

Collinear ferromagnetism and spin orientation in the molecule-based magnets $M[\text{N}(\text{CN})_2]_2$ ($M = \text{Co}, \text{Ni}$)

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Zero-field unpolarized neutron powder diffraction has been used to study the low- T magnetic structure and T -dependent crystal structure of $M[\text{N}(\text{CN})_2]_2$ ($M = \text{Co}, \text{Ni}$). Both compounds show collinear ferromagnetism with spin orientation along the c axis. The results provide the determination of a complete magnetic structure in the ordered state for a molecule-based magnet. The c lattice parameter exhibits negative thermal expansion, explained by a wine-rack-like deformation. [S0163-1829(99)10225-X]

Since the discovery of the first room-temperature molecule-based magnets,^{1,2} there has been growing interest in understanding the origin of the magnetic ordering in these emerging magnetic materials, with the aim of designing new high- T_c molecule-based magnets.³ For this purpose, it is essential to obtain *complete* magnetic structures in the ordered state. A complete magnetic structure consists of quantitative determination of: (a) the direction of the spins with respect to each other, (b) the direction of the spins with respect to the crystallographic axes, and (c) the magnitude of the magnetic moment per ion. Important progress toward this goal has been made by Refs. 4–9, which accomplished (a) and (c) but not (b). Knowledge of (b) is crucial in elucidating the microscopic interactions responsible for the magnetic ground state, since the spatial orientation of the spins gives insight into the sign and strength of the superexchange interactions, the strength of single-ion magnetocrystalline anisotropy, and optimal atomic orbital overlaps. In the present work, we report the determination of the direction of the spins with respect to the crystallographic axes in the ordered state, as well as (a) and (c), for a molecule-based magnet. These results provide a basis for the design of high- T_c molecule-based magnets.

The prototype family of molecule-based magnets, $M[\text{N}(\text{CN})_2]_2$, where M is the transition-metal ion, has two members for which the ground state is ferromagnetic, $M = \text{Co}$ and $M = \text{Ni}$.^{10,11} We show that the low- T magnetic behavior of these systems is described by a collinear ferromag-

netic structure with spin orientation parallel to the c axis, in accord with the local anisotropy expected to originate with the neighboring atoms and lattice distortions. The magnitudes of the magnetic moments of the metal ions are in agreement with the crystal-field theoretical predictions. At low- T , while $\text{Ni}[\text{N}(\text{CN})_2]_2$ has the expected total angular momentum $J = 1$ with corresponding Landé g factor $g_1 = 2.21$ at each Ni^{2+} site, we demonstrate that $\text{Co}[\text{N}(\text{CN})_2]_2$ has an effective $J = 1/2$ with $g_{1/2} = 5.34$ at each Co^{2+} site. We also present the T -dependent crystal structure obtained via neutron powder diffraction techniques and show that it has an unusual wine-rack-like deformation.¹² The complete magnetic and crystal structures together with static magnetization, dynamic susceptibility,¹⁰ and specific heat studies¹³ demonstrate the unusual ability to control the magnetic ground state in molecule-based magnets.

The neutron powder diffraction (NPD) measurements were carried out at the National Institute of Standards and Technology's (NIST) research reactor. For *crystal* structure determination, the NPD measurements were made with the 32-detector BT-1 high-resolution powder diffractometer using incident neutron beams of wavelength 1.5401 Å. Full diffraction patterns ($3^\circ < 2\theta < 165^\circ$) were recorded at a few selected temperatures in order to determine both the nuclear and magnetic structures, and to detect possible structural and magnetic phase transitions. Crystal structures were refined by the Rietveld technique, using the General Structure Anal-

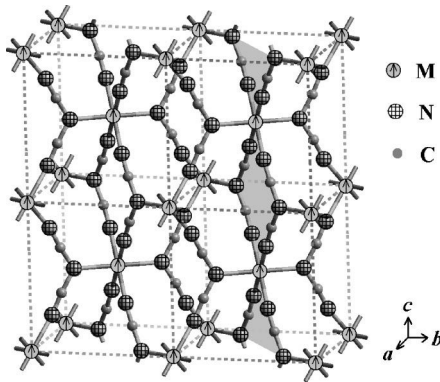


FIG. 1. Four unit cells of the crystal and magnetic structures of $M[\text{N}(\text{CN})_2]_2$ ($M=\text{Co}, \text{Ni}$). The shaded part represents a “chain,” and the arrows on the metal ions indicate the direction of the spins.

system (GSAS) program¹⁴ and adopting as initial model the room-temperature structure for $\text{Co}[\text{N}(\text{CN})_2]_2$ derived previously.¹⁰ For *magnetic* structure determination, the NPD experiments were carried out on the BT-2 triple-axis spectrometer utilizing an incident neutron beam with wavelength of 2.3591 Å, which provided much higher intensity than BT-1. Diffraction patterns ($3^\circ < 2\theta < 65^\circ$) collected at 1.6 K and $\sim 2T_C$ were used to determine the orientation of the spins and the magnitude of the magnetic moment per ion. The intensity of one of the strong magnetic Bragg peaks for each sample was monitored as a function of temperature. Two ~ 4.5 g polycrystalline samples were prepared¹⁰ and were sealed in vanadium (BT-1) or aluminum (BT-2) containers filled with He-exchange gas. An Institut Laue-Langevin-type top loading cryostat with a low-temperature capability of 1.6 K was used to control the sample environment.

We determined that both Co and Ni compounds have the same crystal structure at all temperatures studied (Fig. 1). The crystal structure, described by the space group $Pnmm$, consists of hinged rhombus-shaped repeats of $M[\text{N}(\text{CN})_2]_2$ that form “chains” (shaded in Fig. 1) oriented parallel to the c axis. There are two chains (one repeat per chain) in the orthorhombic unit cell, one passing through the origin and the other passing through the center of the unit cell, with the metal ions located at $(0,0,0)$ and $(1/2, 1/2, 1/2)$. The environment around each of the two metal ions in each unit cell is an axially elongated octahedron, $M\text{N}_6$, with the longer axis tilted by the same angle, but in opposite senses of rotation about the c axis. These lattice distortions, i.e., axial elongation and opposite tilting of the octahedra in each unit cell, affect the resulting magnetic structure. The crystal structure for $\text{Co}[\text{N}(\text{CN})_2]_2$ obtained from our profile refinements is in good agreement with the room-temperature single-crystal x-ray determination.¹⁰

Figure 2 shows the orthorhombic lattice parameters and unit-cell volume as a function of temperature for Co and Ni compounds. The volume of the unit cell in each case increases monotonically with increasing temperature, but the c -lattice parameter exhibits *negative thermal expansion*. The fractional changes in length between 1.5 and 300 K are: $\Delta a/a=0.89\%$ (Co) and 0.70% (Ni), $\Delta b/b=0.55\%$ (Co) and 0.42% (Ni), $\Delta c/c=-0.21\%$ (Co) and -0.14% (Ni). The bond lengths show no significant variation with temperature.

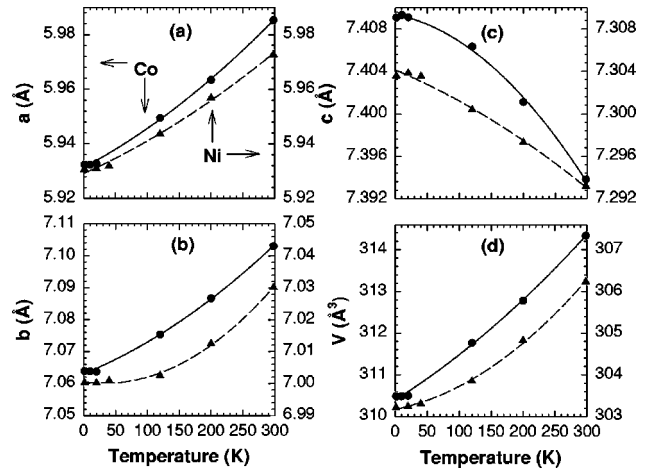


FIG. 2. Temperature dependence of the orthorhombic lattice parameters (a), (b), and (c) and unit-cell volume (d) for $\text{Co}[\text{N}(\text{CN})_2]_2$ (circles, left axis) and $\text{Ni}[\text{N}(\text{CN})_2]_2$ (triangles, right axis). The lines are guides for the eye.

The contraction along the c axis, accompanied by the expansion along the a and b crystal directions with increasing temperature, may be due to a wine-rack-like deformation¹² of each rhombus-shaped repeat of $M[\text{N}(\text{CN})_2]_2$. Another effect of increasing temperature is the change in the angle of the planar chains with respect to the ac plane by $\sim 0.5(2)^\circ$. No structural phase transitions were detected over the entire range of temperatures studied.

To obtain the magnetic diffraction patterns (Fig. 3), we made one diffraction measurement at $\sim 2T_C$ in the paramagnetic regime and another at the lowest attainable temperature (1.6 K) in the ordered state. A subtraction of the high- T data from the low- T data yielded six magnetic Bragg peaks with the scattering angle lying between 25° and 60° on top of a negative background. As there is no significant temperature

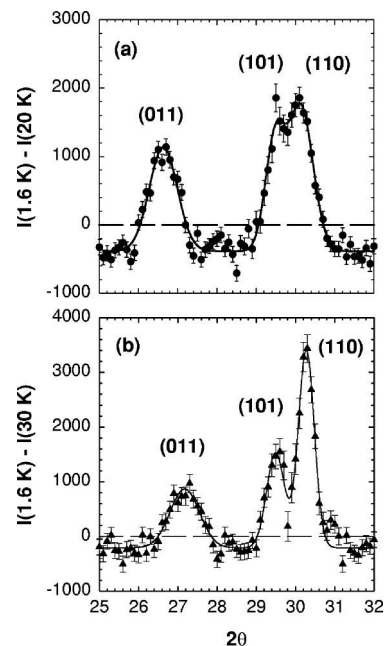


FIG. 3. Part of the magnetic diffraction pattern of (a) $\text{Co}[\text{N}(\text{CN})_2]_2$ and (b) $\text{Ni}[\text{N}(\text{CN})_2]_2$. Lines are Gaussian fits to the peaks.

variation of the lattice parameters over this temperature range, the nuclear Bragg peaks subtract out, leaving only the magnetic Bragg peaks. The negative background is assigned to the shift from (incoherent) diffuse magnetic scattering in the paramagnetic regime to coherent magnetic Bragg peaks in the ordered state.¹⁵ The magnetic Bragg peaks obtained correspond to the Miller indices (011), (101), (110), (020), overlap of (112) and (121), and overlap of (211) and (022). We note here that magnetic reflections are present for $h+k+l=2n$ and absent for $h+k+l=2n+1$. In addition, the nuclear and magnetic Bragg peaks occur at the same angular positions. The above analysis establishes that the magnetic lattice consists of two metal ions, one located at (0,0,0) and the other at (1/2,1/2,1/2), in an orthorhombic unit cell with ferromagnetic interactions between them.

We determined the spin orientation and the value of the ordered moment for the samples studied. For all calculations we assumed that the magnetic moments are localized on the metal ions. The observed integrated intensities and positions of the magnetic and nuclear Bragg peaks were obtained by fitting a resolution-limited Gaussian to each peak. The calculated integrated intensities of the magnetic peaks were obtained by using Eqs. (3) and (4) from Ref. 16. For the magnetic form factors of the metal ions we used the calculated free-ion values.¹⁷ The orientation of the spins was determined by finding the best agreement between the ratios of the integrated intensities of magnetic Bragg peaks in the experimental diffraction pattern and the patterns calculated at different spin orientations. This method is very sensitive to the spin orientation even for the difficult case of small ferromagnetic moments, for which weak magnetic peaks occur on top of strong nuclear peaks. We have found that each compound has a *collinear* ferromagnetic structure below the ordering temperature, with the magnetic moments of the metal ions of $\mu = g_J \mu_B J = 2.67(5) \mu_B$ for Co and $2.21(10) \mu_B$ for Ni, oriented along the *c* axis (arrows in Fig. 1).

From the values of the magnetic moments, we extracted the total angular momenta (J) and corresponding Landé g factors (g_J). Assuming *LS* coupling, the angular momentum state of an ion is specified by the quantum numbers S , L , and J . For high-spin Co^{2+} ($S=3/2$) in octahedral geometry, the orbital angular momentum is only partially quenched, $L=1$. By the theory of the addition of angular momenta, the possible values of J are $1/2$, $3/2$, and $5/2$. From $\mu(\text{Co}^{2+}) = 2.67(5) \mu_B$ and $g_J > 2$ for large negative spin-orbit coupling,¹⁸ we then obtain $J=1/2$ with $g_{1/2}=5.34$. For Ni^{2+} ($S=1$) in octahedral geometry, the orbital angular momentum is totally quenched $L=0$, leading to $J=S=1$. From $\mu(\text{Ni}^{2+}) = 2.21(10) \mu_B$ we then get $g_1=2.21$. These magnetic moments are only 3% higher than the magnetic moments obtained from the saturation magnetization.¹⁰ Consistency is obtained from the magnetic specific heat, which yields a transition entropy of $R \ln 2$ ($J=1/2$) for Co and $R \ln 3$ ($J=1$) for Ni.¹³ At high- T , static magnetization measurements¹⁰ show that $J=3/2$ with $g_{3/2}=2.49$ (Co) and $J=1$ with $g_1=2.21$ (Ni).

We verified that there is no spin canting in these systems with respect to the *c* axis through three observations. (i) Careful inspection of the magnetic diffraction pattern shows that a weak (200) peak is present, while the (002) peak is missing. Equation (4) from Ref. 16 reveals that $\hat{\tau} \cdot \hat{\mathbf{M}} = 1$ for

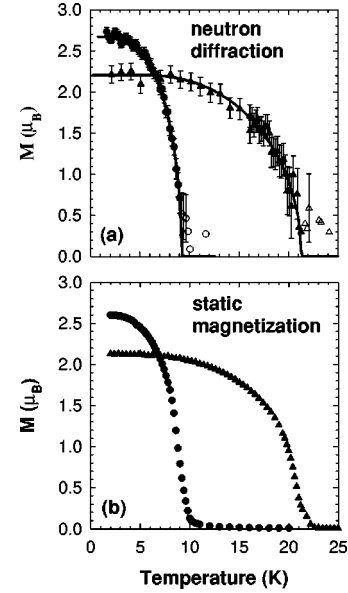


FIG. 4. (a) Temperature dependence of the magnetic moment per metal ion obtained from NPD in zero magnetic field. The data are shown for the magnetic Bragg peaks (011) for $\text{Co}[\text{N}(\text{CN})_2]_2$ (circles) and (101) for $\text{Ni}[\text{N}(\text{CN})_2]_2$ (triangles). The solid curves are Brillouin function fits to the data. (b) Temperature dependence of the bulk magnetization obtained by static magnetization measurements in 5 Oe for $\text{Co}[\text{N}(\text{CN})_2]_2$ (circle) and $\text{Ni}[\text{N}(\text{CN})_2]_2$ (triangle) compounds.

the (002) peak, which implies that the magnetic moments are fully aligned along the *c* axis. (ii) From the classification of magnetic space groups,¹⁹ a nuclear space group of $Pnmm$ for a ferromagnetic system allows only two magnetic space groups: $*Pn'n'm$ (spin along *c* axis) and $*Pnn'm'$ (spin in the *ab* plane), of which the latter is easily ruled out based on our computed ratios of the integrated intensities. Hence the magnetic structure of our compounds is described by the magnetic space group $*Pn'n'm$, which does not allow a canting of the magnetic moments. (iii) Bulk magnetic measurements¹⁰ do not show any evidence of spin canting in these systems.

Figure 4(a) shows the magnetic moment per metal ion corresponding to the (011) magnetic Bragg peak for Co and (101) peak for Ni as a function of temperature. To obtain an estimate of the magnetic ordering temperature T_C we fitted a Brillouin function to the data by varying the exchange parameter, T_C , and saturation magnetization. The solid curves are fits of the Brillouin functions to corresponding NPD data, and the fitted ordering temperatures are $9.22(4)$ K for Co and $21.3(2)$ K for Ni. The apparent nonzero moment above T_C (open symbols) is attributed to critical scattering and the data close to and above T_C were not used in the fitting procedure. These values are in very good agreement with the ordering temperatures obtained from specific-heat measurements.¹³ The NPD results are nearly identical to the static magnetization data, Fig. 4(b), which further confirms that there is no spin canting in these systems.

In summary, we have determined that $M[\text{N}(\text{CN})_2]_2$ ($M = \text{Co}, \text{Ni}$) crystallize in isomorphous wine-rack-like structures (space group $Pnmm$), no structural phase transitions accompany the magnetic ordering down to 1.6 K, and both com-

pounds have a collinear ferromagnetic structure below the transition temperature (magnetic space group $*Pn'n'm$) with metal-ion moments of $\mu(\text{Co}^{2+})=2.67(5)\mu_B$ and $\mu(\text{Ni}^{2+})=2.21(10)\mu_B$ directed parallel to the c axis. The low-temperature magnetism corresponds to an effective $J=1/2$ with $g_{1/2}=5.34$ for Co^{2+} , and $J=1$ with $g_1=2.21$ for

Ni^{2+} . These results are in excellent agreement with the static magnetization, dynamic susceptibility and specific-heat results.

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