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Intramolecular Antiferromagnetic Coupling in Supramolecular Grid Structures with Co^{2+} Metal Centers

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The magnetization of novel supramolecular grid structures consisting of four bis(bipyridyl)-pyrimidine ligands and four Co^{2+} ions was measured. We provide evidence for an antiferromagnetic coupling of the Co^{2+} spins. Investigations of microcrystals, powders, and solutions with the mean distance of the grids varying from 20 to 160 Å showed that the coupling is solely of intramolecular origin and is not affected by long-range ordering. Thus, these grids form an almost ideal quantum spin system of four spins. This is further supported by low-temperature field-sweep measurements.　[S0031-9007(97)03039-1]

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For the past decade, the properties of low-dimensional antiferromagnetic quantum spin systems have attracted a growing interest. From an experimental as well as theoretical point of view, it has been shown by many authors that these systems can reveal many spectacular phenomena. For example, the interest in one-dimensional (1D) systems has been greatly stimulated by Haldane's conjecture that integer-spin Heisenberg chains show a gap in their excitation spectra [1]. The first observation of a spin-Peierls transition in an inorganic material, $CuGeO_3$, has raised the interest in this field even more [2]. Further examples are the experimental realization of several 1D antiferromagnetic spin systems in single crystals, e.g., $Sr_{n-1}Cu_{n+1}O_{2n}$ [3,4]. Moreover, the possibility that two-dimensional antiferromagnetic fluctuations are responsible for superconductivity in the high-temperature superconductors is being considered [5].

Further insight into the properties of antiferromagnetic spin systems can be gained by investigating systems with a small number of spins. Such systems can be created by supramolecular chemistry which is able to produce, by self-assembly, metallorganic complexes with a defined number of magnetic metal centers [6]. In investigations on crystals or powders of supramolecular arrays, bulk properties have been observed so far, i.e., long-range intermolecular coupling. For example, antiferromagnetic ordering was found in polycrystalline samples of $[Fe^{II}(d_8\text{-}bpy)_3]_n^{2+}[Mn_2^{II}(ox)_3]_n^{2n-}$ [7].

In this work, we investigated a novel self-assembled supramolecular grid structure with four Co^{2+} metal centers, denoted as Co-$[2 \times 2]$. We observed antiferromagnetic coupling of the Co^{2+} spins. We provide strong experimental evidence that the coupling is of intramolecular origin and that the Co-$[2 \times 2]$ system thus forms an almost ideal quantum spin system. To our knowledge, this is the first experimentally realized quantum spin system with exactly four spins in a well-defined geometry.

The structure of the Co-$[2 \times 2]$ grids [8] consists of four bis(bipyridyl)-pyrimidine ligands [9] and four Co^{2+} metal centers (Fig. 1). Each metal center is situated in the crossing point of two ligands and is enclosed by six N donor atoms in an almost octahedral geometry. The positive charges are countered by eight PF_6^- ions. The grids were formed by self-assembly in methanol and investigated in acetonitrile (CH_3CN) solution [8]. They were completely characterized by x-ray crystallography, UV spectroscopy, mass spectrometry, elemental analysis, and electrochemical methods [8]. The distance between the Co^{2+} ions is about 6.5 Å. The average bond length from the N donors to the Co^{2+} ions is 2.0 Å. In single crystals of Co-$[2 \times 2]$ grids, the size of the unit cell is
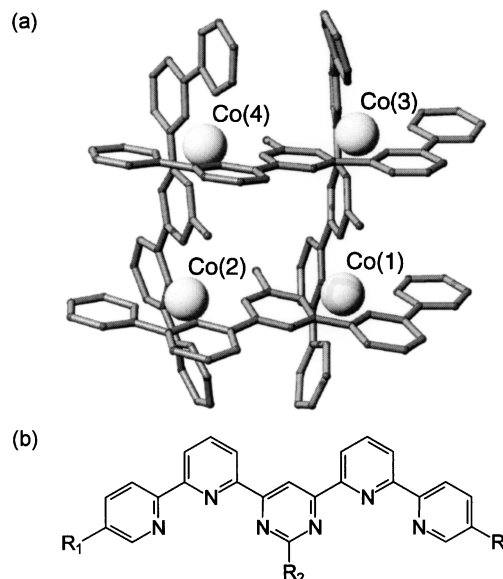

FIG. 1. (a) Crystal structure of the Co-$[2 \times 2]$ grid. (b) Bis(bipyridyl)-pyrimidine ligand with $R_1 = H$ and $R_2 = CH_3$.

approximately $20.6 \times 18.2 \times 18.6$ Å^3. Three different forms of Co-[2 × 2] samples were prepared:

(1) Powder samples with a typical weight of ≈ 1 mg.

(2) Microcrystals with sizes of approximately $(200 \ \mu m)^3$. The samples used contain several randomly oriented microcrystals with a total weight of <0.5 mg. The average grid-to-grid distance is ≈ 20 Å.

(3) Solutions in CH_3CN. The sample presented in this work was 4×10^{-4} M with 0.45 mg of Co-[2 × 2] grids dissolved. The average grid-to-grid distance was estimated to be about 160 Å.

We also performed measurements on the mononuclear analog of the Co-[2 × 2] grids, the $Co(terpyridyl)_2(PF_6)_2$ complex, denoted here as Co-[1 × 1]. For synthesis, a method analogous to that for the Co-[2 × 2] grids was used [10]. The weight of the powder samples was typically 2.5 mg.

The temperature and magnetic field dependence of the magnetic moment, $m(T, H)$, was measured with a commercial SQUID magnetometer (Quantum Design). The temperature range was $T = 2$–250 K and the maximum field 5.5 T. The powder and microcrystal samples were fixed with apiezon grease on a plastic straw. The solution was filled into a gel cap, closed carefully by a second cap, and then put into a straw. In this way, sublimation of the frozen solution could be avoided. The background signal of the sample holders was checked independently. For the powder and crystal samples the background never exceeded 5% of the sample signal. As the magnetic contribution of the ligands and counter ions is only inaccurately known, the data were not corrected for either background or other contributions. In the case of the solution, the background of the gel caps and the solvent is considerable and was treated as described below. Fortunately, the arguments we present here are not affected by background, ligands, or solvent contributions. In this work we use μ_B/spin as a unit for the magnetic moment where μ_B is the Bohr magneton. For Co-[2 × 2], $1\mu_B$/spin correspond to 2.234×10^4 cm^3 G/mol and for Co-[1 × 1], $1\mu_B$/spin correspond to 5.585×10^3 cm^3 G/mol.

In Fig. 2 we present the temperature dependence of the magnetic moment for Co-[2 × 2] powder [Fig. 2(a)], for a sample consisting of several Co-[2 × 2] microcrystals [Fig. 2(b)] and for the solution of Co-[2 × 2] grids [Fig. 2(c)]. Figure 2(c) is obtained by subtracting $\chi = -0.34\mu_B$/(spin T) from the data in order to take into account the contribution of the gel caps and the solvent. The significantly smaller value of the magnetic moment of the solution at low temperatures is attributed to this rough correction of the background. The measured zero-field-cooled and field-cooled curves are identical. All three samples show essentially the same behavior. Especially, the low-field magnetization curves exhibit maxima at $T^* \approx 7$ K (Fig. 2, insets), T^* being independent on the mean distance of the Co-[2 × 2] grids which was
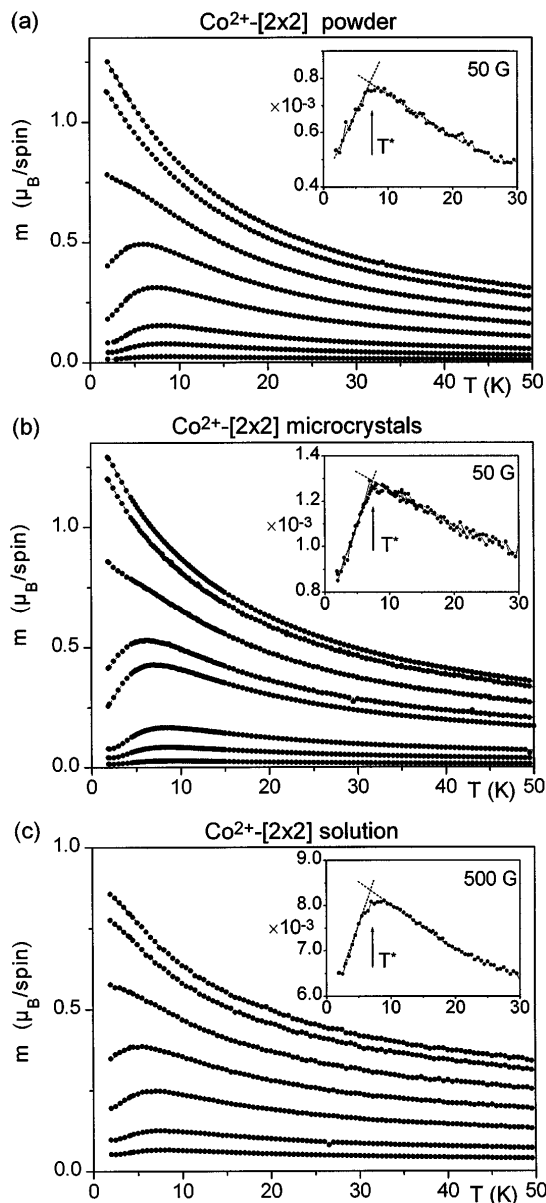

FIG. 2. Temperature dependence of the magnetic moment of the Co-[2 × 2] complex (a) as powder, (b) as a sample of microcrystals, and (c) in dilute CH_3CN solution. Magnetic fields were 0.15, 0.5, 1, 2, 3, 4, 5, and 5.5 T from bottom to top. For the microcrystals, 2.5 T was used instead of 2 T. For the solution, 0.15 T is not shown. The insets show the magnetization at low fields and the definition of T^*. The lines are guides to the eye.

increased from 20 Å in the microcrystal sample to 160 Å in the solution. The maxima at T^* are interpreted as a signature of antiferromagnetic coupling. This will be discussed in detail below. T^* is directly related to the antiferromagnetic coupling strength, and Fig. 2 represents the main result of this work: Since the coupling strength does not depend on the intermolecular distance, we conclude that antiferromagnetism in Co-[2 × 2] is due predominantly to intramolecular coupling of the four

Co^{2+} spins and is not affected by long-range effects. A formation of clusters of Co-[2 × 2] grids in the solution, which might lead to long-range antiferromagnetism, can be excluded because of the high solubility of the grids in CH_3CN [8] and because of their high dilution in our sample. Furthermore, an optical investigation of a frozen solution gave no indications of any cluster formation.

A fit of the high-temperature tail of the magnetization curves (100−250 K) with a Curie-Weiss law, $\chi = C/(T - \Theta)$, did produce good agreement with data. We obtained $\Theta = -15$ to -25 K depending slightly on the particular temperature range used for the fit and the particular background correction [$C = 4-5(\mu_B$ K$)/($spin T$)$]. A negative Θ is usually taken as evidence for antiferromagnetism. On the other hand, such small values of Θ might also be an effect of ligand field splitting [11]; i.e., in the presence of crystal fields, the susceptibility of magnetic ions without any coupling is often better described by a Curie-Weiss law instead of a Curie law. Furthermore, the magnetization of a system where ligand fields lead to a nonmagnetic ground state can look very similar to that in Fig. 2. A simple example is a system described by the Hamiltonian $\hat{H} = D(\hat{S}_z)^2 + g\mu_B H_z \hat{S}_z$ with $S = 1$ and $D > 0$. Its susceptibility exhibits a maximum at $T^* \approx 2/3D$, and the high temperature susceptibility follows a Curie-Weiss law with $\Theta = -1/3D$. However, in the following discussion, we show that the maximum at T^* is not an effect of ligand fields but is most likely due to antiferromagnetic coupling.

Crystallographic data [8,10] show an irregular arrangement of the six nitrogen atoms surrounding a Co^{2+} ion leading to a ligand field which is only roughly cubic but, in fact, has no symmetries. This suggests that in Co-[2 × 2] the ligand field splitting is essentially the same as in Co-[1 × 1], because degeneracies of energy levels are removed as far as possible in both systems. Thus, without interactions the magnetic behavior of both Co-[2 × 2] and Co-[1 × 1] should be similar. We have measured the magnetization of Co-[1 × 1] powder and obtained good agreement with the magnetization of Co-[2 × 2] for temperatures $T > 100$ K, confirming the above suggestions. However, the typical maximum in the magnetization of Co-[2 × 2] is not present in Co-[1 × 1] [Fig. 3(a)]. This provides clear evidence that the magnetization of Co-[2 × 2] is a consequence of antiferromagnetic coupling.

A second argument against ligand fields is obtained by considering the ground state of the Co^{2+} ions. If ligand fields lead to a ground state with, e.g., effective spin $S = 1/2$, the magnetization at low temperatures is Curie-like and does not exhibit a maximum. Antiferromagnetic coupling, however, still yields a maximum. In Fig. 3(b) magnetization data for Co-[1 × 1] is plotted against the reduced variable $x = \mu_B H/k_B T$. A constant magnetic moment of $\chi = 0.017\mu_B/($spin T$)$ has been subtracted. This is a reasonable value for the combined contributions of sample holder, ligands, and a Van Vleck term. The
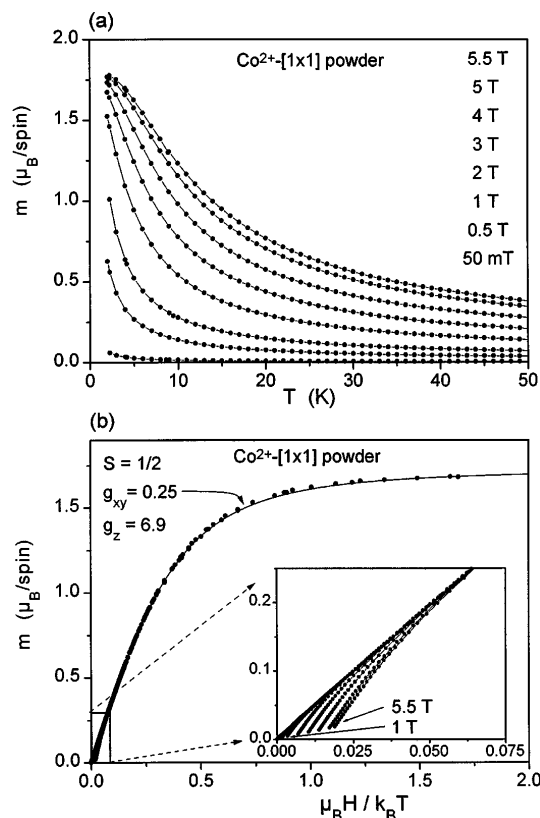

FIG. 3. (a) Temperature dependence of the magnetic moment of Co-[1 × 1] powder; magnetic fields were the same as in Fig. 2; the lines are guides to the eye. (b) Magnetic moment of Co-[1 × 1] powder vs the reduced variable $x = \mu_B H/k_B T$; plotted data were obtained by subtracting $\chi = 0.017\mu_B/($spin T$)$; the solid line is a fit to the data (see text); the inset shows the deviation from scaling for temperatures $T > 100$ K.

data can be well reproduced by the effective spin Hamiltonian $\hat{H}_0 = g_{xy}\mu_B(H_x\hat{S}_x + H_y\hat{S}_y) + g_z\mu_B H_z\hat{S}_z$ after averaging over the randomly oriented grids [Fig. 3(b)]. We obtain $S = 1/2$, $g_{xy} \approx 0.25$, and $g_z \approx 6.9$. We note that it was not possible to obtain reasonable fits for $S > 1/2$. The deviation from scaling for temperatures above 100 K [Fig. 3(b), inset] indicates thermal excitation of higher energy levels.

An effective spin $S = 1/2$ is also expected from theoretical considerations. In ligand field theory, the ground state of a Co^{2+} ion exposed to a low symmetric ligand field is a doublet with effective spin $S = 1/2$ for intermediate or strong ligand fields, independent on whether covalent binding has to be taken into account [11]. The twofold degeneracy cannot be removed by ligand fields because of Kramers theorem: For a system with an odd number of electrons, the ligand field splitting leaves an even degeneracy of the energy levels [11]. Therefore, the ground state of Co^{2+} with its seven valence electrons should be at least a doublet.

Summarizing the above results, the magnetization of Co-[2 × 2] can be described by an effective spin Hamiltonian of the form $\hat{H} = \hat{H}_{af} + \hat{H}_0$, where $\hat{H}_0$ is given above and $\hat{H}_{af}$ describes the antiferromagnetic coupling of four $S = 1/2$ spins. This property of $\hat{H}_{af}$ can be further confirmed without specifying $\hat{H}_{af}$ explicitly. Assuming that $\hat{H}$ and $\Sigma \hat{S}_z^{(i)}$ commute, the magnetization at zero temperature can be understood as follows [12]. $\Sigma \hat{S}_z^{(i)}$ is the total spin operator with magnetic quantum number M. M varies between $-NS$ and NS, where N is the number of spins and S is the spin quantum number of a single spin. An odd N does not have to be considered here because, in this case, the spins cannot couple to zero total spin and, in contrast to our experiments (Fig. 2), the magnetization at low temperatures would be Curie-like. The antiferromagnetic ground state has $M = 0$. Then, with increasing magnetic field, energy levels with $M < 0$ decrease in energy and cross the ground state at certain characteristic fields, leading to steps in the zero-temperature magnetization. The maximum number of steps is NS.

In Fig. 4 we present a field-sweep measurement at $T = 2$ K for a Co-[2 × 2] powder sample. At $H_2 \approx 3.5$ T, a clear step arises corresponding to the transition into the paramagnetic state (also to be seen in Fig. 2). Subtracting the initial slope from the data, a kink at $H_1 \approx 0.35$ T appears (inset of Fig. 4) which is interpreted as a second "step," smeared out not only due to the nonzero temperature but also because of the anisotropy of $\hat{H}_0$. It is worth noting that we didn't observe any indication of hysteresis. Therefore, $NS = 2$, and the magnetization of Co-[2 × 2] is consistent with that of four $S = 1/2$ spins.

To summarize, we have studied the magnetization of two supramolecular structures: Co-[2 × 2] grids containing four Co^{2+} ions and a Co-[1 × 1] complex containing a single Co^{2+} ion. The magnetization of Co-[1 × 1] was observed to be Curie-like, whereas Co-[2 × 2] exhibited antiferromagnetic coupling. The effective spin of the Co^{2+} ions was identified as $S = 1/2$. Comparing microcrystal, powder, and dilute solution samples of Co-[2 × 2] grids, the antiferromagnetic coupling strength was found to be independent of the mean intermolecular distance. We showed that the magnetization of Co-[2 × 2] is consistent with that of a quantum spin system consisting of four antiferromagnetically coupled $S = 1/2$ spins.

We conclude that Co-[2 × 2] represents an almost ideal model system for investigating magnetic interactions in a discrete entity. We believe that supramolecular systems with a defined number of magnetic ions are suitable for future investigations, contributing to a deeper insight into molecular magnetic coupling mechanisms.
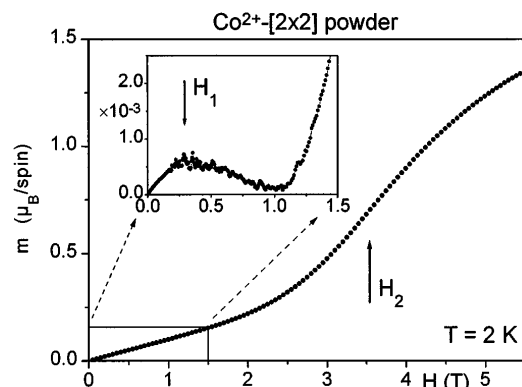
FIG. 4. Field dependence of the magnetic moment of Co-[2 × 2] powder at $T = 2$ K. The solid arrows indicate two features of the magnetization discussed in the text. The data in the inset was obtained by subtracting $\chi = 0.1 \mu_B/(\text{spin T})$.

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