Magnetic Properties of Diruthenium(II,III) Carboxylate Compounds with Large Zero-Field Splitting and Strong Antiferromagnetic Coupling

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The magnetic properties of mixed-valent compounds of general formula $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH_2-CH_3 (**1**), C(Me)=CHEt) (**2**)] have been studied in the 2−300 K temperature range. This magnetic study also includes a revision of the magnetic properties of the complex $Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4$ (**3**). Compounds **1**−**3** show a linear structure and a strong antiferromagnetic coupling between the diruthenium units through the chlorine atoms according to previous studies. Two fitting models to explain the magnetic properties of these complexes that incorporate a large zero-field splitting together with a strong antiferromagnetic coupling are described. These models consider that each diruthenium unit ($S = {}^3/_2$) is magnetically coupled to the nearest diruthenium unit and ignores the longer distance magnetic coupling. The fitting models were found to be successful in fitting the magnetic data of the linear diruthenium(II,III) complexes. The zero-field splitting, *D*, and the antiferromagnetic coupling, *zJ*, vary from 37.8 to 48.0 cm^{-1} and from −7.43 to −13.30 cm^{-1}, respectively, for complexes. The *D* values are similar to those calculated for the nonlinear diruthenium(II,III) compounds and confirm the validity of the proposed fitting models.

Introduction

The syntheses and properties of numerous mixed-valent diruthenium(II,III) carboxylates have been reported.[2−4] Among the properties of these complexes, the magnetic behavior has been the subject of considerable interest for several years.[2−4] These complexes show at room temperature a very high magnetic moment ($\mu_{eff} \approx 4\ \mu_B$ per dimer unit) due to the presence of three unpaired electrons in a $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ electron configuration for the dimetallic unit according to the theoretical studies carried out by Norman et al.[5] The magnetic properties of all diruthenium(II,III) complexes are consistent with an $S = {}^3/_2$ ground state of the dimer unit and a large zero-field splitting[2−4] (ZFS) of about 70 cm^{-1}. The $S = {}^3/_2$ units can be linked into chains using appropriate bridging ligands to give molecular magnetic wires. Following this idea, several magnetic studies on diruthenium(II,III) units linked by ligands such as phenazine,[6] pyrazine,[7] nitroxide radicals,[8−11] 4,4′-dipyridine,[12] or 1,4-diazabicyclooctane[12] have been published.

Several variable-temperature magnetic susceptibility measurements on the chlorotetracarboxylatodiruthenium(II,III) compounds have shown[13−17] that these complexes present three different types of magnetic behavior.

(i) For compounds without or with extremely weak antiferromagnetic coupling, this behavior has been observed in some complexes[17] that form isolated molecules such as in $Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4$ and in some zigzag polymeric compounds[15] such as in $Ru_2Cl(\mu\text{-}O_2CC_6H_2(OMe)_3)_4$. The magnetic properties of these complexes is satisfactorily explained on the basis of isolated $S = {}^3/_2$ units undergoing a large ZFS.

(ii) For compounds with weak antiferromagnetic coupling, this behavior has been usually observed in zigzag polymeric[15,17] compounds such as in $Ru_2Cl(\mu\text{-}O_2CC_4H_9)_4$ and $Ru_2Cl(\mu\text{-}O_2CCH{=}CHCH{=}CHCH_3)_4$, but it also has been observed in some nonpolymeric[17] complexes such as $Ru_2Cl(\mu\text{-}O_2CC_4H_3N)_4$. A large ZFS and a weak antiferromagnetic exchange through chlorine bridging or through space are responsible for this magnetic behavior. This behavior can be adequately treated by a model based on a molecular field approximation developed by O'Connor,[18] corrected later by Telser et al.,[19] and used primarily by Cukiernik et al.[15]

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(iii) For compounds with a large antiferromagnetic coupling, this magnetic behavior has been observed only when there is a linear chain (Ru−Cl−Ru angle ≅ 180°) such as in $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH_2-CH_3, C(Me)=CHEt, $CMePh_2$]. The electronic density of each diruthenium unit is connected by the chlorine atom, giving a strong antiferromagnetic coupling. This magnetic behavior cannot be explained by O'Connor's model because the model's mathematical expression does not predict a maximum in the $\chi(T)$ curve. Cotton et al.[14] have studied the magnetic properties of the complex $Ru_2Cl(\mu\text{-}O_2CCMePh_2)_4$ using the one-dimensional Ising model for an infinite chain of coupled $S = {}^3/_2$ units. This last model considers a strong antiferromagnetic coupling but neglects the ZFS, which is always present in the diruthenium(II,III) complexes. Therefore, a more accurate fitting model is needed.

Although several crystal structure determinations have been carried out on the $Ru_2Cl(\mu\text{-}O_2CR)_4$ (R = alkyl or aryl) compounds,[14,15,17,20−30] only four complexes have linear structure: one form of the acetato complex,[24] the propionate,[25] 2-methylpentadienoate,[26] and diphenylpropionate[14] derivatives. These last three derivatives show, in the representation of the magnetic susceptibility versus temperature plot, a turning point at very low temperature, indicating a strong antiferromagnetic coupling. In this paper we describe two fitting models to explain the magnetic properties of compounds $Ru_2Cl(\mu\text{-}O_2CR)_4$ [R = CH_2-CH_3 (**1**), C(Me)=CHEt (**2**), $CMePh_2$ (**3**)]. The acetato derivative has not been included in this study because, as observed by Cukiernick et al.,[15] the solid forms a mixture of zigzag and linear chains. The developed models are valid for linear chains of $S = {}^3/_2$ units having both a strong antiferromagnetic coupling and a large zero-field splitting.

Experimental Section

The complexes $Ru_2Cl(\mu\text{-}O_2CR)_4$ were prepared according to literature procedures.[14,25,26,31] Compounds **1**−**3** were crystallized as indicated in the literature[14,25,26] before carrying out the magnetic measurements. The variable-temperature magnetic susceptibility data were measured on a Quantum Design MPMS*XL* SQUID (superconducting quantum interference device) susceptometer over a temperature range 2−300 K. Magnetic susceptibility measurements were taken using field strengths of 10 000 and 3000 G, and no field dependence was observed. Each raw data field was corrected for the diamagnetic contribution of both the sample holder and the compound to the susceptibility. The molar diamagnetic corrections for the complexes were calculated on the basis of Pascal's constants. The fit of experimental data was carried out using the commercial MATLAB, V.5.1.0.421, program, fitting all *g*, *D*, *zJ*, TIP, and *P* parameters simultaneously in the 2−300 K temperature range. Magnetization measurements at 14 field strengths between 0 and 50 kG were made at T_c and lower temperatures for compounds **1**−**3**.

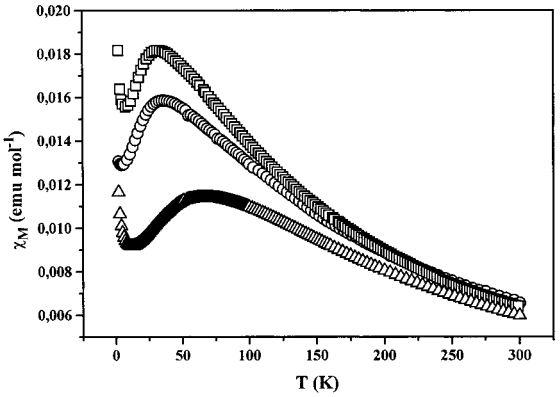

Figure 1. Experimental temperature dependence of the magnetic susceptibility for the complexes **1** (○), **2** (□), and **3** (△).

Results and Discussion

The magnetic measurements of compounds **1**−**3** show a magnetic moment at room temperature of ca. 4.0 μ_B corresponding to the presence of three unpaired electrons for a dimer unit, in good agreement with the published results on these complexes. The temperature dependence of the magnetic susceptibility data for compounds **1**−**3** is shown in Figure 1. It is worth noting the turning point (T_c) observed in the representation of the three complexes. The T_c appears at 35 and 32 K for compounds **1** and **2**, whereas it is observed at 67 K for compound **3**. The observed T_c values for complexes **1**−**3** are in excellent accordance with previous studies.[14,25,26]

In general, the magnetic properties of the zigzag and molecular chlorotetracarboxylatediruthenium(II,III) compounds can be correctly interpreted[7,12,15,17] using the equation described by O'Connor[18] and corrected later by Telser et al.[19] for an $S = {}^3/_2$ spin system with an axial ZFS. However, in the case of the linear compounds **1**−**3** this equation cannot be used because, as mentioned above, the mathematical expression of this model does not predict a maximum in the molar susceptibility versus temperature curve.

Three models could be used to analyze the magnetic properties of the linear compounds **1**− **3**. The first model considers a Heisenberg linear chain that must be scaled to the value of $S = {}^3/_2$. In addition this model can be modified to include a term corresponding to an *inter*chain interaction. However, in complexes **1**−**3**, the chains are well separated[14,25,26] and the *inter*chain interactions must be insignificant with respect to the *intra*chain coupling. On the other hand this model, similar to the one-dimensional Ising model used by Cotton et al.[14] for complex **3**, does not consider a ZFS term. As a consequence, we have decided not to use this model.

The second model considers a full-spin Hamiltonian for a linear chain that must include antiferromagnetic coupling and ZFS on all dimer units. This model could be very useful, but the introduction of the ZFS term makes the quantitative treatment very complex. However, several examples of the exchange interaction model in dinuclear complexes,[35−37] includ-

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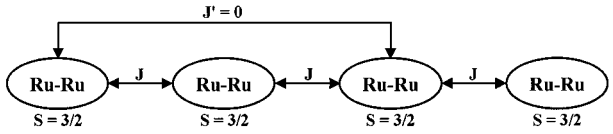
Table 1. Experimental Magnetic Data and Magnetic Parameters for Complexes **1**−**3** Obtained from Fits to the Magnetic Moment[a]

	R = CH_2−CH_3 (**1**)		R = C(Me)=CHEt (**2**)		R = $CMePh_2$ (**3**)	
parameter	model A	model B	model A	model B	model A	model B
μ_B, room temp	3.9		4.0		3.8	
T_c (K)	35		32		67	
g	1.90 (1.66)	1.90 (1.67)	2.04 (1.84)	2.04 (1.85)	2.06 (1.82)	2.07 (1.82)
D (cm^{-1})	46.7 (21.5)	46.6 (21.2)	48.0 (19.2)	47.9 (19.0)	38.1 (35.4)	37.8 (35.6)
zJ (cm^{-1})	−8.05 (−7.39)	−8.02 (−7.44)	−7.46 (−7.19)	−7.43 (−7.20)	−13.28 (−12.00)	−13.30 (−11.97)
TIP (cm^3 mol^{-1})	1.7×10^{-3} (3.3×10^{-3})	1.7×10^{-3} (3.3×10^{-3})	6.0×10^{-4} (2.0×10^{-3})	6.0×10^{-4} (2.0×10^{-3})	5.0×10^{-4} (2.1×10^{-3})	5.0×10^{-4} (2.1×10^{-3})
P (%)	1.8 (0.8)	1.8 (0.8)	2.7 (1.5)	2.7 (1.5)	1.7 (1.0)	1.7 (1.0)
σ^2	7.3×10^{-5} (9.5×10^{-4})	7.4×10^{-5} (9.4×10^{-4})	4.6×10^{-5} (8.5×10^{-4})	4.6×10^{-5} (8.5×10^{-4})	3.1×10^{-5} (9.1×10^{-4})	3.1×10^{-5} (9.1×10^{-4})

[a] Values obtained from fits to the molar susceptibility curves are given in parentheses. For model A, the magnetic susceptibility is calculated according to Boltzman statistics (see Appendix). For model B, the magnetic susceptibility is calculated according to the Van Vleck approximation (see Appendix). T_c is the temperature corresponding to the maximum magnetic susceptibility. P is the paramagnetic impurity. $\sigma^2 = \sum(\mu_{eff,calc} - \mu_{eff,exp})^2/\sum\mu_{eff,exp}^2$ ($\sigma^2 = \sum(\chi_{mol,calc} - \chi_{mol,exp})^2/\sum\chi_{mol,exp}^2$).

Scheme 1



ing some Cr(III) dimer compounds[38] ($S = {}^3/_2$), have been published. In these metal dimers the magnetic interactions usually lead to nonlinear variation of the magnetization versus magnetic field plot and it was necessary to calculate the magnetic susceptibility using the thermodynamic expression instead of using Van Vleck's equation. We have used, as model A, a similar approach; each diruthenium unit ($S = {}^3/_2$) is magnetically coupled only to the nearest diruthenium unit ($S = {}^3/_2$), with zero magnetic coupling over longer distances (Scheme 1). In this approach a ZFS and an antiferromagnetic coupling is considered (see Appendix).

The third model considers the same spin Hamiltonian used in model A, but the theoretical magnetic susceptibility is calculated using the Van Vleck approximation. This model has been applied[39] to a dimer of Mn(IV) ($S_1 = S_2 = {}^3/_2$) but without including the ZFS effect. Some diruthenium(II,III) ($S = {}^3/_2$) and diruthenium(II,II) ($S = 1$) dimers coupled to nitroxide radicals ($S = {}^1/_2$) have been studied[8−11] by the Van Vleck approximation. We have used, as model B, a similar approximation using the magnetic coupling showed in Scheme 1 and the Van Vleck formula, including ZFS and antiferromagnetic coupling, developed in the Appendix.

In the compounds **1**−**3** the variation of magnetization versus magnetic field is linear at least until 50 kG. Figure 2 shows, as an example, this behavior for the compound **1**. Thus, models A and B can be used to calculate the theoretical magnetic susceptibility.

A term corresponding to the temperature-independent paramagnetism (TIP) has been added to the expressions of the magnetic susceptibility shown in the Appendix.

$$\chi'_M = \chi_M + \mathrm{TIP}$$

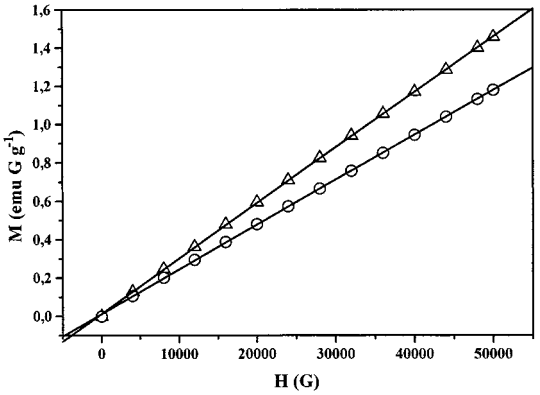


Figure 2. Magnetization vs magnetic field for the complex **1** at T_c (△) and 5 K (○).

As one can observe in Figure 1, the measured susceptibility plot shows a typical paramagnetic tail at low temperature, and therefore, we have included a paramagnetic impurity (P) in the expression of the molar susceptibility with $g_{mo} = 2$.

$$\chi_{mol} = (1 - P)\chi'_M + P\frac{Ng_{mo}^2\beta^2}{4kT}$$

By use of this expression, a satisfactory agreement was observed between experimental and calculated curves of the molar magnetic susceptibility and the magnetic moment, using models A and B. At higher temperatures only (from ca. 250 to 300 K) the experimental data are lower than the calculated values. Table 1 contains the values of the magnetic parameters (g, D, zJ, TIP, and P) together with σ^2, which indicates the quality of the fits. The magnetic parameters obtained using models A and B are very similar, showing the validity of both models to explain the magnetic properties of the complexes. Figures 3 and 4 show experimental and calculated curves for the complex **3**. The theoretical curves, showed in these figures, were simulated using the magnetic parameter values calculated in the fits of the magnetic susceptibility curves.

However, a better agreement between the experimental and calculated curves of the molar magnetic susceptibility and magnetic moment, over the entire range of temperatures, is obtained when the theoretical curves were simulated using the magnetic parameter values calculated in the fits of the magnetic moment[40] curves (Table 1). A similar behavior has been found

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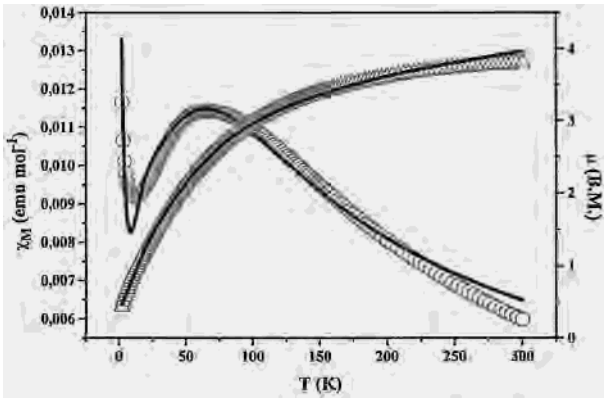

Figure 3. Temperature dependence of the molar susceptibility χ_M (○) and μ_{eff} (△) for complex **3**. Solid lines result from least-squares fits of the magnetic susceptibility using the model A described in the text, with $g = 1.82$, $D = 35.4$ cm^{-1}, $zJ = -12.00$ cm^{-1}, TIP $= 2.1 \times 10^{-3}$ cm^3 mol^{-1}, and $P = 1.0\%$.

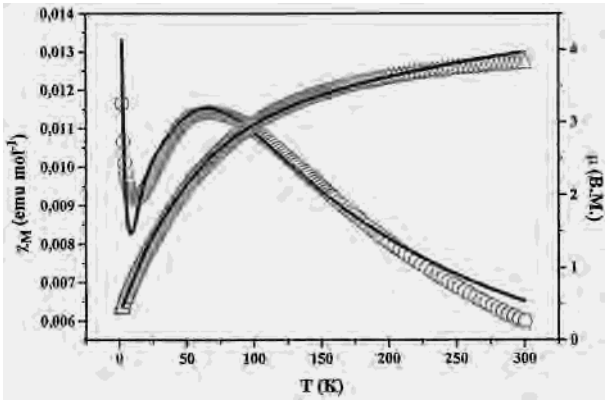

Figure 4. Temperature dependence of the molar susceptibility χ_M (○) and μ_{eff} (△) for complex **3**. Solid lines result from least-squares fits of the magnetic susceptibility using the model B described in the text, with $g = 1.82$, $D = 35.6$ cm^{-1}, $zJ = -11.97$ cm^{-1}, TIP $= 2.1 \times 10^{-3}$ cm^3 mol^{-1}, and $P = 1.0\%$.

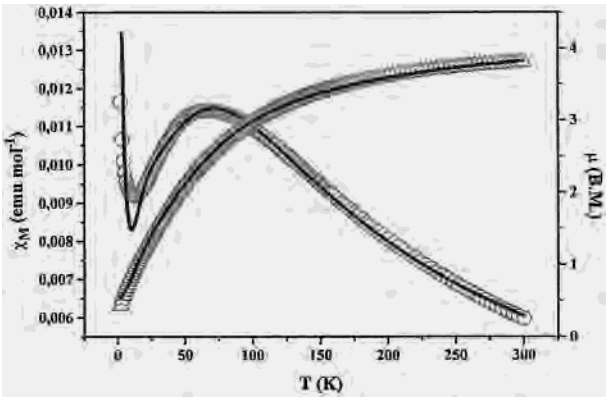

Figure 5. Temperature dependence of the molar susceptibility χ_M (○) and μ_{eff} (△) for complex **3**. Solid lines result from least-squares fits of the magnetic moment using the model A described in the text, with $g = 2.06$, $D = 38.1$ cm^{-1}, $zJ = -13.28$ cm^{-1}, TIP $= 5.0 \times 10^{-4}$ cm^3 mol^{-1}, and $P = 1.7\%$.

in a previous paper[17] on the magnetic properties of diruthenium compounds with weak antiferromagnetic coupling between dirutheniun units. Figures 5 and 6 show experimental and calculated curves for complex **3** using models A and B.

Some differences in the magnetic parameters values are observed depending on the mode of experimental data fits (Table 1). The greatest differences are observed in the D and P parameters of compounds **1** and **2**. In these complexes the D values obtained in the fit of the magnetic susceptibility are lower than those observed previously in other diruthenium(II,III) compounds. The g values are also too low. Finally the σ^2 values are in the range 8.5×10^{-4} to 9.5×10^{-4}. In contrast, these parameters are better in the fit of the magnetic moment curves; D is similar to that described for other diruthenium(II,III) complexes, g is very close to 2, and the σ^2 values are in the range 3.1×10^{-5} to 7.4×10^{-5}. Thus, although the magnetic parameters obtained in the fits of the measured quantity, χ, could be more representative than the ones obtained from the derived quantity μ_{eff}, we believe that the last parameters are more accurate. The explanation of this fact could be the following. At very low temperatures the contribution of the paramagnetic impurity to the magnetic susceptibility values is very important and the values of the magnetic parameters obtained in the fits of the magnetic susceptibility could be inaccurate. The fits of the magnetic moment curves minimize the significance of the data at very low temperatures and allow us to obtain more representative magnetic parameters. In fact, if the experimental susceptibility data from 2 to 6 K are not considered in the fits of the magnetic susceptibility, then the magnetic parameter values are very similar to those obtained in the fits of the magnetic moment over the entire range of temperatures.

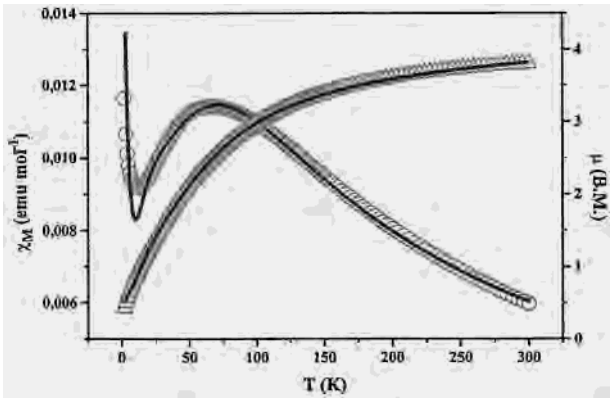

Figure 6. Temperature dependence of the molar susceptibility χ_M (○) and μ_{eff} (△) for complex **3**. Solid lines result from least-squares fits of the magnetic moment using the model B described in the text, with $g = 2.07$, $D = 37.8$ cm^{-1}, $zJ = -13.30$ cm^{-1}, TIP $= 5.0 \times 10^{-4}$ cm^3 mol^{-1}, and $P = 1.7\%$.

Compounds **1**−**3** show D values between 37.8 and 48.0 cm^{-1}, slightly lower than those described for other chlorotetracarboxylatediruthenium(II,III) compounds,[12,14,16] which vary from 54 to 80 cm^{-1}. The large ZFS values observed in all diruthenium(II,III) complexes are due to the presence of two second-row transition metals and a large number of closely spaced electronic states in the dimetallic unit.[5]

The zJ values vary from -7.46 to -13.30 cm^{-1} for complexes **1**−**3**. The antiferromagnetic coupling for complex **3** is slightly higher than that described previously by Cotton et al.[14] ($J = -10.9$ cm^{-1}). However, because the one-dimensional Ising model for an infinite chain of coupled $S = {}^3/_2$ units, used by Cotton et al.,[14] does not consider a ZFS term, the zJ value obtained using models A and B must be more accurate. In any event, the zJ values obtained for complexes **1**−**3** are higher than the zJ values described for the zigzag or molecular diruthenium compounds. This is consistent with previous studies[14−17] that indicate that the linear compounds must have a strong antiferromagnetic coupling.

The TIP values vary from 1.7×10^{-3} to 6.0×10^{-4} cm^3 mol^{-1}. Similar high TIP values (ca. 10^{-3} cm^3 mol^{-1}) have been previously found[41,42] in reduced diruthenium(II,II) complexes. TIP values near 10^{-4} are also common in diruthenium complexes.[12,15,17]

The amount of paramagnetic impurity obtained in the fits varies from 1.7% to 2.7%. The presence of similar or higher (up to 4.3%) quantities of paramagnetic impurity is usually observed in diruthenium complexes.[7,12,15,17,42]

Conclusion

In this work, we have reported a magnetic study of linear chlorotetracarboxylatodiruthenium(II,III) compounds. We have used two satisfactory models to explain the magnetic susceptibility of these types of complexes as a function of the temperature, confirming the existence of both a strong antiferromagnetic coupling and a large zero-field splitting.

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Appendix

1. Eigenstates of the Coupled System. The Hamiltonian is given by

$$H = H_0 + \mu g \vec{S} \vec{H}$$

where the unperturbed Hamiltonian H_0 is given, up to an additive constant, by

$$H_0 = -2J\vec{S}_1\vec{S}_2 + D(\vec{S}_{z1}{}^2 + \vec{S}_{z2}{}^2)$$

where J represents the ferromagnetic coupling, D the zero-field splitting, and $\vec{H}$ the applied magnetic field.

Using the basis $|S_1S_2\rangle$, where $S_i = -3/2, -1/2, 1/2, 3/2$ for $i = 1, 2$ and defining ϕ_i for $i = 1, ..., 16$ as

$$\begin{array}{llll}
\phi_1 = |\frac{3}{2}, \frac{3}{2}\rangle & \phi_2 = |\frac{3}{2}, \frac{1}{2}\rangle & \phi_3 = |\frac{3}{2}, -\frac{1}{2}\rangle & \phi_4 = |\frac{3}{2}, -\frac{3}{2}\rangle \\
\phi_5 = |\frac{1}{2}, \frac{3}{2}\rangle & \phi_6 = |\frac{1}{2}, \frac{1}{2}\rangle & \phi_7 = |\frac{1}{2}, -\frac{1}{2}\rangle & \phi_8 = |\frac{1}{2}, -\frac{3}{2}\rangle \\
\phi_9 = |-\frac{1}{2}, \frac{3}{2}\rangle & \phi_{10} = |-\frac{1}{2}, \frac{1}{2}\rangle & \phi_{11} = |-\frac{1}{2}, -\frac{1}{2}\rangle & \phi_{12} = |-\frac{1}{2}, -\frac{3}{2}\rangle \\
\phi_{13} = |-\frac{3}{2}, \frac{3}{2}\rangle & \phi_{14} = |-\frac{3}{2}, \frac{1}{2}\rangle & \phi_{15} = |-\frac{3}{2}, -\frac{1}{2}\rangle & \phi_{16} = |-\frac{3}{2}, -\frac{3}{2}\rangle
\end{array}$$

we obtain 16 states but only 9 energy levels for the unperturbed Hamiltonian. The following parameters are very useful to express the eigenstates and eigenmodes of H_0:

$$x = (D^2 + 2DJ + 25J^2)^{1/2}, \quad y = (4D^2 + 9J^2)^{1/2}, \quad z = (4D^2 + 16DJ + 25J^2)^{1/2}$$

$$\alpha = \frac{6J}{\sqrt{72J^2 + 3(x - D - J)^2}}$$

$$\beta = \frac{\sqrt{3}(D + J - x)}{\sqrt{72J^2 + 3(x - D - J)^2}}$$

$$\gamma = \frac{6J}{\sqrt{72J^2 + 3(x + D + J)^2}}$$

$$\delta = \frac{\sqrt{3}(x + D + J)}{\sqrt{72J^2 + 3(x + D + J)^2}}$$

$$\epsilon = \frac{3J}{\sqrt{2}\sqrt{9J^2 + (2D - y)^2}}$$

$$\eta = \frac{2D - y}{\sqrt{2}\sqrt{9J^2 + (2D - y)^2}}$$

$$\theta = \frac{3J}{\sqrt{2}\sqrt{9J^2 + (2D + y)^2}}$$

$$\iota = \frac{2D + y}{\sqrt{2}\sqrt{9J^2 + (2D + y)^2}}$$

$$\lambda = \frac{2D + 4J - z}{\sqrt{2}\sqrt{9J^2 + (z - 2D - 4J)^2}}$$

$$\xi = \frac{3J}{\sqrt{2}\sqrt{9J^2 + (z - 2D - 4J)^2}}$$

$$\pi = \frac{z + 2D + 4J}{\sqrt{2}\sqrt{9J^2 + (z + 2D + 4J)^2}}$$

$$\sigma = \frac{3J}{\sqrt{2}\sqrt{9J^2 + (z + 2D + 4J)^2}}$$

We have eigenstates, multiplicities, and eigenmodes as shown in Table 2.

The coefficients S_i are obtained through the standard perturbation theory, and for this case we obtain the following values.

$$S_1 = \frac{3}{E_1 - E_3}$$

$$S_2 = \frac{2(l_3)^2}{E_2 - E_6} + \frac{2(l_4)^2}{E_2 - E_7}$$

$$S_3 = \frac{3}{E_3 - E_1} + \frac{2(l_1)^2}{E_3 - E_4} + \frac{2(l_2)^2}{E_3 - E_5}$$

$$S_4 = \frac{2(l_1)^2}{E_4 - E_3} + \frac{2(l_5)^2}{E_4 - E_8} + \frac{2(l_6)^2}{E_4 - E_9}$$

$$S_5 = \frac{2(l_2)^2}{E_5 - E_3} + \frac{2(l_7)^2}{E_5 - E_8} + \frac{2(l_8)^2}{E_5 - E_9}$$

$$S_6 = \frac{2(l_3)^2}{E_6 - E_2}$$

$$S_7 = \frac{2(l_4)^2}{E_7 - E_2}$$

(41) Maldivi, P.; Giroud-Godquin, A. M.; Marchon, J. C.; Guillon, D.; Skoulios, A. *Chem. Phys. Lett.* **1989**, *157*, 552.
(42) Bonnet, L.; Cukiernik, F. D.; Maldivi, P.; Giroud-Godquin, A. M.; Marchon, J. C.; Ibn-Elhaj, M.; Guillon, D.; Skoulios, A. *Chem. Mater.* **1994**, *6*, 31.

Table 2.

Eigenstates	Multiplicity	Eigenmodes	
$E_1 = \frac{9}{2}D - \frac{9}{2}J$	$m_1 = 2$	$V_1 = \phi_1$	$V_2 = \phi_{16}$
$E_2 = \frac{5}{2}D + \frac{3}{2}J$	$m_2 = 4$	$V_3 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_5)$	$V_4 = \frac{1}{\sqrt{2}}(\phi_3 - \phi_9)$
		$V_5 = \frac{1}{\sqrt{2}}(\phi_8 - \phi_{14})$	$V_6 = \frac{1}{\sqrt{2}}(\phi_{12} - \phi_{15})$
$E_3 = \frac{5}{2}D - \frac{9}{2}J$	$m_3 = 2$	$V_7 = \frac{1}{\sqrt{2}}(\phi_2 + \phi_5)$	$V_8 = \frac{1}{\sqrt{2}}(\phi_{12} + \phi_{15})$
$E_4 = \frac{3}{2}D + \frac{1}{2}J + x$	$m_4 = 2$	$V_9 = \alpha\phi_3 + \beta\phi_6 + \alpha\phi_9$	$V_{10} = \alpha\phi_8 + \beta\phi_{11} + \alpha\phi_{14}$
$E_5 = \frac{3}{2}D + \frac{1}{2}J - x$	$m_5 = 2$	$V_{11} = \gamma\phi_3 + \delta\phi_6 + \gamma\phi_9$	$V_{12} = \gamma\phi_8 + \delta\phi_{11} + \gamma\phi_{14}$
$E_6 = \frac{5}{2}D + \frac{9}{2}J + y$	$m_6 = 1$	$V_{13} = \varepsilon\phi_4 + \eta\phi_7 - \eta\phi_{10} - \varepsilon\phi_{13}$	
$E_7 = \frac{5}{2}D + \frac{9}{2}J - y$	$m_7 = 1$	$V_{14} = \theta\phi_4 + \iota\phi_7 - \iota\phi_{10} - \theta\phi_{13}$	
$E_8 = \frac{5}{2}D + \frac{1}{2}J + z$	$m_8 = 1$	$V_{15} = \xi\phi_4 + \lambda\phi_7 + \lambda\phi_{10} + \xi\phi_{13}$	
$E_9 = \frac{5}{2}D + \frac{1}{2}J - z$	$m_9 = 1$	$V_{16} = \sigma\phi_4 + \pi\phi_7 + \pi\phi_{10} + \sigma\phi_{13}$	

$$S_8 = \frac{2(l_5)^2}{E_8 - E_4} + \frac{2(l_7)^2}{E_8 - E_5}$$

$$S_9 = \frac{2(l_6)^2}{E_9 - E_4} + \frac{2(l_8)^2}{E_9 - E_5}$$

where

$$l_1 = \sqrt{2}\alpha + \frac{\sqrt{6}\beta}{2}$$

$$l_2 = \sqrt{2}\gamma + \frac{\sqrt{6}\delta}{2}$$

$$l_3 = \frac{\sqrt{6}(\epsilon + \eta)}{2}$$

$$l_4 = \frac{\sqrt{6}(\iota + \theta)}{2}$$

$$l_5 = \sqrt{3}\alpha(\xi + \lambda) + 2\beta\lambda$$

$$l_6 = \sqrt{3}\alpha(\sigma + \pi) + 2\beta\pi$$

$$l_7 = \sqrt{3}\gamma(\xi + \lambda) + 2\delta\lambda$$

$$l_8 = \sqrt{3}\gamma(\sigma + \pi) + 2\delta\pi$$

2. Calculation of Magnetic Susceptibility. The molar magnetic susceptibility of a powdered sample can be expressed as

$$\chi_M = \frac{1}{3}(\chi_{||} + 2\chi_{\perp})$$

where $\chi_{||}$ and $\chi_{\perp}$ have been calculated for two methods.

2.A. Susceptibility According to Boltzman Statistics. With the analysis done above we can write the asymptotic expansion up to second order in H of the eigenstates.

We will denote by $e_i = e_i(H)$, $i = 1, ..., 16$ the expression of the asymptotic expansion of the eigenstates, and $\mu_i = \mu_i(H) = \partial e_i(H)/\partial H$. We will need to distinguish between the parallel and perpendicular perturbations, and we will denote by e_i^z, μ_i^z the parallel and by e_i^x, μ_i^x the perpendicular. The first case considers a perturbation of the type μgHS_z, and the second one considers the perturbation μgHS_x.

For parallel perturbation, we have the following second-order approximation of e_i and first-order approximation of μ_i:

$e_1^z = E_1 + 3\mu gH$	$\mu_1^z = 3\mu g$
$e_2^z = E_1 - 3\mu gH$	$\mu_2^z = -3\mu g$
$e_3^z = E_2 + 2\mu gH$	$\mu_3^z = 2\mu g$
$e_4^z = E_2 + \mu gH$	$\mu_4^z = \mu g$
$e_5^z = E_2 - \mu gH$	$\mu_5^z = -\mu g$
$e_6^z = E_2 - 2\mu gH$	$\mu_6^z = -2\mu g$
$e_7^z = E_3 + 2\mu gH$	$\mu_7^z = 2\mu g$
$e_8^z = E_3 - 2\mu gH$	$\mu_8^z = -2\mu g$
$e_9^z = E_4 + \mu gH$	$\mu_9^z = \mu g$
$e_{10}^z = E_4 - \mu gH$	$\mu_{10}^z = -\mu g$
$e_{11}^z = E_5 + \mu gH$	$\mu_{11}^z = \mu g$
$e_{12}^z = E_5 - \mu gH$	$\mu_{12}^z = -\mu g$
$e_{13}^z = E_6$	$\mu_{13}^z = 0$
$e_{14}^z = E_7$	$\mu_{14}^z = 0$
$e_{15}^z = E_8$	$\mu_{15}^z = 0$
$e_{16}^z = E_9$	$\mu_{16}^z = 0$

Using Boltzman statistics to obtain the molar parallel susceptibility, we get

$$\chi_{||} = \frac{N_c \sum_{i=1}^{16} \mu_i^z \exp[-e_i^z/(kT)]}{H \sum_{i=1}^{16} \exp[-e_i^z/(kT)]}$$

where N_c is the number of moles of the compound, that is, the number of moles of the two coupled dimeric units. Note that $N_c = N_u/2$ if N_u represents the number of moles of the diruthenium units.

For perpendicular perturbation, we have the following second-order approximation of e_i and first-order approximation of μ_i:

$e_1^x = E_1 + (1/2)S_1(\mu g)^2H^2$	$\mu_1^x = S_1(\mu g)^2H$
$e_2^x = E_1 + (1/2)S_1(\mu g)^2H^2$	$\mu_2^x = S_1(\mu g)^2H$
$e_3^x = E_2 + \mu gH + (1/4)S_2(\mu g)^2H^2$	$\mu_3^x = \mu g + (1/2)S_2(\mu g)^2H$
$e_4^x = E_2 - \mu gH + (1/4)S_2(\mu g)^2H^2$	$\mu_4^x = -\mu g + (1/2)S_2(\mu g)^2H$
$e_5^x = E_2 + \mu gH + (1/4)S_2(\mu g)^2H^2$	$\mu_5^x = \mu g + (1/2)S_2(\mu g)^2H$
$e_6^x = E_2 - \mu gH + (1/4)S_2(\mu g)^2H^2$	$\mu_6^x = -\mu g + (1/2)S_2(\mu g)^2H$

$$e_7^x = E_3 + (^1/_2)S_3(\mu g)^2H^2 \qquad \mu_7^x = S_3(\mu g)^2H$$
$$e_8^x = E_3 + (^1/_2)S_3(\mu g)^2H^2 \qquad \mu_8^x = S_3(\mu g)^2H$$
$$e_9^x = E_4 + (^1/_2)S_4(\mu g)^2H^2 \qquad \mu_9^x = S_4(\mu g)^2H$$
$$e_{10}^x = E_4 + (^1/_2)S_4(\mu g)^2H^2 \qquad \mu_{10}^x = S_4(\mu g)^2H$$
$$e_{11}^x = E_5 + (^1/_2)S_5(\mu g)^2H^2 \qquad \mu_{11}^x = S_5(\mu g)^2H$$
$$e_{12}^x = E_5 + (^1/_2)S_5(\mu g)^2H^2 \qquad \mu_{12}^x = S_5(\mu g)^2H$$
$$e_{13}^x = E_6 + S_6(\mu g)^2H^2 \qquad \mu_{13}^x = 2S_6(\mu g)^2H$$
$$e_{14}^x = E_7 + S_7(\mu g)^2H^2 \qquad \mu_{14}^x = 2S_7(\mu g)^2H$$
$$e_{15}^x = E_8 + S_8(\mu g)^2H^2 \qquad \mu_{15}^x = 2S_8(\mu g)^2H$$
$$e_{16}^x = E_9 + S_9(\mu g)^2H^2 \qquad \mu_{16}^x = 2S_9(\mu g)^2H$$

Using Boltzman statistics to obtain the susceptibility, we get

$$\chi_\perp = \frac{N_c\sum_{i=1}^{16}\mu_i^x \exp[-e_i^x/(kT)]}{H\sum_{i=1}^{16}\exp[-e_i^x/(kT)]}$$

2.B. Susceptibility According to Van Vleck Approximation.

$$\chi_{\parallel} = \frac{N_c g^2\mu^2}{kTZ}(18e^{-E_1/(kT)} + 10e^{-E_2/(kT)} + 8e^{-E_3/(kT)} + 2e^{-E_4/(kT)} + 2e^{-E_5/(kT)})$$

$$\chi_\perp = \frac{N_c g^2\mu^2}{kTZ}(4e^{-E_2/(kT)} - 2kT\sum_{i=1}^{9}S_i\, e^{-E_i/(kT)})$$

where

$$Z = \sum_{i=1}^{9} m_i\, e^{-E_i/(kT)}$$

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