Magnetic Properties of the Two-Dimensional Bimetallic Compounds $(NBu_4)[M^{II}Ru^{III}(ox)_3]$ (NBu_4 = Tetra-*n*-butylammonium; M = Mn, Fe, Cu; ox = Oxalate)

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Three compounds of general formula $(NBu_4)[M^{II}Ru^{III}(ox)_3]$ have been synthesized; NBu_4^+ stands for tetra-*n*-butylammonium, M for Mn, Fe, and Cu, and ox^{2-} for the oxalate dianion. The X-ray powder patterns for the three derivatives have revealed that these compounds are isostructural with $(NBu_4)[Mn^{II}Cr^{III}(ox)_3]$, whose crystal structure was known, and the cell parameters have been refined in the *R*3*c* space group. The $(NBu_4)[M^{II}Ru^{III}(ox)_3]$ compounds are new examples of two-dimensional bimetallic assemblies with oxalate bridges. The temperature (*T*) dependences of the magnetic susceptibility (χ_M) in both the dc and ac modes and the field dependences of the magnetization have been investigated. The local spins are $S_{Ru} = S_{Cu} = {}^1/_2$, $S_{Mn} = {}^5/_2$, and $S_{Fe} = 2$. The $Ru^{III}-M^{II}$ interaction has been found to be antiferromagnetic for M = Fe and Cu and ferromagnetic for M = Mn. The two compounds $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ and $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$ exhibit a ferrimagnetic behavior, characterized by a minimum in the χ_MT versus *T* plots. $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ exhibits a long-range magnetic ordering at $T_c = 13 \pm 1$ K. A slight frequency dependence of the out-of-phase ac magnetic response has been observed. The field dependence of the magnetization in the magnetically ordered state has revealed a rather strong coercivity, with a coercive field of 1.55 kOe at 2 K. A theoretical model has been used to determine the magnitude of the $Ru^{III}-M^{II}$ interactions, with M = Mn and Fe. This model is based on a quantum−classical spin approach together with Monte Carlo simulations. The interaction parameters have been found as $J = 1.04$ cm^{-1} for $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ and -9.7 cm^{-1} for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$, with a spin Hamiltonian of the type $-J\sum_{i,j}\mathbf{S}_{Ru,i}\cdot\mathbf{S}_{M,j}$. The magnetic properties of these compounds have been discussed. In particular, it has been emphasized that the symmetry rules governing the nature and the magnitude of the interaction between two 3d magnetic metal ions seem not to be valid anymore for 4d ions such as Ru^{III}.

Introduction

In 1990 Okawa, Kida, and co-workers reported on the synthesis and the magnetic properties of oxalate-bridged polymeric compounds of general formula $cat[M^{II}Cr^{III}(ox)_3]$, where cat^+ stands for a monovalent cation, ox^{2-} stands for the oxalate dianion, and M^{II} stands for a divalent metal ion. For M = Mn, Fe, Co, and Cu, the $Cr^{III}-M^{II}$ interaction was found to be ferromagnetic, and long-range ferromagnetic orderings were observed in the 6−14 K temperature range.[1−3] A three-dimensional structure was postulated. Subsequently, it has been shown by Atovmyan et al.[4] and then by Decurtins *et al.*[5] that the structure was two-dimensional with honeycomb layers and cat^+ cations located between the layers. The Cr^{III} and M^{II} ions alternate at the corners of the hexagons. Within each layer all the Cr^{III} sites have the same chirality (Λ or Δ) and all the M^{II} sites have the other chirality. The whole structure is nonchiral. If Cr^{III} and M^{II} had the same chirality, the hexagons of the honeycomb structure could no longer be closed, and the structure would be three- instead of two-dimensional. This structure would obviously be chiral. Such a chiral three-dimensional structure has been reported for the first time by Decurtins et al.[6−10]

The compounds $cat[M^{II}Cr^{III}(ox)_3]$ are synthesized using $[Cr^{III}(ox)_3]^{3-}$ as a precursor. Other oxalate-bridged polymeric compounds were obtained using $[Fe^{III}(ox)_3]^{3-}$ as a precursor. Their formula is $cat[M^{II}Fe^{III}(ox)_3]$.[11−15] In all the cases where M^{II} is magnetic, the $Fe^{III}-M^{II}$ interaction has been found to be antiferromagnetic, and the compounds behave as ferrimagnets

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with long-range orderings around 40 K for M = Fe and Ni or canted antiferromagnets for M = Mn.

In the field of molecular magnetism the most extensively used spin carriers are organic radicals along with 3d transition metal ions. In a few cases lanthanide ions were also utilized.[16] On the other hand, the number of studies dealing with 4d and 5d metal ions are still rather limited.[17−21] That is why we have decided to initiate a new project dealing with such 4d and 5d metal ions. This paper is the first one along this line; it is devoted to oxalate-bridged polymeric compounds synthesized from the precursor $[\mathrm{Ru^{III}(ox)_3}]^{3-}$. More precisely, three compounds will be investigated, of formula $(\mathrm{NBu_4})[\mathrm{M^{II}Ru^{III}(ox)_3}]$, with $\mathrm{NBu_4}^+$ = tetra-*n*-butylammonium and M = Mn, Fe, and Cu.

The questions we ask ourselves concerning the magnetic properties of molecular species involving 4d or 5d metal ions may be summed up as follows: (i) The orbital diffuseness follows the sequence 5d > 4d > 3d. Does the more diffuse character of singly occupied orbitals affect the magnitude of the interaction between magnetic centers? (ii) The ground state of species containing 4d or 5d metal ions derives from a strong-field configuration. For instance, while the ground state of $[\mathrm{Fe^{III}(ox)_3}]^{3-}$ is $^6A_1$, referring to the octahedral symmetry, that of $[\mathrm{Ru^{III}(ox)_3}]^{3-}$ is $^2T_2$. The metal−ligand bonds around 4d and 5d metal ions are more covalent. What is the consequence of this strong-field (low-spin) configuration on the magnitude of the magnetic interaction? Of course, this point is strongly correlated to the previous one concerning the diffuseness of the d orbitals. (iii) The spin−orbit coupling is more important for 4d and 5d than for 3d ions, and the relativistic effects may become crucial. This spin−orbit coupling mixes the symmetry orbitals, so that the eigenfunctions of the system do not transform as the irreducible representations of the symmetry group anymore. To what extend does the relativistic effects affect the symmetry rules governing the nature and the magnitude of the interaction between 3d metal ions?

Experimental Section

Syntheses. The precursor $\mathrm{K_3[Ru(ox)_3]\cdot4.5H_2O}$ was synthesized according to a procedure significantly different from that already described.[22] The first step consisted in the synthesis of pure $\mathrm{Ru^{III}}$ hydroxide. A solution of 370 × 10^{-3} g of potassium hydroxide dissolved in 2 mL of water was added dropwise to a solution of 500 × 10^{-3} g of $\mathrm{Ru^{III}}$ chloride dissolved in 4 mL of water. The mixture was stirred for 20 min. The $\mathrm{Ru^{III}}$ hydroxide was then filtered out and washed several times with water under rigorous stirring, until the $\mathrm{AgNO_3}$ test showed the absence of chloride ions. $\mathrm{K_3[Ru(ox)_3]\cdot4.5H_2O}$ was then synthesized as follows: 100 × 10^{-3} g of freshly prepared $\mathrm{Ru^{III}}$ hydroxide was added to a boiling solution of 220 × 10^{-3} g of oxalic acid in 2 mL of water, and the mixture was refluxed (130 °C) until the solution became limpid with a olive-green color (ca. 30 mn). A 120 × 10^{-3} g amount of potassium oxalate was then slowly added, and the solution was refluxed again for 20 min. Afterward, this solution was cooled to 40 °C and then poured into 25 mL of ethanol. $\mathrm{K_3[Ru(ox)_3]\cdot4.5H_2O}$ precipitated as a yellow-green solid and was recrystallized in water. The yield with respect to $\mathrm{Ru^{III}}$ was 70%.

Table 1. Unit Cell Parameters (Å) in the *R*3*c* Space Group for the Compounds $(\mathrm{NBu_4})[\mathrm{M^{II}Ru^{III}(ox)_3}]$ with M = Mn, Fe, and Cu

	M = Mn	M = Fe	M = Cu
a = *b*	9.381	9.432	9.312
c	53.99	53.49	53.98

$(\mathrm{NBu_4})[\mathrm{Fe^{II}Ru^{III}(ox)_3}]$ was obtained by adding successively 44 × 10^{-3} g of $\mathrm{Fe^{II}}$ sulfate and 66 × 10^{-3} g of tetra-*n*-butylammonium chloride to a solution of 100 × 10^{-3} g of $\mathrm{K_3[Ru(ox)_3]\cdot4.5H_2O}$ dissolved in 2 mL of water. The resulting solution was stirred for 30 min, and a microcrystalline powder precipitated. The compound was filtered out, washed with water and methanol, and dried under vacuum. The yield was 60%. Anal. Calcd for $\mathrm{C_{22}H_{36}NO_{12}FeRu}$: C, 39.83; H, 5.47; N, 2.11; Fe, 8.42; Ru, 15.23. Found: C, 39.51; H, 5.21; N, 1.93; Fe, 8.57; Ru, 15.11.

$(\mathrm{NBu_4})[\mathrm{Mn^{II}Ru^{III}(ox)_3}]$ and $(\mathrm{NBu_4})[\mathrm{Cu^{II}Ru^{III}(ox)_3}]$ were synthesized in the same way, replacing $\mathrm{Fe^{II}}$ sulfate by $\mathrm{Mn^{II}}$ sulfate and $\mathrm{Cu^{II}}$ sulfate, respectively. Anal. Calcd for $\mathrm{C_{22}H_{36}NO_{12}MnRu}$: C, 39.88; H, 5.48; N, 2.11; Mn, 8.29; Ru, 15.25. Found: C, 39.39.; H, 5.01; N, 1.95; Mn, 8.17; Ru, 15.01. Calcd for $\mathrm{C_{22}H_{36}NO_{12}CuRu}$: C, 39.37; H, 5.41; N, 2.09; Cu, 9.47; Ru, 15.06. Found: C, 39.02; H, 5.05; N, 1.95; Cu, 9.61; Ru, 15.21.

Magnetic Measurements. These were carried out on powder samples with a Quantum Design MPMS-5S SQUID magnetometer working down to 2 K in both dc and ac modes. The $\chi_M T$ versus T curves, χ_M being the molar magnetic susceptibility (defined as the ratio M/H of the magnetization by the magnetic field) and T the temperature, were recorded with a magnetic field of 1 kOe. The diamagnetic correction was estimated as 305 × 10^{-6} emu mol^{-1} for the three compounds. The EPR spectra were recorded with a Bruker ER 200 spectrometer equipped of a frequency meter and a hall probe.

X-ray Data. The powder diffraction profiles were recorded at room temperature on a Philips PW 1050 diffractometer using Cu Kα radiation. For the three compounds the X-ray powder patterns were found to be very close to that of $(\mathrm{NBu_4})[\mathrm{Mn^{II}Cr^{III}(ox)_3}]$, whose crystal structure has been solved by Atovmyan *et al.*[4] $(\mathrm{NBu_4})[\mathrm{Mn^{II}Cr^{III}(ox)_3}]$ crystallizes in the *R*3*c* space group, and for each of our compounds the reflections were indexed and the unit cell parameters were refined in this space group. These cell parameters are given in Table 1.

Magnetic Properties: A Qualitative Approach

In this section we will treat first $(\mathrm{NBu_4})[\mathrm{Fe^{II}Ru^{III}(ox)_3}]$, which is a magnet with $T_c = 13 \pm 1$ K, and then the manganese and copper derivatives, which show no long-range magnetic ordering above 2 K.

$(\mathbf{NBu_4})[\mathbf{Fe^{II}Ru^{III}(ox)_3}]$. We will successively discuss the temperature dependence of the molar magnetic susceptibility both in dc and ac modes and the field dependence of the magnetization.

The $\chi_M T$ versus T curve is shown in Figure 1. At room temperature $\chi_M T$ is equal to 3.4 emu K mol^{-1}, which roughly corresponds to what is expected for isolated $\mathrm{Ru^{III}}$ and $\mathrm{Fe^{II}}$ magnetic centers, with the local spins $S_{\mathrm{Ru}} = {}^1/_2$ and $S_{\mathrm{Fe}} = 2$, respectively. As T is lowered, $\chi_M T$ remains constant down to ca. 130 K, then decreases very smoothly, and reaches a minimum value around 62 K with $\chi_M T = 3.24$ emu K mol^{-1}. As T is lowered further, $\chi_M T$ increases very rapidly up to a maximum value around 10 K. This maximum value of $\chi_M T$ depends on the applied field. The minimum in the $\chi_M T$ versus T curve, even if it is weakly pronounced, indicates a ferrimagnetic behavior with a $\mathrm{Ru^{III}}$−$\mathrm{Fe^{II}}$ antiferromagnetic interaction. The low-temperature data suggest that the compound exhibits a long-range magnetic ordering. This is confirmed by the field-cooled-magnetization (FCM) and remnant (REM) magnetization curves displayed in Figure 2. The FCM curve obtained in

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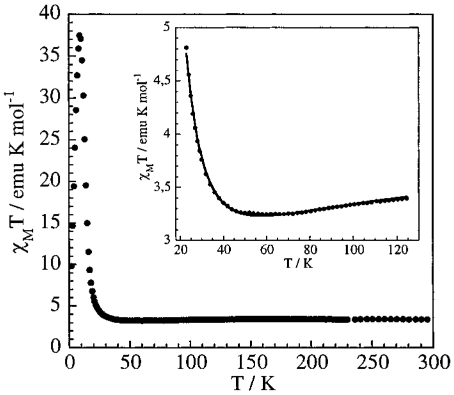

Figure 1. $\chi_M T$ versus T curve for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$. The insert emphasizes the minimum of $\chi_M T$ together with the calculated curve as a full line.

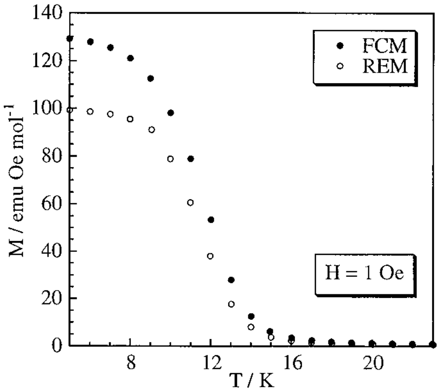

Figure 2. Field-cooled-magnetization (FCM) and remnant magnetization (REM) curves for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$. The applied magnetic field is 1 Oe.

cooling the sample within a field of 1 Oe shows a break around 13 K. The REM curve obtained in turning the field off at 2 K and then warming the sample in zero field is typical of a magnet. The remnant magnetization vanishes around 13 K.

Further information on the three-dimensional ordering is provided by the temperature dependences of the ac magnetic responses shown in Figure 3. Both the in-phase, χ', and out-of-phase, χ'', ac magnetic susceptibilities present a maximum which depends very slightly on the frequency of the oscillating field. For instance, the maximum of χ' passes from 10 K at 1 Hz up to 12 K at 1000 Hz, and the maximum of χ'' passes from 10 K at 1 Hz to 9.2 K at 1000 Hz. Let us note that χ'' is different from zero below 14 K. The frequency dependence may arise either from a structural disorder conferring a certain spin glass character to the material or from the very small size of the microcrystalline particles conferring a certain superparamagnetic character to this material. The X-ray powder pattern reveals that the compound is very well crystallized, so that the latter interpretation seems to us to be more likely. In any case, this frequency dependence is weakly pronounced as compared to what is expected for a genuine superparamagnet.[23] The problem we are faced with is to determine the critical temperature T_c from the dc and ac magnetic data. Some authors (including ourselves in some previous papers) determine T_c as the maximum of χ''. Such an approach might be questionable, in particular for magnets involving magnetically anisotropic spin carriers. For such compounds, we observed that the vanishing of the remnant magnetization systematically occurs at a few kelvin above the maximum of χ'' but corresponds to the temperature below which χ'' is not longer zero. In the present case, owing to the slight frequency dependence of the ac magnetic responses and the magnetic anisotropy of the compound (vide infra), T_c is determined with a certain uncertainty as 13 ± 1 K.

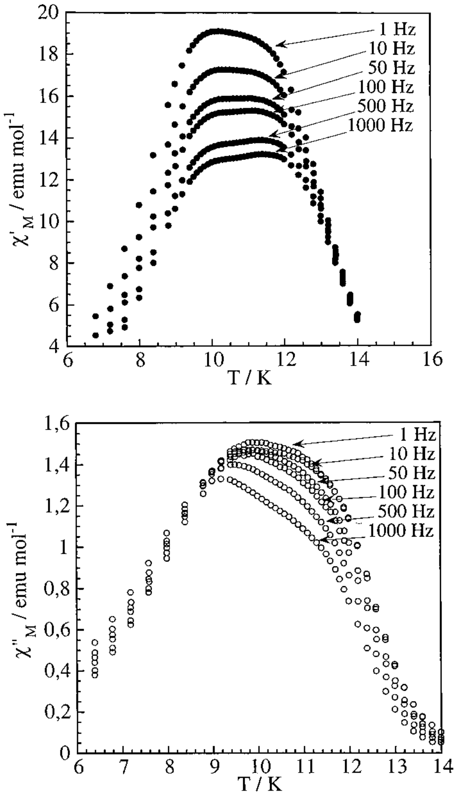

Figure 3. In-phase, χ', and out-of-phase, χ'', ac molar magnetic susceptibilities at different frequencies for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$.

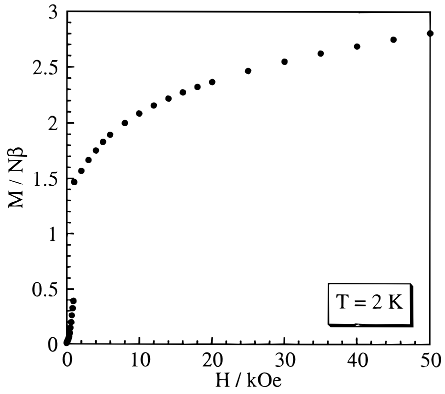

Figure 4. Field dependence of the magnetization at 2 K for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$.

The field dependence of the magnetization, $M = f(H)$, at 2 K is given in Figure 4. The magnetization increases very rapidly in low field, as expected for a magnet, and then increases much smoother above 10 kOe. The magnetization under 50 kOe is found equal to $2.8N\beta$, which is slightly below the expected saturation value (about $3N\beta$). The maximum of $\partial M/\partial H$ is not observed in zero field but around 1 kOe. This behavior indicates that a certain coercive field is required to orient the domains. The coercivity is confirmed by the magnetic hysteresis loop at 2 K of Figure 5. The coercive field is found as 1.55 kOe. It is well established that the coercivity of a magnet is governed by

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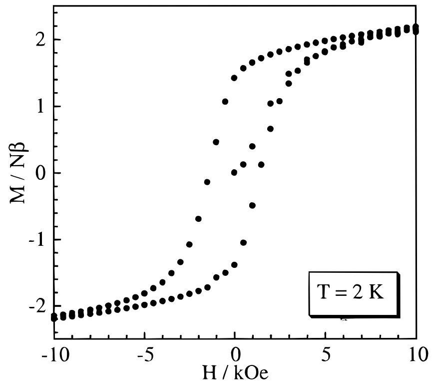

Figure 5. Magnetic hysteresis loop at 2 K for (NBu$_4$)[Fe^{II}Ru^{III}(ox)$_3$].

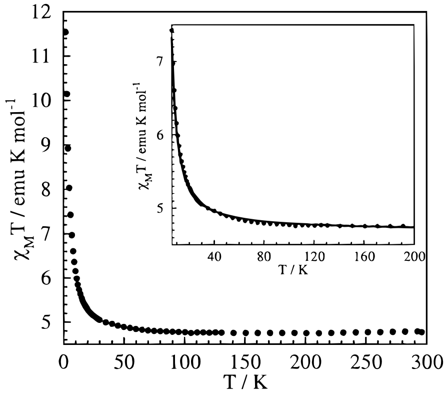

Figure 6. $\chi_M T$ versus T curves for (NBu$_4$)[Mn^{II}Ru^{III}(ox)$_3$]. The insert shows the calculated curve as a full line.

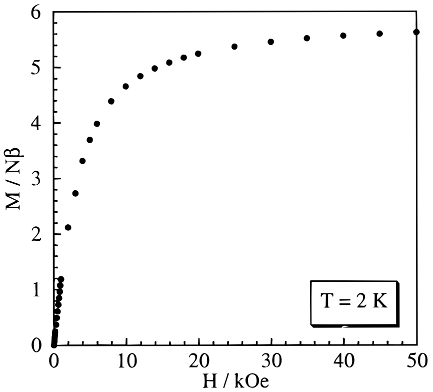

Figure 7. Field dependence of the magnetization at 2 K for (NBu$_4$)[Mn^{II}Ru^{III}(ox)$_3$].

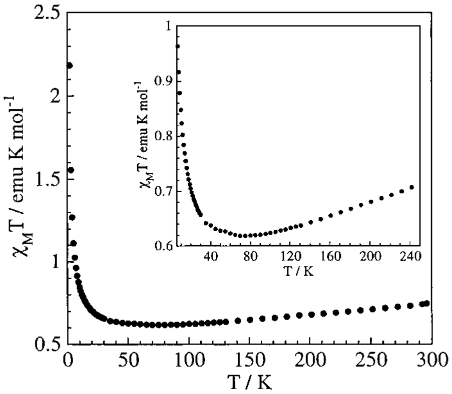

Figure 8. $\chi_M T$ versus T curve for (NBu$_4$)[Cu^{II}Ru^{III}(ox)$_3$]. The insert emphasizes the minimum of $\chi_M T$.

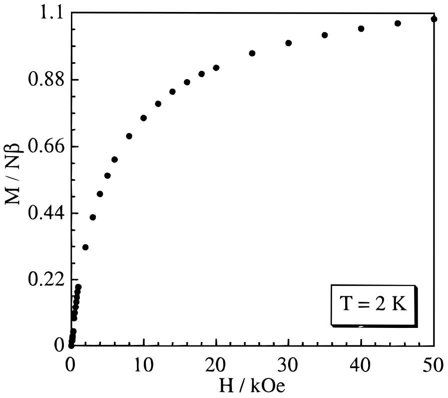

Figure 9. Field dependence of the magnetization at 2 K for (NBu$_4$)[Cu^{II}Ru^{III}(ox)$_3$].

both chemical and structural factors. The chemical factors refer to the magnetic anisotropy of the spin carriers, and the structural factors to the size and the shape of the particles.[24,25] In the present case, both Ru^{III} and Fe^{II} in distorted octahedral surroundings are orbital triplet ions, with a first-order orbital momentum; therefore, these ions possess a certain magnetic anisotropy.[26]

(NBu$_4$)[Mn^{II}Ru^{III}(ox)$_3$]. The $\chi_M T$ versus T curve for this compound is shown in Figure 6. In contrast with the preceding case, the shape of the curve reveals Ru^{III}−Mn^{II} ferromagnetic interactions. As a matter of fact, $\chi_M T$ is equal to 4.8 emu K mol^{-1} at room temperature and increases continuouly and more and more rapidly as T is lowered. At 2 K, however, the $\chi_M T$ value is only equal to 11.7 emu K mol^{-1}; the correlation length within the two-dimensional lattice is still limited, and the long-range ordering most likely occurs much below 2 K. The ac magnetic response does not show any peak down to 2 K.

The field dependence of the magnetization, $M = f(H)$, at 2 K given in Figure 7 shows a very rapid increase of M in low field and then a saturation at higher field, with a saturation magnetization of the order of $6N\beta$, in perfect agreement with a parallel alignment of the Ru^{III} and Mn^{II} magnetic moments. It was checked that the magnetization curve is above the sum of the Brillouin functions for $S_{Mn} = {}^5/_2$ and $S_{Ru} = {}^1/_2$ uncorrelated spins.

(NBu$_4$)[Cu^{II}Ru^{III}(ox)$_3$]. The $\chi_M T$ versus T curve for this compound is shown in Figure 8. At room temperature $\chi_M T$ is equal to 0.75 emu K mol^{-1}, which is a little bit smaller than expected for isolated Ru^{III} and Cu^{II} ions. As T is lowered, $\chi_M T$ decreases, reaches a minimum around 75 K with $\chi_M T = 0.61$ emu K mol^{-1}, and then increases. The $\chi_M T$ value at 2 K is 2.18 emu K mol^{-1}. Again, this curve reveals a ferrimagnetic behavior. What is particularly interesting in the present case is that both the Ru^{III} and Cu^{II} ions carry a local spin ${}^1/_2$, but the magnetic moments $g_{Ru}S_{Ru}$ and $g_{Cu}S_{Cu}$ do not exactly compensate owing to the difference in the local Zeeman factors, g_{Ru} and g_{Cu}.

The field dependence of the magnetization at 2 K is given in Figure 9. The magnetization varies linearly with the field up to ca. 6 kOe and then progressively saturates. The magnetization at 50 kOe is equal to $1.08N\beta$.

Let us also mention that for the three compounds the powder EPR spectra were recorded at various temperatures in X band.

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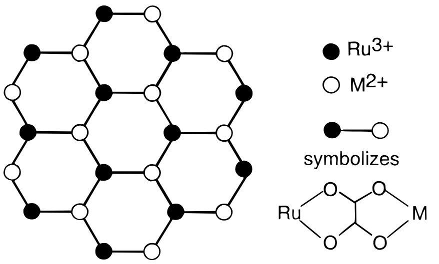

Figure 10. Spin topology in the $(NBu_4)[M^{II}Ru^{III}(ox)_3]$ compounds.

The Fe^{II} and Cu^{II} derivatives are EPR silent, while the Mn^{II} derivative gives a single symmetric feature centered at $g = 2.00$.

Magnetic Properties: A Quantative Approach

Two of us have recently developed a theoretical model in order to interpret the thermodynamical properties of various types of two-dimensional mixed-spin lattices, including the honeycomb lattice of the $(NBu_4)[M^{II}Ru^{III}(ox)_3]$ compounds,[27,28] for which the spin topology is recalled in Figure 10. The requirements of this model are the following: (i) One of the two magnetic centers should have a spin large enough to be treated as a classical spin. (ii) Each quantum spin should only interact with classical spins. (iii) The interaction between adjacent spins carriers should be of the Heisenberg type. When these requirements are fulfilled, the quantum Hamiltonian can be replaced by a classical Hamiltonian with effective ferromagnetic interactions. The thermodynamical properties can then be computed using Monte Carlo simulations.

We do not intend to develop here the formalism which can be found elesewhere.[28] On the other hand, we would like to see to what extend the model is valid for our compounds. The first requirement may be assumed to be fulfilled for $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ and $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$. Both $S_{Mn} = {}^5/_2$ and $S_{Fe} = 2$ will be treated as classical spins, and of course S_{Ru} must be treated as a quantum spin. In contrast, the quantum−classical model is clearly not adapted to $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$. The second requirement is obviously fulfillled for the honeycomb topology considered in this paper (see Figure 10). The third requirement, on the other hand, is the most questionable. The spin Hamiltonian considered in the model is

$$\mathbf{H} = -J\sum_{i,j}\mathbf{S}_{\mathrm{Ru},i}\cdot\mathbf{S}_{\mathrm{M},j} + \left(g_{\mathrm{Ru}}\sum_{i}\mathbf{S}_{\mathrm{Ru},i} + g_{\mathrm{M}}\sum_{j}\mathbf{S}_{\mathrm{M},j}\right)\cdot\beta H \quad (1)$$

where the index M refers to the classical spin ion, Mn^{II} or Fe^{II}. In eq 1 both single-ion anisotropy for the M^{II} ion and anisotropic interaction have been neglected. The single-ion anisotropy is very weak for Mn^{II} with a $^6A_1$ ground state (referring to the octahedral symmetry) but may be nonnegligible for Fe^{II} with a $^5T_2$ ground state. Moreover, not only Fe^{II}, but also Ru^{III} with a $^2T_2$ ground state, has a first-order orbital momentum, which could induce an anisotropic component to the $Ru^{III}-M^{II}$ interaction. In the following, we assume that the Hamiltonian (1) is valid. In ref 28 the Monte Carlo simulation results are given in the form of a list of numbers. It is obviously more convenient to use an algebraic expression to fit the experimental data. We propose here such an expression, valid for honeycomb lattices with alternation of quantum S_{Ru} and classical S_M spins at the corners of the hexagons and for $T \gg |J|S/2$. This expression is

$$\chi_M T = (3/8)[S^2 g_M^2 y_1 - S g_M g_{Ru} y_2/2 + g_{Ru}^2 y_3/4] \quad (2)$$

with

$$y_1 = 0.3353 + 0.0186K + 0.5049K^2 + 0.4534K^3$$

$$y_2 = -0.0009 + 2.0583K - 0.3351K^2 + 1.8454K^3$$

$$y_3 = 1.0095 + 0.0214K + 1.1352K^2 + 0.5341K^3 \quad (3)$$

and

$$K = -JS/2kT \quad (4)$$

$$S = [S_M(S_M + 1)]^{1/2} \quad (5)$$

For $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ a least-squares fitting of the magnetic susceptibility data down to 20 K led to $J = -9.7$ cm^{-1}, $g_{Ru} = 2.10$, and $g_{Fe} = 2.13$. For $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ the fitting was performed down to 5 K. The parameters were found as $J = 1.04$ cm^{-1}, $g_{Ru} = 2.1$, and $g_{Mn} = 1.97$. The experimental and calculated magnetic susceptibility data are compared in Figures 1 and 6. In both cases the agreement is quite satisfying. In particularly, in the case of $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ the minimum in the $\chi_M T$ versus T curve is vell described.

Discussion

In this last section we would like to discuss about the new insights arising from this work, as compared to what was already known concerning the two-dimensional oxalate-bridged compounds. At least three aspects deserve to be approached, namely the nature of the $Ru^{III}-M^{II}$ interactions, the quantitative interpretation of the magnetic susceptibility data for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ and $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$, and the very peculiar case of the $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$ compound.

Nature of the $Ru^{III}-M^{II}$ Interaction. It is now well understood that the nature of the interaction between two 3d magnetic centers to a large extend is governed by the relative symmetries of the magnetic orbitals.[26] A nonzero overlap integral between two magnetic orbitals favors an antiferromagnetic (AF) contribution, while a zero overlap integral favors a ferromagnetic (F) contribution, provided that the overlap density between these orbitals is important. When the interaction occurs between ions carrying more than one unpaired electron, the nature of this interaction is given by the weighted sum of the various contributions involving pairs of magnetic orbitals. Most often, when both AF and F contributions are present, the former dominate, and the overall interaction is AF. These rules explain why the $Cr^{III}-Cu^{II}$ or $Cr^{III}-Ni^{II}$ interaction through the oxalate bridge is F. Indeed, Cr^{III} in octahedral surroundings has three unpaired electrons occupying t_{2g} orbitals; Cu^{II} in Jahn−Teller distorted surroundings has one unpaired electron occupying a $d_{x^2-y^2}$-type orbital arising from the e_g subset, and Ni^{II} in octahedral surroundings has two unpaired electrons occupying e_g orbitals. The $Cr^{III}-Mn^{II}$ and $Cr^{III}-Fe^{II}$ interactions through the oxalate bridge were also found to be F. In these two cases the symmetry analyses are not straigthforward. Both some AF and many more F contributions are involved, and those latter apparently dominate. In the case of compounds prepared from the $[Fe^{III}(ox)_3]^{3-}$ precursor, the interaction seems to be always AF. Fe^{III} in octahedral surroundings has five unpaired electrons occupying the five d-type orbitals. There is always at least one

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of these magnetic orbitals which gives a nonzero overlap integral with any magnetic orbital centered on the other magnetic ion. To sum up the situation observed with the oxalate-bridged species involving two 3d ions, one can say that when the orthogonality of the magnetic orbitals is achieved, the interaction is F.

For the compounds with M = Fe and Cu studied in this paper the $Ru^{III}-M^{II}$ interaction was found to be AF, and for M = Mn it was found to be F. The case of $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ is rather difficult to analyze. Indeed, the very weak interaction involves both AF and F contributions, assuming that the symmetry rules are valid. On the other hand, the case of $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$ is particularly interesting since the nature of the interaction does not respect the symmetry rules recalled above. Indeed, Ru^{III} in octahedral surroundings has a low-spin state arising from the $(t_{2g})^5$ configuration. Each of the t_{2g} orbitals centered on the Ru atom is orthogonal with the $d_{x^2-y^2}$-type magnetic orbital of Cu^{II}. The symmetry rules which have been proved to be so heuristic to analyze the magnetic properties of polymetallic compounds containing only 3d metal ions seem to be no longer valid for Ru^{III}. Probably, the relativistic effects become crucial. A simple formulation would be that the strong spin−orbit coupling mixes the symmetry orbitals, so that the eigenfunctions cannot be labeled anymore with the irreducible representations of the symmetry point groups.

Quantitative Interpretation of the Magnetic Susceptibility Data for $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ and $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$. To the best of our knowledge this paper is the very first one dealing with two-dimensional oxalate-bridged compounds in which a quantitative interpretation of some magnetic susceptibility data is proposed. One of the aims of molecular magnetism is to create new spin topologies, and in most of the cases no theoretical model is available to interpret quantitatively the thermodynamical properties associated with these topologies. It is perhaps the mission of the researchers working in this area to create not only their chemical objects but also the theoretical models adapted to these objects. Up to know, most of the models were limited to one-dimensional compounds; such models do exist for regular and alternating chains, mixed spin chains, ladder-type double chains, etc.[26] We recently decided to focus on models suitable to two-dimensional lattices. Two types of such lattices are of particular interest to us, because they correspond to real systems. Both refer to honeycomb spin topologies, with quantum and classical spins. The former lattice corresponds to the $cat_2Mn[Cu(opba)]_3 \cdot S$ compounds, where opba stands for *ortho*-phenylenebis(oxamato) and S for solvent molecules; the classical spins are located at the corners of the hexagons, and the quantum spins at the middles of the edges.[25] The latter lattice corresponds to two-dimensional oxalate-bridged compounds cat[MM′(ox)$_3$]. In the present work a very satisfying theoretical simulation of the $\chi_M T$ versus T curve was obtained for both $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ with AF interactions and $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ with F interactions.

At this stage, we may wonder whether the fact that $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ exhibits a long-range magnetic ordering at 13 K and $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ does not order down to 2 K is due to the differences of $|J|$ values. Actually, the situation is more complicated. The long-range magnetic ordering results from three factors, the intra- and interlayer interactions and the two-dimensional magnetic anisotropy.[25] In $(NBu_4)[Fe^{II}Ru^{III}(ox)_3]$ not only the intralayer interaction is larger (in absolute value) than in the Mn^{II} derivative but also the magnetic anisotropy is expected to be more pronounced.

To obtain more information on the interlayer interactions, we synthesized a large number of cat$[M^{II}Ru^{III}(ox)_3]$ compounds with cat$^+$ cations of various sizes. All the cat$[Fe^{II}Ru^{III}(ox)_3]$ compounds present a three-dimensional magnetic transition in the 8−12 K temperature range; no cat$[Mn^{II}Ru^{III}(ox)_3]$ compound orders down to 2 K.

Ferrimagnetic Behavior of $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$. As already emphasized, $(NBu_4)[Cu^{II}Ru^{III}(ox)_3]$ represents an interesting case of ferrimagnetic behavior in a compound comprising only $^1/_2$ local spins. It would not be quite correct to analyze the situation in terms of classical $g_{Ru}S_{Ru}$ and $g_{Cu}S_{Cu}$ magnetic moments, which would tend to be antiparallel but would not compensate due to the difference between the local Zeeman factors, g_{Ru} and g_{Cu}. Actually, the zero-field ground state of the compound is nonmagnetic, despite the different Zeeman factors. On the other hand, in the presence of a magnetic field the spin functions of the system are not eigenfunctions of the $\mathbf{S}^2$ operator, and the nonmagnetic ground state couples with the magnetic excited state through the Zeeman perturbation.

So far, we can interpret quantitatively neither the magnetic susceptibility nor the magnetization data. The quantum−classical approach is obviously irrelevant. We hope to be able in the rather near future to propose a model for such a compound, possibly using a density matrix renormalization group (DMRG) approach.[29−31] Perhaps, a purely Heisenberg description of the interaction is not appropriate, so that it would be necessary to take into account an antisymmetrical component capable to cant the S_{Ru} and S_{Cu} spins. We are particularly concerned by the field dependence of the magnetization at very low temperature. If the Ru^{III} and Cu^{II} ions were not antiferromagnetically coupled, the saturation magnetization would be $N\beta(g_{Ru} + g_{Cu})/2$, i.e., about $2N\beta$. If the antiferromagnetic coupling was large, and the two Zeeman factors equal, the saturation magnetization would be very small. In the present case an extrapolation of the $M = f(H)$ curve suggests a saturation magnetization of the order of $1.1N\beta$.

Another family of oxalate-bridged compounds containing two metal ions with the same local spin has been reported, of formula cat$[Mn^{II}Fe^{III}(ox)_3]$ with the local spins $S_{Fe} = S_{Mn} = {}^5/_2$. These compounds exhibit a short range antiferromagnetic coupling characterized by a broad maximum of the magnetic susceptibility, to which is superimposed a weak canting between the antiparallely aligned spins.

Concluding Remark

Perhaps the most important information arising from this work is the breakdown of the symmetry rules governing the nature and the magnitude of the interaction between magnetic ions. This breakdown is certainly due to the presence of the Ru^{III} ion. It seems to us to be worthwhile to confirm this situation on a large number of coupled systems involving 4d and 5d metal ions and then to rationalize this phenomenon.

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