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Article

Magnetic Studies on Hexahalorhenate(IV) Salts of Ferrocenium Cations $[Fe(C_5R_5)_2]_2[ReX_6]$ (R = H, CH_3; X = Cl, Br, I)

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The hexahalorhenate(IV) salts of formula $[Fe(C_5H_5)_2]_2[ReX_6]$, with X = Cl (**1**), Br (**2**), and I (**3**), and $[Fe(C_5Me_5)_2]_2[ReX_6]$, with X = Cl (**4**), Br (**5**), and I (**6**) ($[Fe(C_5Me_5)_2]^+$ = decamethylferrocenium cation), have been synthesized and the structures of **1**, **2**, and **4** determined by single-crystal X-ray diffraction. **1**, **2**, and **4** crystallize in the orthorhombic system, space groups *Pbca* (**1** and **2**) and *Ibam* (**4**), with $a = 14.099(2)$ Å, $b = 16.125(2)$ Å, and $c = 22.133(15)$ Å, for **1**, $a = 14.317(3)$ Å, $b = 16.848(3)$ Å, and $c = 22.099(2)$ Å for **2**, and $a = 15.8583(5)$ Å, $b = 15.9368(5)$ Å, and $c = 16.9816(6)$ Å for **4**. The three structures are made up of discrete $[ReX_6]^{2-}$ anions and ferrocenium cations held together by electrostatic forces. There are anion–anion contacts in **1** and **2** but only through one direction. The $[ReX_6]^{2-}$ octahedra are arranged along the *y* axis forming chains of Re and X atoms, –Re–X···X–Re–X···X–Re–, where the intermolecular X···X distances are shorter than the van der Waals distances. A somewhat greater separation between the anions occurs in **4**. The magnetic properties of **1**–**6** were investigated in the temperature range 2.0–300 K. **1**, **2**, **4**, and **5** exhibit an antiferromagnetic coupling between the anions, whereas a ferromagnetic coupling between anions and cations is the dominant interaction in **3**. **6** behaves as a magnetically isolated compound, its susceptibility being the simple addition of the independent contributions of the uncoupled paramagnetic cations and anions.

Introduction

Molecular magnetism has been an active research field during the last 15 years. One of the main goals in this area is the study of magnetic interactions between different spin carriers present in a lattice. These spin carriers may be organic, organometallic, or inorganic, and the magnetic interactions between them may occur either through chemical bridges or through space.[2] Considerable efforts have been devoted to the study of the magnetic properties of the polynuclear complexes of transition metals, where the spin carriers, i.e., the metal ions, are connected by bridging ligands. The nature of the magnetic coupling has been explained in terms of the symmetry of the interacting magnetic orbitals, and now it is reasonably well understood.[2−4]

Compounds which only present through-space interactions have received much less attention. Very little work has been done, in comparison with through-bond interactions, due probably to their weaker nature. In 1986, it was reported that $[Fe(C_5Me_5)_2][TCNE]$ shows a ferromagnetic ordering below 4.8 K.[5] In this compound, decamethylferrocenium cations, $[Fe(C_5Me_5)_2]^+$ ($S = 1/2$), and planar tetracyanoethenide anions, $TCNE^-$ ($S = 1/2$), are alternatively stacked in chains, being exclusively linked by electrostatic forces.[5−8]

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Miller explained the ferromagnetic exchange between $[Fe(C_5Me_5)_2]^+$ and $TCNE^-$ ions in terms of the McConnell's type II mechanism,[9] i.e., a configuration mixing through a virtual charge transfer (between the assumed lowest excited state $[Fe(C_5Me_5)_2]^{2+}[TCNE]^{2-}$ and the ground state $[Fe(C_5Me_5)_2]^+[TCNE]^-$) operates to stabilize a $S = 1$ state. However, Hoffman pointed out that the proposed mechanism is not valid for these charge-transfer compounds.[10] Kahn also disagreed with this mechanism and suggested that another alternative could be effective.[2,11,12] Using McConnell's type I mechanism,[13] he proposed that, due to a spin polarization mechanism in the cation, a residual negative spin density could exist on the rings. This magnetic moment could interact with the spin of the anion in an antiferromagnetic way, leading to an overall ferromagnetic coupling between the metal ion and the organic anion. NMR experiments agree with Kahn's explanation,[14] and recent neutron diffraction experiments confirm partially this mechanism.[15] After Miller's work, metallocenium ions were widely used as molecular bricks toward the design of molecular magnetic materials.[16−23]

Ionic compounds where the cation is a nitronyl nitroxide radical derivative and the anion is a transition metal complex, $[M(CN)_6]^{3-}$ (M = Fe, Co, and Cr)[24] and $[MCl_4]^{2-}$ (M = Co and Mn),[25] are other examples where the magnetic interactions are purely transmitted through space. Again, different theoretical mechanisms have been proposed by the different authors[24,25] in the analysis of the nature of the magnetic coupling between the radical cation and the anions.

Another interesting and different example of this kind of interaction concerns the halocomplexes of Re(IV), a $5d^3$ metal ion. Magnetic properties of $[ReX_6]^{2-}$ (X = Cl and Br) salts of monocations have been investigated and show strong antiferromagnetic interactions.[26] Magnetic susceptibility,[27] heat capacity,[28,29] and neutron diffraction measurements[30] on $K_2[ReCl_6]$ and $K_2[ReBr_6]$ confirm the existence of antiferromagnetic ordering below 12 and 14 K, respectively. In these compounds there are magnetic interactions between the anions, the cations being diamagnetic. These interactions are transmited through space via a Re−X···X−Re pathway. The coupling depends on the spin densities lying on the X ligands (neutron diffraction experiments[31] and density functional calculations[32] show a significant spin delocalization from the metal to the coordinated ligands) and on the X···X distance. Despite the small number of known structures, it can be pointed out that, for a given $[ReX_6]^{2-}$ anion, the X···X distance is controlled by the size of the countercation and so the strength of the magnetic interactions is strongly dependent on the nature of the cation. Bulky cations such as tetrabutylammonium, NBu_4^+, or tetraphenylarsonium, $AsPh_4^+$, preclude any interaction between neighbor paramagnetic anions, and no magnetic coupling is observed in compounds such as $(AsPh_4)_2[ReCl_6]$ and $(NBu_4)_2[ReCl_6]$. The decrease in the effective magnetic moment observed in these compounds when lowering the temperature is due exclusively to the zero-field splitting, which is very large in Re(IV) complexes. $|D|$ values of 13, 9, and 60 cm^{-1} have been found for $(AsPh_4)_2[ReCl_6]$, $(NBu_4)_2[ReCl_6]$, and $(AsPh_4)_2[Re(ox)Cl_4]$ (ox = oxalate anion), respectively.[32]

Recently, the magnetic properties of a series of salts of the hexaiodorhenate(IV) complex, $M_2[ReI_6]$ (M = Li, Na, K, Rb, Cs, and NH_4), have been investigated. A maximum in the susceptibilty curves at 28 K (Li), 27 K (Na), 21 K (Rb), 16 K (Cs), and 20 K (NH_4) reveals the occurrence of an antiferromagnetic ordering in these compounds. A quite remarkable result concerns the potassium salt, $K_2[ReI_6]$, which behaves as a weak ferromagnet below 24 K, exhibiting an hysteresis loop at 15 K with a coercive field of 5000 G.[33]

The magnetic interactions in all the above cited compounds occur either between the cations and the anions or between the anions of an ionic lattice. It seemed interesting to study the behavior of systems in which both types of interactions could exist in the same compound. Thus, in the framework of our current research interest in the magnetic properties of Re(IV) compounds, we tried to substitute paramagnetic ferrocenium cations for the diamagnetic alkali metal ions in the $M_2[ReX_6]$ salts. Our first results concerning the syntheses and magnetic properties of six novel compounds of formula $[Fe(C_5H_5)_2]_2[ReX_6]$ [with X = Cl (**1**), Br (**2**), and I (**3**)] and $[Fe(C_5Me_5)_2]_2[ReX_6]$ [with X = Cl (**4**), Br (**5**), and I (**6**)] as well as the crystal structures of **1**, **2**, and **4** are presented here.

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Experimental Section

Materials. All reagents were purchased from commercial sources and used as received. $K_2[ReX_6]$ (X = Cl, Br, and I), $[Fe(C_5H_5)_2]PF_6$, and $[Fe(C_5Me_5)_2]BF_4$ were obtained by using previously reported methods.[33−35]

Synthesis. $[Fe(C_5H_5)_2]_2[ReCl_6]$ (1). A solution of ferrocenium chloride was prepared by mixing a solution of 50 mg (0.27 mmol) of ferrocene in 3 mL of acetone with a solution of 73 mg (0.27 mmol) of $FeCl_3 \cdot 6H_2O$ in 10 mL of water. The resulting dark blue solution was carefully added to a solution of 64 mg (0.134 mmol) of $K_2[ReCl_6]$ in 5 mL of water. The final solution was left overnight in an ice bath, and then the blue microcrystalline solid which precipitates slowly was filtered out, washed with water and ethanol, and dried in the air. Yield: 40%. Anal. Calcd for $H_{20}C_{20}Fe_2Cl_6Re$ (**1**): H, 2.61; C, 31.16. Found: H, 2.2; C, 30.7. Crystals suitable for X-ray diffraction were obtained by slow evaporation at room temperature from an ethanol/acetone (1/1 v/v) solution.

$[Fe(C_5H_5)_2]_2[ReBr_6]$ (2). A solution of ferrocenium chloride prepared as above was carefully added to a solution of 100 mg (0.134 mmol) of $K_2[ReBr_6]$ in 5 mL of 0.5 M HBr. The green microcrystalline solid which appeared immediately was filtered out, washed first with 0.1 M HBr and then with 2-propanol, and dried in air. Yield: 60%. Anal. Calcd for $H_{20}C_{20}Fe_2Br_6Re$ (**2**): H, 1.9; C, 23.1. Found: H, 2.0; C, 23.1. Slow evaporation of the filtrate yields X-ray-quality crystals.

$[Fe(C_5H_5)_2]_2[ReI_6]$ (3). A solution of 67 mg (0.20 mmol) of $[Fe(C_5H_5)_2]PF_6$ in 30 mL of 4.5 M HBr was slowly added to a cold, well-stirred solution of 100 mg (0.098 mmol) of $K_2[ReI_6]$ in 10 mL of 4.5 M HBr. The black microcrystalline solid which appeared instantaneously was filtered off with a sintered glass funnel, washed with 0.5 M HBr and 2-propanol, and dried in a vacuum for 1 day. Yield: 45%. Anal. Calcd for $H_{20}C_{20}Fe_2I_6Re$ (**3**): H, 1.5; C, 18.2. Found: H, 1.2; C, 18.4. The instability of the solutions of **3**, which undergo slow decomposition, precluded the preparation of single crystals of this compound.

IR spectra of **1**−**3** are nearly identical and show the characteristic bands of the ferrocenium ion.[36,37]

$[Fe(C_5Me_5)_2]_2[ReCl_6]$ (4). A 70 mg (0.169 mmol) amount of $[Fe(C_5Me_5)_2]BF_4$ dissolved in 15 mL of methanol was added to a solution of 40 mg (0.084 mmol) of $K_2[ReCl_6]$ in 15 mL of H_2O. The resulting solution was left to evaporate slowly at room temperature, and green needles appeared after 1 day. The solid was filtered off, washed with water and ethanol, and dried in the air. Yield: 30%. Anal. Calcd for $H_{60}C_{40}Fe_2Cl_6Re$ (**4**): H, 5.7; C, 45.7. Found: H, 5.7; C, 45.1. X-ray-quality crystals of **4** were obtained by slow evaporation of an ethanol/acetone (1/1 v/v) solution.

$[Fe(C_5Me_5)_2]_2[ReBr_6]$ (5). A 44 mg (0.106 mmol) amount of $[Fe(C_5Me_5)_2]BF_4$ dissolved in 5 mL of methanol was added to a solution of 40 mg (0.053 mmol) of $K_2[ReBr_6]$ in 5 mL of 0.5 M HBr. The green microcrystalline solid formed was separated from the solution by filtration. A second crop of crystals was obtained by evaporation at room temperature during 1 day. The collected solid was washed with 0.1 M HBr and ethanol and dried in the air. Yield: 70%. Anal. Calcd for $H_{60}C_{40}Fe_2Br_6Re$ (**5**): H,4.6; C, 36.4. Found: H, 4.0; C, 36.5.

$[Fe(C_5Me_5)_2]_2[ReI_6]$ (6). This compound was obtained in the same way as **3**, using a solution $[Fe(C_5Me_5)_2]BF_4$ (40 mg, 0.097 mmol) in 4.5 M HBr (40 mL) and a solution of $K_2[ReI_6]$ (50 mg, 0.048 mmol) in 4.5 M HBr (30 mL). A dark brown microcrystalline solid was obtained. Yield: 70%. Anal. Calcd for $H_{20}C_{20}Fe_2I_6Re$ (**1**): H, 3.8; C, 30.0. Found: H, 3.6; C, 29.3.

Table 1. Crystal Data and Structure Refinement for $[Fe(C_5H_5)_2]_2[ReCl_6]$ (**1**), $[Fe(C_5H_5)_2]_2[ReBr_6]$ (**2**), and $[Fe(C_5Me_5)_2]_2[ReCl_6]$ (**4**)

	1	**2**	**4**
formula	$C_{20}H_{20}Cl_6Fe_2Re$	$C_{20}H_{20}Br_6Fe_2Re$	$C_{10}H_{15}Cl_{1.5}Fe_{0.5}Re_{0.25}$
space group	Pbca	Pbca	Ibam
M_r	770.96	1037.72	262.87
a, Å	14.099(2)	14.317(3)	15.8583(5)
b, Å	16.125(3)	16.848(3)	15.9368(5)
c, Å	22.133(6)	22.099(4)	16.9816(6)
V, Å^3	5031.9(15)	5331(2)	4291.8(2)
T	293	293	150
Z	8	8	16
D_c, g cm^{-3}	2.035	2.586	1.627
μ, cm^{-1}	65.81	14.606	143.79
R1[a] $[I > 2\sigma(I)]$	0.0542	0.0669	0.0462
wR2[b,c]	0.1190	0.1342	0.1235

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/[(w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [F_o^2 + 2F_c^2]/3$, $a = 0.0568$ (**1**), 0.021 (**2**), and 0.0782 (**4**), and $b = 16.7566$ (**1**), 0 (**2**), and 25.840 (**4**).

IR spectra of **4**−**6** are nearly identical and show the characteristic bands of the decamethylferrocenium cation.[37,38]

Physical Techniques. The IR spectra of **1**−**6** (CsI pellets) were recorded with a Bomen MB-102 FTIR spectrometer. Elemental analysis (C, H) were carried out on a Carlo Erba model 1108 elemental analyzer. Magnetic susceptibility measurements (2.0−300 K) were carried out with a Quantum Design SQUID magnetometer under an applied magnetic field of 1 T at high temperatures and only 100 G at low temperatures to avoid any problem of magnetic saturation. The device was calibrated with $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$. The corrections for the diamagnetism were estimated from Pascal's constants.

X-ray Data Collection and Structure Refinement. Diffraction intensity data were collected at room temperature with a Bruker R3m/V automatic four circle diffractometer, by using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) with the $\omega-2\theta$ scan method for **1** and **2**, and at 150 K with a Bruker Smart CCD diffractometer, by using graphite-monochromated Cu Kα radiation ($\lambda = 1.5418$ Å) for **4**. A summary of the crystallographic data and structural parameters is given in Table 1. Lorentz−polarization and empirical absorption corrections through the ψ-scan program[39] (**1** and **2**) and through the SADABS program[40] (**4**) were applied.

The structures were solved by the standard Patterson method and subsequently completed by Fourier recycling. The hydrogen atoms were not defined. All the other atoms have been refined anisotropically in **1**. Cyclopentadienyl rings have been defined as rigid groups and the carbon atoms refined isotropically in **2**. Decamethylferrocenium cations are disordered in **4**; two positions with identical occupancy (SOF = 0.5) have been defined for each carbon atom, but only the methyl C atoms have been refined anisotropically.

Full-matrix least-squares refinements on F^2, which were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, reached convergence with values of the discrepancy indexes given in Table 1. The goodness-of-fit is 1.105 for **1**, 0.993 for **2**, and 1.182 for **4**. Solutions and refinements were performed with the SHELXTL NT

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system.[41] The final geometrical calculations were carried out with the PARST program.[42] The graphical manipulations were performed using the XP utility of the SHELXTL NT system. Main interatomic bond distances and angles for **1**, **2**, and **4** are given as Supporting Information (Tables S1 and S2). Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 221511, 221512, and 221513 for compounds **1**, **2**, and **4**, respectively.

Results and Discussion

Description of the Structures of $[Fe(C_5H_5)_2]_2[ReCl_6]$ (1) and $[Fe(C_5H_5)_2]_2[ReBr_6]$ (2). The structure of compounds **1** and **2** consist of discrete ferrocenium cations and $[ReCl_6]^{2-}$ (**1**) or $[ReBr_6]^{2-}$ (**2**) anions held together by electrostatic forces. The two compounds are isostructural. Perspective drawings showing the atom numbering are given as Supporting Information in Figures S1 and S2. Rhenium(IV) centers are surrounded by six chloride or bromide anions in a slightly distorted octahedral environment, with the bond lengths varying in a narrow range [2.345(3)−2.366(3) Å for **1** and 2.484(8)−2.507(4) Å for **2**]. These values are in agreement with those found in the literature for Re−X bond lengths.[43]

Two nonequivalent ferrocenium cations are present in the asymmetric unit. The cyclopentadienyl rings of each cation are almost parallel to each other. The rings are staggered in one ferrocenium cation, whereas they are almost eclipsed in the second one. The distances between the mean planes of cyclopentadienyl rings for both compounds are in the 3.35−3.40 Å range.

The ReX_6 octahedra are arranged in chains developing along *b* axis, with adjacent anions showing different orientations: each anion is related to its neighbors in the chain by a glide operation, giving rise to a zigzag motif (Figure 1). The shortest intrachain X···X distances, 3.382(4) Å [Cl(1)···Cl(2a), (a) = 0.5 − *x*, −0.5 + *y*, *z*] for **1** and 3.464(9) Å [Br(1)···Br(2a)] for **2**, are shorter than the van der Waals contacts (3.62 Å for Cl and 3.90 Å for Br) whereas the shortest interchain X···X distances, 4.147(6) [Cl(4)···Cl(5b)] and 3.955(5) Å [Br(4)···Br(5b); (b) = 0.5 + *x*, *y*, 0.5 − *z*], are longer. The corresponding Re···Re intrachain distances are 8.072(1) (**1**) and 8.428(4) Å (**2**), while the interchain distances are 8.288(1) and 8.443(3) Å in **1** and **2**, respectively. Chains are arranged in such a way that each anion is in the middle of a trigonal prism whose vertexes are occupied by the iron atoms from six ferrocenium cations (Figure 1). The shortest Fe−Fe distances within this polyhedron are 7.224(2) [Fe(1)···Fe(2)], 7.050(2) [Fe(1)···Fe(1b)], and 7.308(2) Å [Fe(2)···Fe(1b)] in **1** and 7.292(7), 7.158(7), and 7.455(7) Å, respectively, in **2**. With regard to the anion−cation interactions, the mean distance between the rhenium atom at the center and the iron atoms at the vertexes of the trigonal prism is 5.792 Å in **1** and 5.95 Å in **2**. A plot showing these interactions is given in Figure 2.

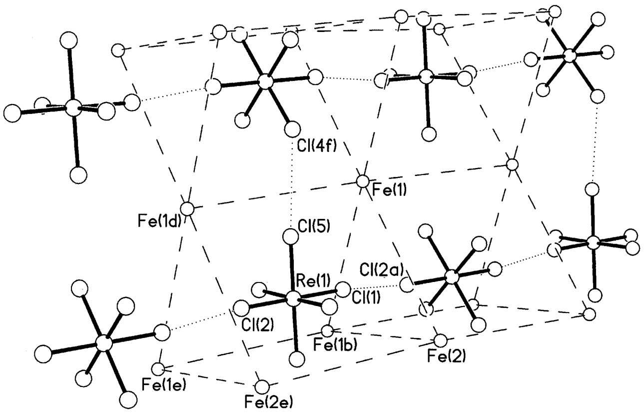

Figure 1. Perspective drawing of $[ReX_6]^{2-}$ [X = Cl (**1**), Br (**2**)] anions developing along the *b* axis, showing the prismatic motif.

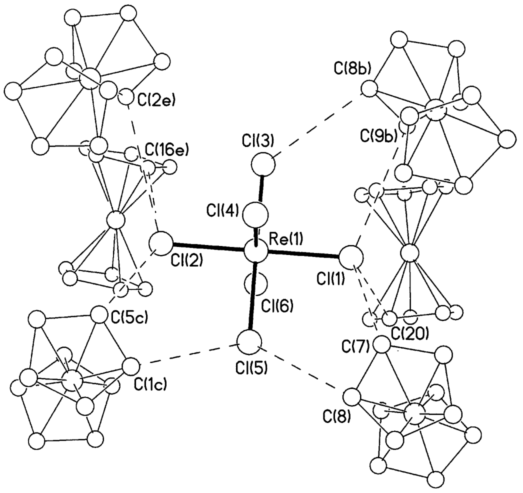

Figure 2. Anion−cation interactions in compounds **1** and **2**.

Description of the Structure of $[Fe(C_5Me_5)_2]_2[ReCl_6]$ (4). The structure of compound **4** consists of decamethylferrocenium cations and $[ReCl_6]^{2-}$ anions. Perspective drawings showing the atom numbering are given as Supporting Information in Figures S3 and S4. Each rhenium atom is six-coordinated in a regular octahedral environment. The Re−Cl bond distances vary in the range 2.328(3)−2.375(3) Å. These bond lengths are in agreement with those reported for analogous complexes.[43] Each anion is in the middle of a quadrangular antiprism, whose vertexes are occupied by iron atoms from eight decamethylferrocenium cations (Figure 3a,b). $ReCl_6$ octahedra are arranged in linear chains developing along *c* axis. The shortest Cl···Cl distance along the chain is 3.836(5) Å [Cl(3)···Cl(3c); (c) = 1 − *x*, 1 − *y*, 1 − *z*] a value longer than the van der Waals distance; the corresponding intrachain Re···Re distance is 8.4908(3) Å. Chains are parallel to each other so that rhenium centers determine ideally a rhombic motif in the *xy* plane (Figure 4), in which the edge length is 11.242 Å and the smallest angle is 89.7°.

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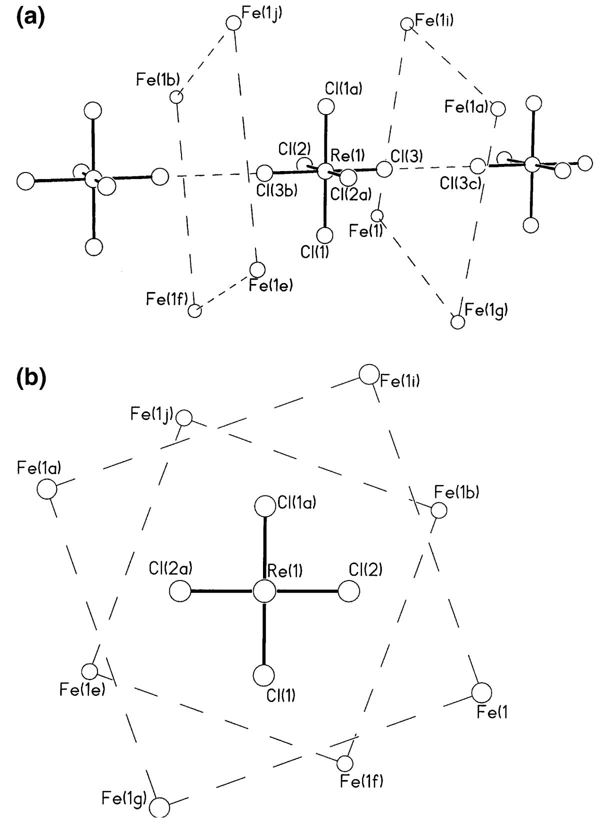

Figure 3. (a) Perspective drawing of $[ReCl_6]^{2-}$ anions developing along the *c* axis in compound **4**. (b) Antiprismatic motif of the iron atoms around each $[ReCl_6]^{2-}$ anion in **4**.

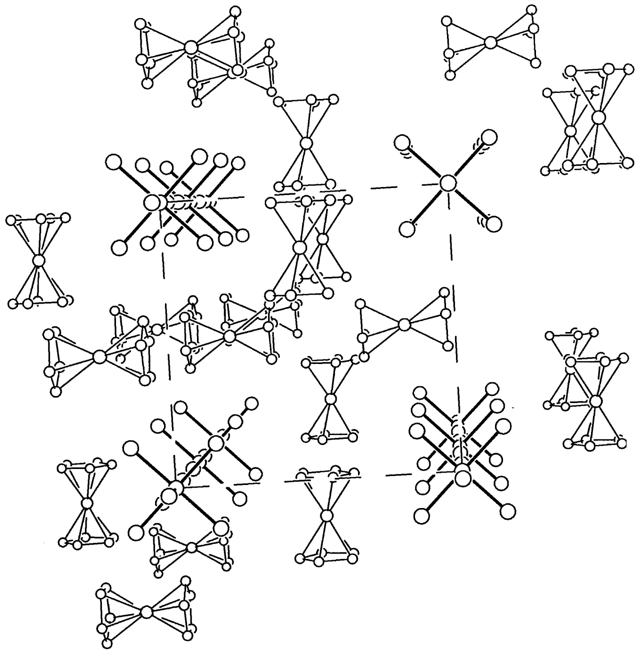

Figure 4. Side view of the rhombic motif in the *xy* plane in **4**.

The shortest Fe···Fe distances within the polyhedron are 8.428(2) and 8.472(2) Å, and the Re···Fe distances are 7.328(1) and 7.332(1) Å. C_5Me_5 rings in each cation are almost parallel, and the Fe−C and the C−C distances are as expected.[44] Decamethylferrocenium cations form pairs in which pentamethylcyclopentadienyl rings are face-to-face. The distance between the nearest rings in a pair is 3.758(2) Å, while the distance between the iron atoms is 7.186(2) Å [Fe(1)···Fe(1d); (d) = 1 − *x*, 2 − *y*, 1 − *z*].

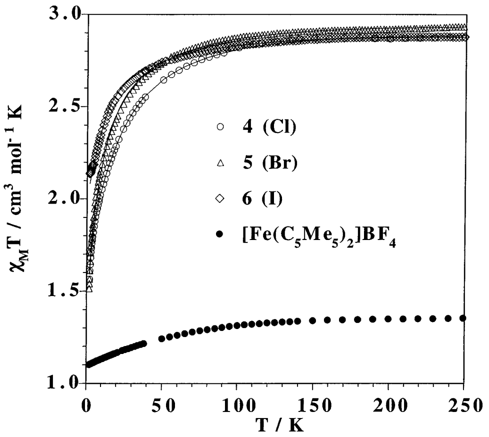

Figure 5. Thermal variation of the $\chi_M T$ product for compounds **4**−**6** and $2\chi_M T$ for $[Fe(C_5Me_5)_2]BF_4$. Continuous lines represent the best theoretical fit (see text).

Magnetic Properties. The magnetic properties of complexes **1**−**6** under the form of $\chi_M T$ versus *T* plot (χ_M being the molar susceptibility) are shown in Figures 5 (**4**−**6**) and 6 and 7 (**1**−**3**). Let us start the analysis and discussion of the magnetic behavior of these compounds with the simpler series, that is the decamethylferrocenium one (**4**−**6**). As seen in Figure 5, $\chi_M T$ at room temperature for **4**−**6** is ca. 2.90 cm^3 mol^{-1} K. This value is as expected for a mononuclear Re(IV) unit ($\chi_M T = 1.60$ cm^3 mol^{-1} K for $S = 3/2$ with g $=1.85$) and two decamethylferrocenium cations ($2\chi_M T =$ 1.35 cm^3 mol^{-1} K value taken from the bottom curve in Figure 5 which shows the magnetic behavior of the decamethylferrocenium as the hexafluorophosphate salt). It should be noted that ferrocenium cations although they have only one unpaired electron ($S_{Fe} = 1/2$) exhibit a large orbital contribution to the magnetic moment.[35,45−47] The value of $\chi_M T$ for **4**−**6** remains practically constant upon cooling until 80 K, and then it decreases abruptly to reach 1.50 (**5**), 1.56 (**4**), and 2.13 cm^3 mol^{-1} K (**6**) at 2.0 K. Two factors can account for this decrease of $\chi_M T$ in **4**−**6**: (i) the zero field splitting of Re(IV); (ii) intermolecular antiferromagnetic interactions between the hexahalorhenate anions. Previous magneto−structural studies on magnetically isolated six-coordinated $[ReX_6]^{2-}$ compounds (X = halogen atom)[32] have shown that $\chi_M T$ at room temperature is ca. 1.6 cm^3 mol^{-1} K ($S_{Re} = 3/2$ and $g = 1.8$−1.9), and it decresases when cooling, due to the large zero-field splitting of Re(IV), tending to a

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Table 2. Best-Fit Magnetic Parameters for Complexes **1**−**6**

compd	*g*	|*D*|, cm^{-1}	Θ, K	$10^{-5}R^{a}$
$[Fe(C_5H_5)_2]_2[ReCl_6]$ (**1**)	1.82	16.6	−4.1	6.4
$[Fe(C_5H_5)_2]_2[ReBr_6]$ (**2**)	1.84	10.2	−5.9	5.1
$[Fe(C_5H_5)_2]_2[ReI_6]$ (**3**)	1.84	13.0	+1.9	0.4
$[Fe(C_5Me_5)_2]_2[ReCl_6]$ (**4**)	1.82	16.0	−1.8	4.3
$[Fe(C_5Me_5)_2]_2[ReBr_6]$ (**5**)	1.85	14.5	−1.9	13
$[Fe(C_5Me_5)_2]_2[ReI_6]$ (**6**)	1.83	12.0	ca. 0	6.2

[a] *R* is the agreement factor defined as $\sum_i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calc}(i)]/\sum_i[(\chi_M T)_{obs}(i)]^2$.

value close to 1.0 cm^3 mol^{-1} K at 2.0 K. The values of $\chi_M T$ at 2.0 K for **4**−**6** after subtracting the contribution of the decamethylferrocenium [0.40 (**5**), 0.46 (**4**), and 1.03 cm^3 mol^{-1} K (**6**)] reveal the occurrence of very weak antiferromagnetic interactions in **4** and **5** and no magnetic coupling in **6**. This is in agreement with the fact that in these solids the anions are separated by bulky decamethylferrocenium cations. The presence of Cl···Cl distances between adjacent anions in **4** along the *c* axis, which are close to the van der Waals value, would account for the antiferromagnetic coupling in this compound. Although the structure of **5** is unknown, it is probably the same as **4**, taking into account that the corresponding ferrocenium derivatives (**1** and **2**) are isostructural and because of the similarity of the magnetic curves of **4** and **5**. In the case of **6**, a different structure is anticipated in the lack of magnetic interactions. Although this assumption could seem surprising at first sight, it deserves to be noted that in a very recent work we showed that the structures of the $K_2[ReCl_6]$ and $K_2[ReI_6]$ are different and that even ammonium and potassium salts of $[ReI_6]^{2-}$ are not isostructural.[33]

Having these considerations in mind, we have analyzed the magnetic data for **4**−**6** (after correction for the paramagnetic contribution of the decamethylferrocenium cations) through the spin Hamiltonian $H = D[S_z^2 - (1/3)S(S+1)] + g\beta HS$, where DS_z^2 represents the splitting into two Kramers doublets in the absence of a magnetic field. A Θ term under the form of $T - \Theta$ was included to account for the magnetic coupling between the anions. Least-squares fitting of the experimental data of **4**−**6** through this Hamiltonian leads to the *g*, *D*, and Θ values listed in Table 2. As seen in Figure 5, the calculated curves reproduce very well the magnetic data in the whole temperature range.

The values of $\chi_M T$ at room temperature for complexes **1**−**3** (see Figure 6) are 2.85 (**1** and **2**) and 3.0 cm^3 mol^{-1} K (**3**). These values are as expected for a mononuclear Re(IV) complex ($S_{Re} = 3/2$) and two ferrocenium cations ($S_{Fe} = 1/2$) which are magnetically uncoupled. Upon cooling, the values of $\chi_M T$ decrease for all three compounds in the high-temperature range but they differ at lower temperatures. In fact, the magnetic plots of **1** and **2** are practically identical with an abrupt decrease of $\chi_M T$ in the lower temperature range to reach values of 1.52 (**1**) and 1.30 cm^3 mol^{-1} K (**2**) (see inset of Figure 6). These values are consistent with the occurrence of a weak but significant antiferromagnetic coupling between the hexahalorhenate(IV) units (see above) in addition to the presence of a large well-known zero-field splitting of the Re(IV) cation. In the case of complex **3**, $\chi_M T$ smoothly decreases, it exhibits a minimum of ca. 2.70 cm^3 mol^{-1} K at 8.0 K, and then sharply increases to reach a maximum of ca. 5.10 cm^3 mol^{-1} K at 3.0 K with a further linear decrease of $\chi_M T$ with *T* (see Figures 6 and 7). The shape of this plot for **3** together with the fact that the value of $\chi_M T$ in the minimum is clearly above that calculated for two ferrocenium cations and a Re(IV) unit magnetically noninteracting shows that a weak ferromagnetic coupling is involved, the smooth decrease of $\chi_M T$ in the high-temperature range being due to the zero-field splitting of the Re(IV). The *M* versus *H* plot at 2.0 K for **1**−**3** (see inset of Figure 7) confirms the presence of antiferro- (**1** and **2**) and ferromagnetic (**3**) interactions: the magnetization at the highest available magnetic field for **3** tends to 5 μ_B (ferromagnetic interaction between $S_{Re} = 3/2$ and two $S = 1/2$ from two ferrocenium cations) whereas those of **1** and **2** tends to values between 2 and 3 μ_B). In light of these features of **1**−**3**, their magnetic data (from 300 to 2.0 K for **1** and **2** and from 300 to 8.0 K for **3**) were analyzed through the same approach used for **4**−**6** but using the $\chi_M T$ values of $[Fe(C_5H_5)_2]PF_6$ to correct the measured values, and the relevant magnetic parameters are listed in Table 2. As one can see, the calculated curves match very well the magnetic data in all three complexes. The crystal structure of complexes **1** and **2** shows the occurrence of X···X distances [X = Cl (**1**) and Br (**2**)] smaller than the van der Waals separation [3.383(5)

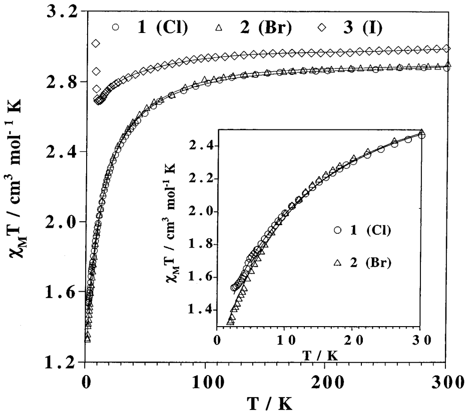

Figure 6. Thermal variation of the $\chi_M T$ product for compounds **1**−**3**. Continuous lines represent the best theoretical fit (see text).

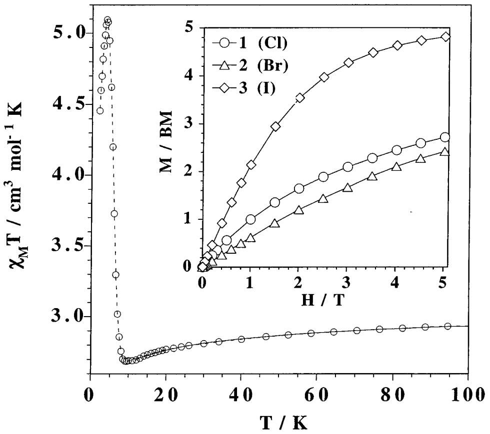

Figure 7. Thermal variation of the $\chi_M T$ product for compound **3** in the low-temperature range and magnetization curves for **1**−**3** at 2 K (inset).

Å in **1** and 3.464(9) Å in **2**] which are certainly responsible for the antiferromagnetic interaction observed in them. The somewhat larger antiferromagnetic coupling in **1** and **2** with respect to those of **4** and **5** is most likely due to the shorter intermolecular X···X separation in the former. As observed in the decamethylferrocenium family, the magnetic behavior of the iodo compound in the ferrocenium series is different from that of its parent chloro and bromo derivatives. Unfortunately, the lack of a crystal structure for compound **3** [the iodo-containing rhenium(IV) complexes undergo easy hydrolysis and redox reactions] precludes a detailed analysis of the exchange pathway for the ferromagnetic interaction observed. Clearly, its structure has to be different from that of the isostructural complexes **1** and **2**, and most likely, the anions will be well separated hindering any antiferromagnetic coupling between them. The nature of the ferromagnetic interaction between the ferrocenium cations and the hexahalorhenate(IV) anions could be similar to that observed in the [Fe(C_5Me_5)$_2$][TCNE].[5] As previously reported, the carbon atoms of cyclopendienyl rings in ferrocenium cations can exhibit some spin density opposite the sign with the metal ion through a polarization mechanism.[2,11,12] An antiferromagnetic coupling between this spin density and that of the iodine atoms in [ReI_6]$^{2-}$ due to direct intermolecular C_{ring}···I contacts creates the parallel disposition of the Re(IV) and Fe(III) spins. This kind of ferromagnetic coupling should occur also in **1** and **2**, but it is negligible against the stronger, in comparison, antiferromagnetic coupling between the anions.

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Supporting Information Available: Perspective views of the structures (Figures S1−S4) and main interatomic bond distances and angles (Tables S1 and S2) for **1**, **2**, and **4** and X-ray crystallographic files of compounds **1**, **2**, and **4** in CIF format. This material is available free of charge via the Internet at htpp://pubs.acs.org.

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