimensions 0.18 x 0.16 x 0.12 (**1**) and 0.61 x 0.25 x 0.18 mm<sup>3</sup> (**2**) were collected on a Bruker-Nonius X8APEXII CCD area detector diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Crystal parameters and refinement results for **1** and **2** are summarized in Table 1. The structures of **1** and **2** were solved by Patterson methods and subsequently completed by Fourier recycling using SHELXTL [22-24]. The final full-matrix least squares refinements based on  $F^2$ , minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , reached convergence with the values of the discrepancy indices given in Table 1. The graphical manipulations were performed with DIAMOND [25].

## 3. Results and discussion

### 3.1. Crystal structure of [Fe(DEA)<sub>6</sub>][ReCl<sub>6</sub>] (**1**) and [Fe(DEA)<sub>6</sub>][ReBr<sub>6</sub>] (**2**)

Compounds **1** and **2** crystallise in the space group  $R(-3)$  of the trigonal crystal system (Table 1). Their structures are made up of [Fe(DEA)<sub>6</sub>]<sup>2+</sup> cations (**1** and **2**) and [ReCl<sub>6</sub>]<sup>2-</sup> (**1**)/[ReBr<sub>6</sub>]<sup>2-</sup> (**2**) anions which are held together by electrostatic forces. A halide ion and a

DEA molecule are present in the asymmetric unit of **1** and **2**, the rhenium(IV) and iron(II) cations being located on special positions (Figures 1 and S1).

Each  $\text{Re}^{\text{IV}}$  ion is six-coordinate and bonded to six chloro (**1**)/bromo (**2**) ions in a regular octahedral geometry. The Re-X bond lengths [2.361(1) (**1**) and 2.509(1) Å (**2**)] are in agreement with those of previously reported compounds containing  $[\text{ReCl}_6]^{2-}$  and  $[\text{ReBr}_6]^{2-}$  units [6].

The  $\text{Fe}^{\text{II}}$  ion in **1** and **2** is six-coordinate and bonded to six oxygen atoms from six DEA molecules in a distorted octahedral geometry. No significant differences were found in the values of the Fe-O bond lengths [the Fe-O(1) distances being 2.100(1) (**1**) and 2.104(2) Å (**2**)] and the O-Fe-O bond angles [values covering the range 85.3(1)-180.0(1)°]. The C-C, C-O, and C-N bond distances of the DEA ligand exhibit the expected values for this molecule when coordinated to an  $\text{Fe}^{\text{II}}$  ion (see Table 2) [26].

The  $[\text{ReX}_6]^{2-}$  and  $[\text{Fe}(\text{DEA})_6]^{2+}$  units in **1** and **2** are intercalated forming anionic and cationic layers, respectively (see Figures 2, S2 and S3). The shortest interionic Re-X $\cdots$ X-Re contacts are quite long, being 7.251(1) (**1**) and 7.273(1) Å (**2**), and the nearest intermetallic Fe $\cdots$ Fe and Re $\cdots$ Re distances show the same value in the lattice of each compound [the Fe $\cdots$ Fe and Re $\cdots$ Re separations are 10.809(1) (**1**) and 10.987(1) Å (**2**)]. The shortest Fe $\cdots$ Re distance is somewhat shorter in **1** than in **2** [8.481(1) (**1**) and 8.586(1) Å (**2**)]. These structural data account for the magnetic isolation of  $\text{Re}^{\text{IV}}$  and  $\text{Fe}^{\text{II}}$  centres in **1** and **2** (see below).

A projection of the crystal packing along the *c* axis shows a different orientation of the CH<sub>3</sub>-CH<sub>2</sub>- fragments [anticlockwise (**1**) vs. clockwise (**2**)] of the DEA molecules in the  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations in **1** and **2** (Figures 3 and 4). Interestingly, each  $[\text{ReX}_6]^{2-}$  anion interacts with six  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations *via* weak X $\cdots$ H-C type contacts in **1** and **2**, the  $[\text{ReX}_6]^{2-}$  anion occupying a cationic cavity of diameter ca. 9.9 (**1**)/10.3 (**2**) Å (see Figure 4).

### 3.2. Magnetic properties

Dc magnetic susceptibility measurements were carried out on microcrystalline samples of **1** and **2** in the 1.9-300 K temperature range, under external magnetic fields of 0.1 T (at  $T > 30$  K) and 0.025 T (at  $T < 30$  K). The  $\chi_{\text{M}}T$  vs.  $T$  plots of **1** and **2** are given in Figures 5 and 6, respectively. At room temperature, the values of  $\chi_{\text{M}}T$  are 5.14 (**1**) and 5.15 cm<sup>3</sup> mol<sup>-1</sup> K (**2**), as expected for a pair of magnetically isolated high-spin  $\text{Fe}^{\text{II}}$  (3d<sup>6</sup>,  $S = 2$  with  $g = 2.2$ )

and  $\text{Re}^{\text{IV}}$  ( $5d^3$ ,  $S = 3/2$  with  $g = 1.8$ ) ions [14-18]. Upon cooling, the values of  $\chi_{\text{M}}T$  decrease very slowly until *ca.* 100 K, and then more abruptly to reach values of 3.14 (**1**) and 3.06  $\text{cm}^3 \text{mol}^{-1} \text{K}$  (**2**) at 1.9 K (Figs. 5 and 6). No maximum of the susceptibility is observed in either case.

Given the isolation of the paramagnetic centres in **1** and **2** (see above), the decrease of  $\chi_{\text{M}}T$  can likely be attributed to the local anisotropy (zero-field splitting effects) of the  $\text{Fe}^{\text{II}}$  and  $\text{Re}^{\text{IV}}$  metal ions [27]. Consequently, the analysis of the magnetic susceptibility data of **1** and **2**, has been performed through the spin Hamiltonian of eq(1)

$$\hat{H} = \hat{H}_{\text{zfs}} + \hat{H}_{\text{Zeeman}} \quad (1)$$

$$\hat{H}_{\text{zfs}} = D_{\text{Fe}}\hat{S}_Z^2 + D_{\text{Re}}\hat{S}_Z^2$$

$$\hat{H}_{\text{Zeeman}} = g_{\text{Fe}}\beta H \hat{S}_Z^{\text{Fe}} + g_{\text{Re}}\beta H \hat{S}_Z^{\text{Re}}$$

where  $D_{\text{Fe}}$  and  $D_{\text{Re}}$  are the zfs of the  $\text{Fe}^{\text{II}}$  and  $\text{Re}^{\text{IV}}$  ions, respectively, and the last term in eq(1) accounts for the Zeeman effects.

In order to avoid overparameterisation, we have assumed that  $g = g_{\parallel} = g_{\perp}$  for the  $\text{Fe}^{\text{II}}$  and  $\text{Re}^{\text{IV}}$  ions. Best least-squares fits of the experimental data in the 4-300 K temperature range afforded the parameters:  $g_{\text{Fe}} = 2.21$ ,  $g_{\text{Re}} = 1.82$ ,  $|D_{\text{Fe}}| = 11.7 \text{ cm}^{-1}$  and  $|D_{\text{Re}}| = 21.8 \text{ cm}^{-1}$  with  $R = 1.1 \times 10^{-5}$  for **1**, and  $g_{\text{Fe}} = 2.20$ ,  $g_{\text{Re}} = 1.89$ ,  $|D_{\text{Fe}}| = 11.3 \text{ cm}^{-1}$  and  $|D_{\text{Re}}| = 15.4 \text{ cm}^{-1}$  with  $R = 4.1 \times 10^{-5}$  for **2** ( $R$  is the agreement factor defined as  $\sum i [(\chi_{\text{M}}T)_{\text{obs}}(i) - (\chi_{\text{M}}T)_{\text{calc}}(i)]^2 / \sum i [(\chi_{\text{M}}T)_{\text{obs}}(i)]^2$ ). The theoretical curves (red solid lines in Figs. 5 and 6) match the experimental data very well in the explored temperature range. The values of  $g$  and  $D$  found for the metal ions are in agreement with those previously reported for compounds based on the  $[\text{Re}^{\text{IV}}\text{X}_6]^{2-}$  anions [6], and for mononuclear  $\text{Fe}^{\text{II}}$  complexes exhibiting a similar distorted  $\{\text{FeO}_6\}$  octahedral geometry [27]. This distorted geometry is mainly due to the small value  $[85.3(1)^\circ]$  of some of the O-Fe-O angles present in the  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations (Figure S4), these angles being very close to those found in  $\text{Fe}^{\text{II}}$  complexes containing bidentate ligands [27]. The magnetic behaviour observed for **1** and **2** is thus due to that of magnetically isolated

Fe<sup>II</sup> and Re<sup>IV</sup> ions with high values of local anisotropy. The large separation between the cations and anions precludes any significant through-space magnetic exchange coupling.

#### 4. Conclusions

We presented two novel Fe<sup>II</sup>-Re<sup>IV</sup> compounds of general formula [Fe<sup>II</sup>(DEA)<sub>6</sub>][Re<sup>IV</sup>X<sub>6</sub>], X being Cl (**1**) and Br (**2**) (DEA = diethylacetamide), which have been magneto-structurally characterised. The study of their magnetic properties showed that **1** and **2** are magnetically isolated complexes with high values of the zero-field splitting of the Fe<sup>II</sup> and Re<sup>IV</sup> ions. The large separation between cations and anions in their crystal lattice accounts for the lack of any significant through-space magnetic exchange coupling between the metal ions. **1** and **2** are the first examples of hexahalorhenate(IV) salts based on Fe<sup>II</sup> cations and, therefore, their preparation is a suitable starting point to pursue the synthesis of future mixed 3d-5d magnetic compounds based on highly anisotropic Fe<sup>II</sup> and Re<sup>IV</sup> ions in which exchange coupling can play a more significant role.

#### Appendix A. Supplementary data

Figures S1-S4. CCDC 1054690 and 1054691 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

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Table 1. Crystal data and structure refinement for [Fe(DEA)<sub>6</sub>][ReCl<sub>6</sub>] (**1**) and [Fe(DEA)<sub>6</sub>][ReBr<sub>6</sub>] (**2**)

Compound	<b>1</b>	<b>2</b>
Formula	C <sub>36</sub> H <sub>78</sub> Cl <sub>6</sub> N <sub>6</sub> O <sub>6</sub> FeRe	C <sub>36</sub> H <sub>78</sub> Br <sub>6</sub> N <sub>6</sub> O <sub>6</sub> FeRe
<i>Mr</i> (g mol <sup>-1</sup> )	1145.79	1412.55
Crystal system	trigonal	trigonal
Space group	<i>R</i> (-3)	<i>R</i> (-3)
<i>a</i> (Å)	15.955(1)	16.245(1)
<i>b</i> (Å)	15.955(1)	16.245(1)
<i>c</i> (Å)	16.963(1)	17.171(1)
<i>α</i> (°)	90.0	90.0
<i>β</i> (°)	90.0	90.0
<i>γ</i> (°)	120.0	120.0
<i>V</i> (Å <sup>3</sup> )	3739.6(2)	3924.2(2)
<i>Z</i>	3	3
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.526	1.793
<i>μ</i> (Mo-K <sub>α</sub> ) (mm <sup>-1</sup> )	3.083	7.214
<i>F</i> (000)	1761	2085
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.085	1.088
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0188 / 0.0399	0.0259 / 0.0541
Largest diff. peak/hole (e Å <sup>-3</sup> )	0.443 and -0.327	1.586 and -1.803

Table 2. Selected bond lengths (Å) for **1** and **2**

	<b>1</b> (X = Cl)	<b>2</b> (X = Br)
Re(1)-X(1)	2.361(1)	2.509(2)
Fe(1)-O(1)	2.100(1)	2.104(2)
O(1)-C(2)	1.248(2)	1.248(3)
N(1)-C(2)	1.331(2)	1.335(3)
N(1)-C(3)	1.465(2)	1.470(3)
N(1)-C(5)	1.466(2)	1.466(3)
C(1)-C(2)	1.497(2)	1.503(3)
C(3)-C(4)	1.512(3)	1.508(3)
C(5)-C(6)	1.513(3)	1.518(4)

Figure 1.

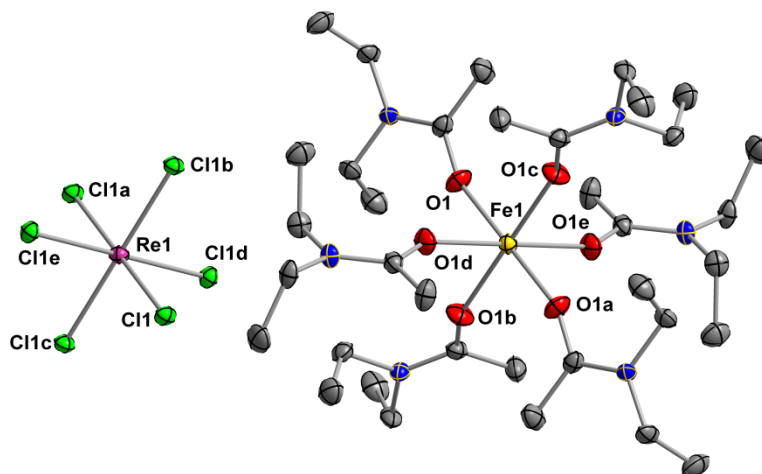
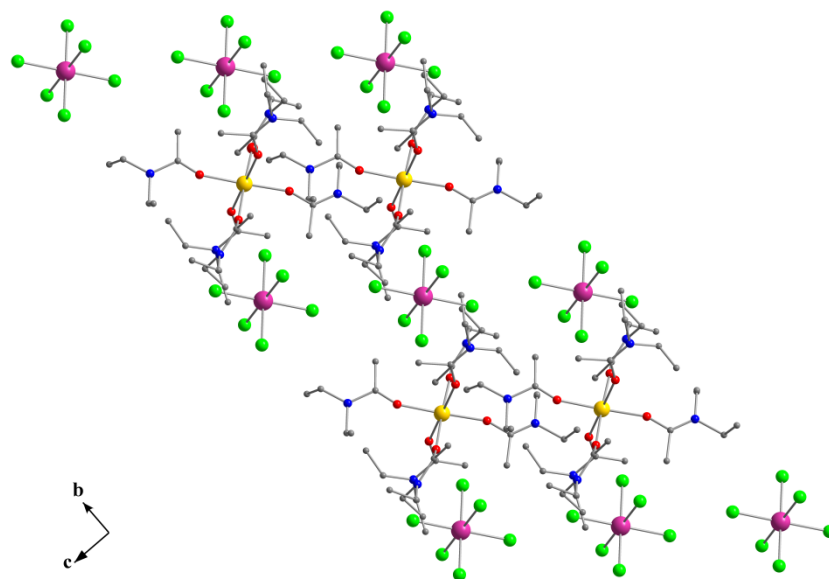
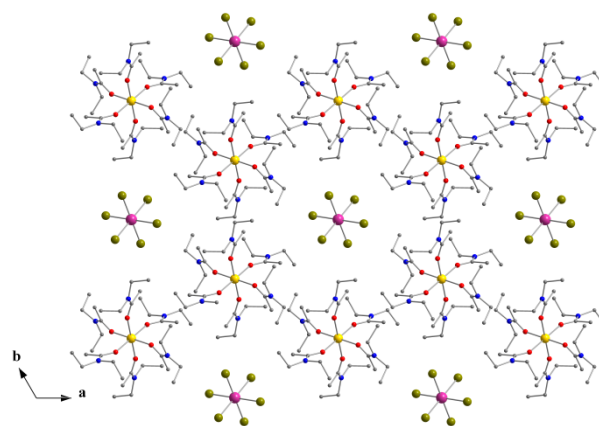
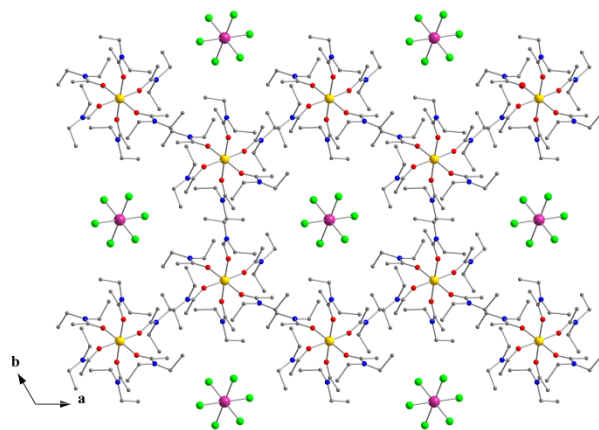


Figure 2.



**Figure 3.**



**Figure 4.**

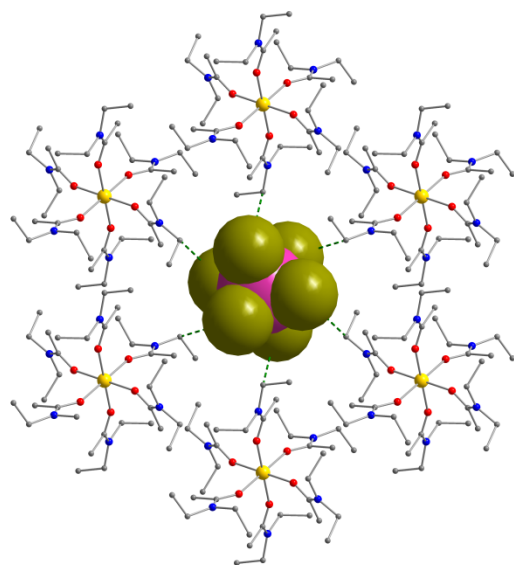
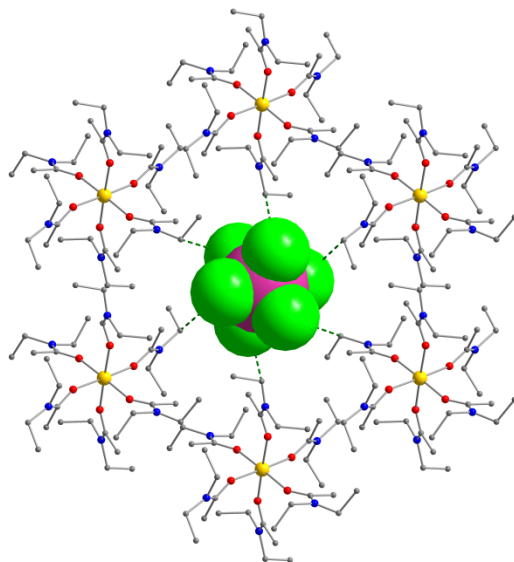


Figure 5.

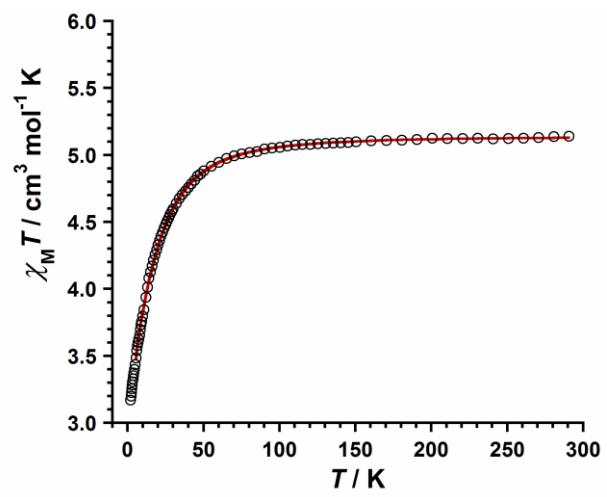
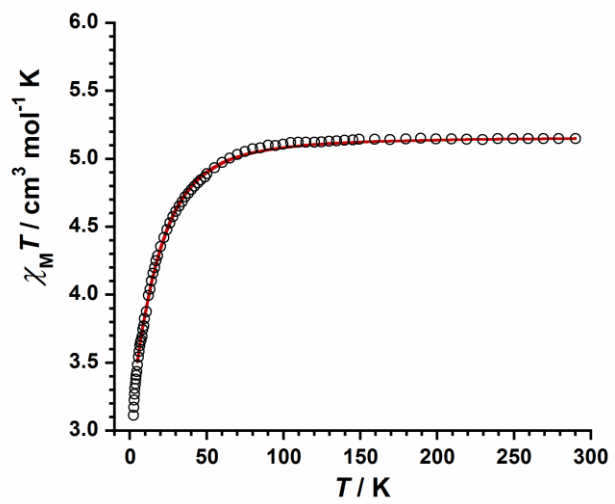


Figure 6.





## Figures captions

**Figure 1.** ORTEP drawing showing the  $[\text{Fe}(\text{DEA})_6]^{2+}$  cation and the  $[\text{ReCl}_6]^{2-}$  anion in **1**. Thermal ellipsoids are depicted at the 50% probability level.

**Figure 2.** View along the crystallographic  $a$  axis of a fragment of the crystal packing of **1** showing the layers of the  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations and  $[\text{ReCl}_6]^{2-}$  anions. The hydrogen atoms have been omitted for clarity. Colour code: pink, Re; yellow, Fe; green, Cl; red, O; blue, N; grey, C.

**Figure 3.** View along the crystallographic  $c$  axis of a fragment of the crystal packing of **1** (top) and **2** (bottom) showing the arrangement of the  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations and  $[\text{ReX}_6]^{2-}$  anions [ $X = \text{Cl}$  (**1**) and  $\text{Br}$  (**2**)]. The hydrogen atoms have been omitted for clarity. Colour code: pink, Re; yellow, Fe; pale green, Cl; olive green, Br; red, O; blue, N; grey, C.

**Figure 4.** View along the crystallographic  $c$  axis of the  $X \cdots \text{H}-\text{C}$  type interactions between the  $[\text{ReX}_6]^{2-}$  anion (space filling model) [ $X = \text{Cl}$  (**1**) and  $\text{Br}$  (**2**)] and  $[\text{Fe}(\text{DEA})_6]^{2+}$  cations in **1** (top) and **2** (bottom). H-atoms are omitted for clarity. Colour code: pink, Re; yellow, Fe; pale green, Cl; olive green, Br; red, O; blue, N; grey, C.

**Figure 5.** Thermal variation of the  $\chi_M T$  product for **1**: (o) experimental; (—) best-fit curve (see text).

**Figure 6.** Thermal variation of the  $\chi_M T$  product for **2**: (o) experimental; (—) best-fit curve (see text).