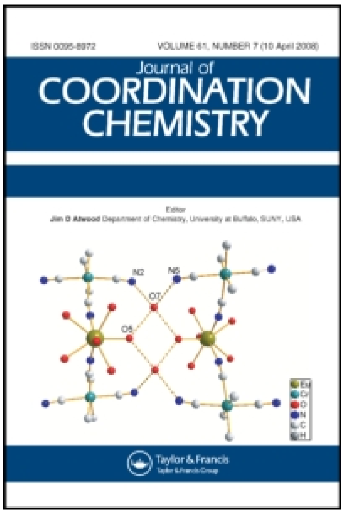

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Spin canting in Re(IV) complexes: magnetic properties of [ReX$_4$(bpym)] (X = Cl and Br; bpym = 2,2′-bipyrimidine)

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The mononuclear complexes [ReCl$_4$(bpym)] (**1**) and [ReBr$_4$(bpym)] (**2**) (bpym = 2,2′-bipyrimidine) are weak ferromagnets. Magnetic ordering occurs below 7.0 (**1**) and 20.0 K (**2**) and good hysteresis loops are observed for the two compounds at 2.0 K. A spin-canting phenomenon, i.e., a non-strict linearity of the individual spins aligned in an anti-parallel way by intermolecular antiferromagnetic coupling occurring in many Re(IV) complexes, accounts for these magnetic features which are unusual in molecular solids such as **1** and **2**.

Keywords: Re(IV) complexes; Magnetic properties; Spin canting

1. Introduction

The magnetic properties of mononuclear Re(IV) complexes are more diverse and interesting than could be thought at first sight. The electronic structure of a d^3 ion in an octahedral environment is characterized by a $^4A_{2g}$ ground term and so, a temperature-independent value of μ_{eff} (i.e., a constant value of $\chi_M T$) which is close but somewhat lower than the spin only value ($\mu_{\mathrm{so}} = 3.87$ BM) could be expected. A d^3 ion has a spin–orbit coupling parameter whose value is positive ($\lambda > 0$) and therefore $g < 2.0$ [1]. Accordingly, the magnetic susceptibility measurements of Re(IV) complexes show $\chi_M T$ values at room temperature varying in the range of 1.5–1.6 cm^3 mol^{-1} K (i.e., $\mu_{\mathrm{eff}} = 3.5$–3.6 BM or $g = 1.8$–1.85) [1, 2]. However, $\chi_M T$ is not constant but decreases significantly upon cooling.

This decrease was ascribed to the presence of intermolecular antiferromagnetic interactions and/or zero-field splitting effects [1], but the limited range of temperatures investigated (from room temperature to 80 K) and the lack of detailed structural knowledge in most of the studied compounds precluded separation and quantification of both factors. This ambiguous situation has been overcome in more recent years. Crystal structures of a good number of Re(IV) complexes have been determined and their magnetic properties have been measured down to 2.0 K providing clear magneto-structural correlations. For those compounds where the paramagnetic

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mononuclear units are well separated from each other in the crystal structure (in general anionic complexes with bulky cations such as NBu_4^+, PPh_4^+, or $AsPh_4^+$), $\chi_M T$ decreases with T reaching a finite value close to $1.0\,cm^3\,mol^{-1}\,K$ at very low temperatures. On the other hand, for those compounds where direct contacts between the paramagnetic entities in the crystal structure occur, i.e., in neutral complexes and also in anionic ones without bulky cations, the decrease of $\chi_M T$ is more pronounced, starting at higher temperatures and vanishing when T approaches 0 K.

In the first case, no magnetic interaction is possible and zero-field splitting must be the only factor accounting for the temperature dependence of $\chi_M T$. This splitting of the $^4A_{2g}$ ground term into two doublets ($M_S = \pm 3/2$ and $M_S = \pm 1/2$) is the combined result of lower symmetry (all the complexes show some distortion of the ideal octahedral geometry) and second-order spin–orbit coupling [2a]. The zero-field splitting parameter ($2D$) measures the energy gap between them. At very low temperatures, only the lower energy doublet will be thermally populated and $\chi_M T$ will reach a non-zero limit. Theoretical fit of the magnetic data affords the $2D$ values which vary between ca $15\,cm^{-1}$ for $[ReCl_6]^{2-}$ and ca $120\,cm^{-1}$ for $[ReCl_4(ox)]^{2-}$ or $[ReCl_4(mal)]^{2-}$ [2a,2b]. This unusually strong zero-field splitting is due to the large value of the spin–orbit coupling constant, λ ca $1000\,cm^{-1}$. Another consequence of these $2D$ values is the great magnetic anisotropy characteristic of the Re(IV) complexes.

As far as the second case is concerned, the intermolecular contacts, usually of the type $Re–X \cdots X–Re$ (X being a halogen atom), mediate antiferromagnetic interactions between the paramagnetic centers [1, 3–6]. This effect coexists with the zero-field splitting and both contribute to the decreasing values of $\chi_M T$ with T. The anti-parallel alignment of the individual spins leads to $\chi_M T = 0$ at very low temperatures. In spite of its intermolecular nature, this antiferromagnetic coupling is relatively strong when compared with that observed in similar complexes of the first row transition metal ions and reflects the large degree of spin delocalization of the Re(IV) on the ligands in its complexes [7].

Moreover, some interesting magnetic phenomena arise in some of the compounds exhibiting intermolecular antiferromagnetic interactions. For instance, it has been reported that $K_2[ReI_6]$ behaves as a weak ferromagnet at $T < 24\,K$ due to a spin canting [8]. *Spin canting* means the anti-parallel spins are not strictly collinear in the lattice but form a certain angle between them. Although it is not possible to predict this phenomenon, it is known that a non-centrosymmetric space group of the resulting solid is required [9]. In addition, a large anisotropy may lead to significant spin canting through increasing the possible anti-symmetric super-exchange interaction [10, 11]. Another peculiar example is represented by $[ReCl_4(NH{=}CMeNHPh)_2]$ which exhibits a metamagnetic transition [7]. *Metamagnetism* means that an external magnetic field overcomes the antiferromagnetic coupling leading to a parallel alignment of the local spins (ferromagnetic phase). Although the spin canting and metamagnetism are different phenomena, both require a large anisotropy and in some occasions they have been observed in the same compound [12].

Recently the synthesis, structure, and reactivity of $[ReX_4(bpym)]$ ($X = Cl$ and Br; bpym = 2,2′-bipyrimidine) have been published [13]. As both complexes crystallize in the non-centrosymmetric $P2_12_12_1$ space group, it seemed interesting to investigate their magnetic properties as a function of temperature. The results are reported herein.

2. Experimental

[$ReCl_4$(bpym)] and [$ReBr_4$(bpym)] were synthesized and crystallized as reported in the literature [13]. Magnetic susceptibility measurements (1.9–300 K) were carried out on a Quantum Design SQUID magnetometer under applied magnetic fields of 1 T (**1** and **2**) in the whole temperature range and at 250 G (**1**) and 100 G (**2**) for $T \leq 20$ K. The magnetization measurements were performed at 2.0 K in the field range 0–5 T. The device was calibrated with $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$. Sealed plastic bags of ca 5 mg each and having a diamagnetism of -8.02×10^{-7} cm^3 g^{-1} were used as sample holders. The diamagnetic contribution (in cm^3 mol^{-1}) of the constituent atoms of the compounds was estimated as half their formula weight per 10^{-6} [14, p. 2].

3. Results and discussion

3.1. *X-ray crystal structures of (1) and (2)*

Compounds **1** and **2** are isostructural and crystallize in the space group $P2_12_12_1$. Their structure is discussed elsewhere [13] and here we present only some structural details which are relevant to the discussion of the magnetic properties. The neutral [ReX_4(bpym)] mononuclear units interact with each other in the crystal lattice by van der Waals forces in such a way that direct contacts between the halogens are observed [figure 1(a)]. Values of the shortest intermolecular $X \cdots X$ distances [X = Cl (**1**) and Br (**2**)] are 3.841(1) and 3.852(1) Å [X(4) $\cdots$ X(3a); (a) = $x + 1/2, -y + 1/2, -z$] for **1** and **2**, respectively [figure 1(b)]. The very short Br $\cdots$ Br distance in **2** is nearly identical to the Cl $\cdots$ Cl distance in **1** and somewhat smaller than the van der Waals value (3.90 Å).

3.2. *Magnetic properties of [$ReCl_4$(bpym)] (1)*

The magnetic properties of **1** under the form of $\chi_M T$ *versus* T plot [χ_M is the magnetic susceptibility per mol of Re(IV) ions] are shown in figure 2. At 290 K, $\chi_M T$ is 1.52 cm^3 mol^{-1} K, a value expected for a magnetically isolated mononuclear Re(IV) complex. Upon cooling, this value continuously decreases first smoothly in the high-temperature region and then sharply at $T < 70$ K to reach a minimum at ca 7.0 K. At lower temperatures, it exhibits an abrupt increase and finally decreases with T. This increase is more pronounced at lower external dc magnetic fields where the saturation effects are minimized. The variation of $\chi_M T$ in the high-temperature range for **1** reveals a significant antiferromagnetic interaction between Re(IV) ions. Moreover, the abrupt increase of $\chi_M T$ in the very low-temperature domain can be attributed to spin canting [8, 9]. The great anisotropy of the Re(IV) ion and the antisymmetric exchange (which is compatible with the lack of inversion center in the structure of **1**) account for this phenomenon [10, 11]. Field-cooled magnetization of **1** under 250 G (see inset of figure 2) shows the occurrence of magnetic ordering below 7.0 K. The magnetization saturates at 500 cm^3 mol^{-1} G (at 250 G), a value which indicates the presence of weak ferromagnetism. The cryomagnetic behavior of **1** obeys the Curie–Weiss law in the temperature range 7.0–290 K, yielding $C = 1.62$ cm^3 mol^{-1} K and $\theta = -15.3$ K. The C value for **1** is in agreement with that expected for a Re(IV) ion with $g = 1.86$ and the negative value of

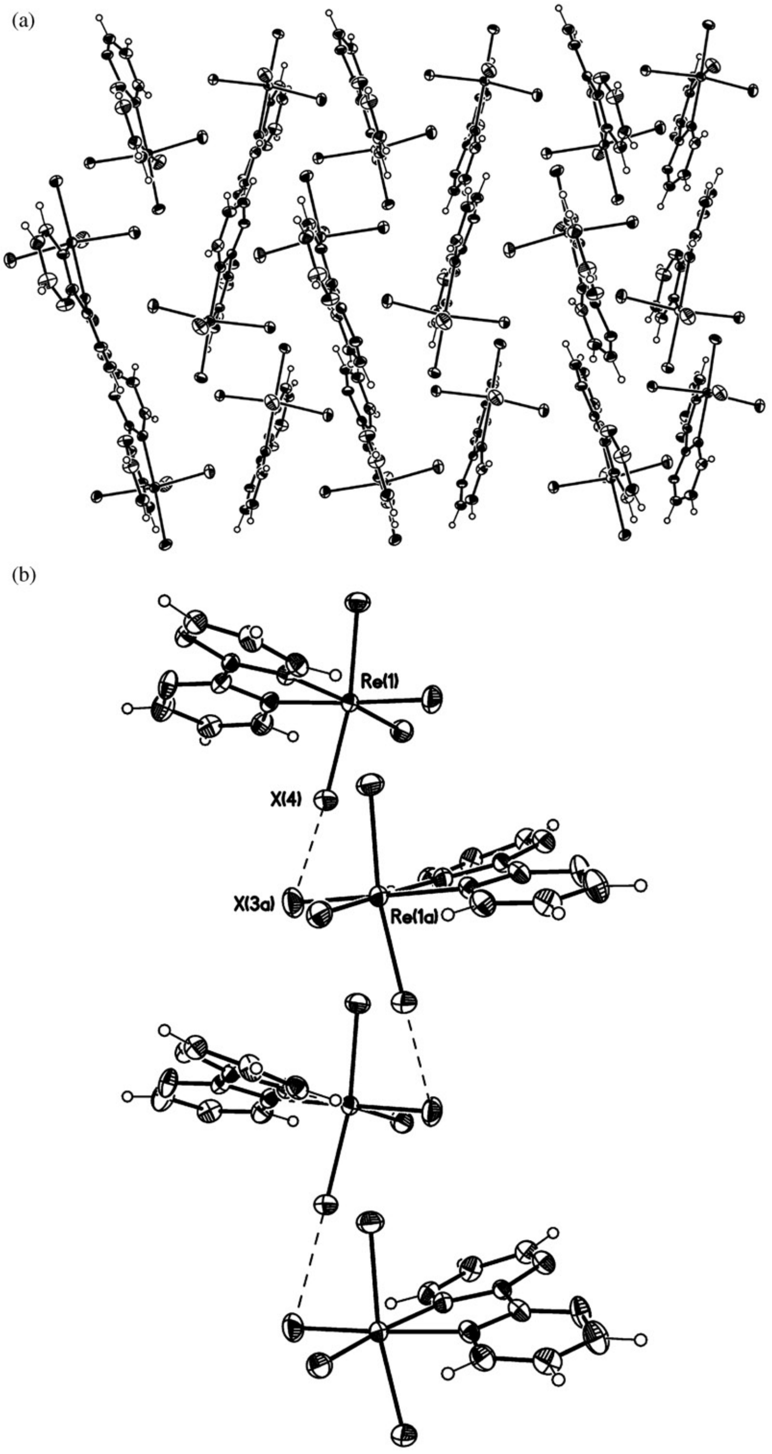

Figure 1. (a) View along the y axis of the crystal packing in **1** and **2**; (b) shortest intermolecular $X\cdots X$ distances [$X=\mathrm{Cl}$ (**1**) and Br (**2**)] shown as broken lines. Thermal ellipsoids are drawn at the 30% probability level.

θ corresponds to the upper value of the intermolecular antiferromagnetic interaction [because of the inclusion in this term of a large zero-field splitting of the Re(IV)].

The hysteresis loop of **1** at 2.0 K (figure 3) shows values of the coercive field (H_c) and remnant magnetization (M_r) of 1750 G and 0.05 μ_B, respectively. The magnetization *versus* H plot shows a saturation value (M_S) of 2.78 μ_B at 5 T (which agrees with a $S = 3/2$ ion with $g = 1.86$). The evaluation of the canting angle (α) in **1** can be obtained through equation (1) [14, p. 322],

$$\sin a = M_c / M_S \tag{1}$$

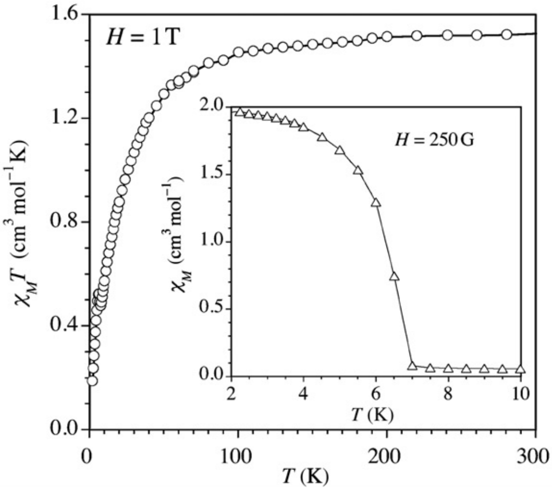

Figure 2. Temperature dependence of the $\chi_M T$ product for **1** at $H = 1$ T. The inset shows theχ_M against T plot at 250 G in the very low-temperature region. The solid lines are visual guides.

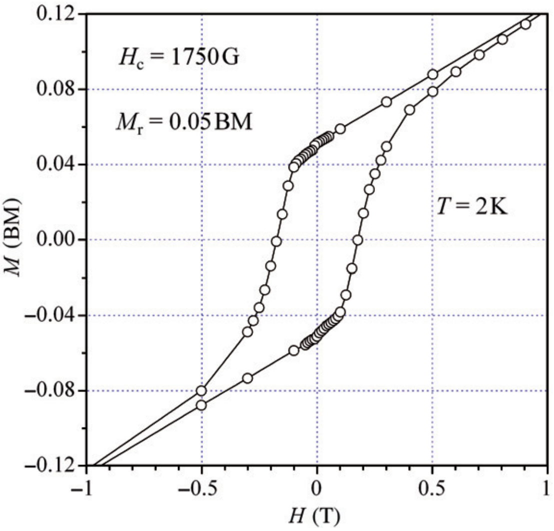

Figure 3. Hysteresis loop of **1** at 2.0 K.

where M_c is the magnetization induced by a weak magnetic field. A value of $\alpha = 1.8°$ can be estimated with $M_c = 0.088\,\mu_B$. This value lies within the range of those usually reported for systems exhibiting weak ferromagnetism [15].

3.3. *Magnetic properties of [ReBr$_4$(bpym)]*

The magnetic properties of **2** (figures 4 and 5) are very close to those of **1**. The $\chi_M T$ *versus* T plot of **2** exhibits a continuous decrease from room temperature ($\chi_M T = 1.49\,\mathrm{cm^3\,mol^{-1}\,K}$) to reach a minimum of $0.75\,\mathrm{cm^3\,mol^{-1}\,K}$ at 20 K, then an

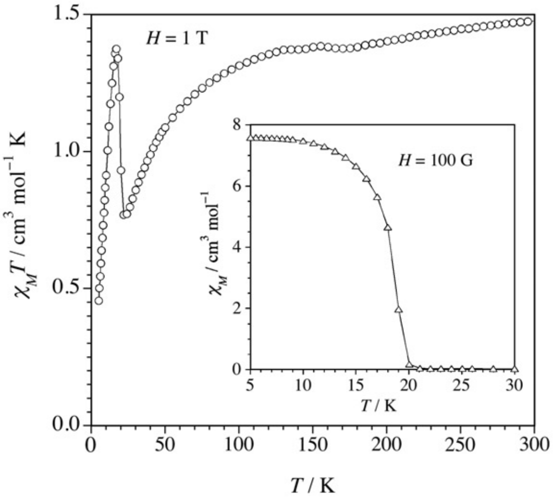

Figure 4. Temperature dependence of the $\chi_M T$ product for **2** at $H = 1$ T. The inset shows the χ_M against T plot at 100 G in the very low-temperature region. The solid lines are visual guides.

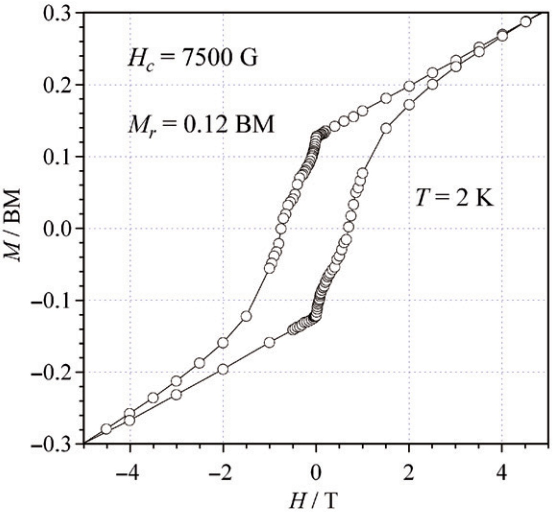

Figure 5. Hysteresis loop of **2** at 2.0 K.

abrupt increase, and finally a sharp decrease to $0.45\,\mathrm{cm^3\,mol^{-1}\,K}$ at 1.9 K. As in **1**, the increase of $\chi_M T$ in the low-temperature region is more pronounced at lower DC magnetic fields where the saturation effects are minimized. The magnetic behavior of **2** corresponds thus to a spin-canted structure. Field-cooled magnetization of **2** under 100 G (see inset of figure 4) shows the occurrence of magnetic ordering below 20.0 K. The magnetization saturates at $750\,\mathrm{cm^3\,mol^{-1}\,G}$ (at 100 G), a value which indicates the presence of a weak ferromagnetism. The magnetic data of **1** follow the Curie–Weiss law in the temperature range 30.0–290 K, yielding $C = 1.58\,\mathrm{cm^3\,mol^{-1}\,K}$ and $\theta = -22.5$ K. The C value for **2** is in agreement with that expected for a Re(IV) ion, with $g = 1.84$ and the negative value of θ corresponds, as in **1**, to the upper value of the intermolecular antiferromagnetic interaction.

The hysteresis loop of **2** at 2.0 K (figure 5) shows values of the coercive field (H_c) and remnant magnetization (M_r) of 7500 G and $0.12\,\mu_B$, respectively. The magnetization *versus* H plot shows a saturation value (M_S) of $2.76\,\mu_B$ at 5 T (which agrees with a $S = 3/2$ ion with $g = 1.84$). The value for the canting angle in **2** through equation (1) with $M_c = 0.124$, μ_B is 2.5°. This value compares well with that estimated for **1**.

We would like to end this discussion by comparing **1** and **2** with the related complex [ReCl$_4$(bpy)] (bpy = 2,2-bipyridine). Although this last compound crystallizes also in a non-centrosymmetric space group [16], it does not exhibit spin canting [2f]. The only remarkable difference in the molecular structure of [ReCl$_4$(bpy)] with respect to that of **1** and **2** is the quasi planarity of the bidentate bpy ligand, whereas the two heterocyclic rings of the bpym ligand form a dihedral angle of 16.0° (**1**) and 16.8° (**2**) [13]. However, it is not clear if this difference is relevant for the magnetism.

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