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Magnetic structure and exchange interactions in quasi-1D $\text{MnCl}_2(\text{urea})_2$

Jamie L. Manson^{1,*}, Qing-zhen Huang², Craig M. Brown^{2,3}, Jeffrey W. Lynn², Matthew B. Stone⁴, John Singleton⁵, and Fan Xiao⁶

¹Department of Chemistry and Biochemistry, Eastern Washington University, Cheney, WA 99004 USA

²NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899 USA

³Department of Chemical and Biochemical Engineering, University of Delaware, Newark, DE 19716 USA

⁴Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830 USA

⁵National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM 87545 USA

⁶Center for Materials Physics, Durham University, Durham DH1 3LE UK

Abstract

$\text{MnCl}_2(\text{urea})_2$ is a new linear chain coordination polymer that exhibits slightly counter-rotated MnCl_4 rhomboids along the chain-axis. The material crystallizes in the non-centrosymmetric orthorhombic space group $Iba2$, with each Mn(II) ion equatorially surrounded by four Cl^- that lead to bi-bridged ribbons. Urea ligands coordinate via O-atoms in the axial positions. Hydrogen bonds of the $\text{Cl}\cdots\text{H-N}$ and $\text{O}\cdots\text{H-N}$ type link the chains into a quasi-3D network. Magnetic susceptibility data reveal a broad maximum at 9 K that is consistent with short-range magnetic order. Pulsed-field magnetization measurements conducted at 0.6 K show that a fully polarized magnetic state is achieved at $B_{\text{sat}} = 19.6$ T with a field-induced phase transition occurring at 2.8 T. Neutron diffraction studies made on a powdered sample of $\text{MnCl}_2(\text{urea})_2$ reveal that long-range magnetic order occurs below $T_N = 3.2(1)$ K. Additional Bragg peaks due to antiferromagnetic (AFM) ordering can be indexed according to the $Ib'a2'$ magnetic space group and propagation vector $\tau = [0, 0, 0]$. Rietveld profile analysis of these data reveal a Néel-type collinear ordering of Mn(II) ions with an ordered magnetic moment of $4.06(6) \mu_B$ ($5 \mu_B$ is expected for isotropic $S = 5/2$) oriented along the b -axis, i.e., perpendicular to the chain-axis that runs along the c -direction. Owing to potential for spatial exchange anisotropy and the pitfalls in modeling bulk magnetic data, we analyzed inelastic neutron scattering data to retrieve the exchange constants; $J_c = 2.22$ K (intrachain), $J_a = -0.10$ K (interchain) and $D = -0.14$ K with $J > 0$ assigned to AFM coupling.

* Contact information for corresponding author: Department of Chemistry and Biochemistry, Eastern Washington University, 226 Science Building, Cheney, WA 99004-2440, phone: (509) 359-2878, fax: (509) 359-6973, jmanson@ewu.edu.

This J configuration is most unusual and contrasts the more commonly observed case of AFM-coupled FM-chains.

Introduction

Low-dimensional (0-, 1- and 2D) molecular magnetic materials continue to attract much attention worldwide.¹ Current interest in such materials is driven by the rich variety of magnetic ground and excited states that can be observed, especially at high magnetic fields, low temperatures or high pressures. In order to better understand the underlying magnetism of these systems it is imperative that we understand the underlying relationship between the lattice and spin dimensionality, and if at all possible, the microscopic magnetic structure, as it can reveal phenomena not observed by macroscopic measurement techniques.

Metal-halide compounds often form low-dimensional crystal structures and continue to elicit interest. For example, anhydrous CuCl_2 has been shown to exhibit spin-driven ferroelectricity and strong magnetoelectric coupling^{2a} whereas CuBr_2 is a multiferroic with a relatively high T_N of 73.5 K.^{2b} Hydrates such as $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ ³, as well as alkali metal salts such as Rb_2MnCl_4 ^{4a} and CsNiCl_3 ^{4b}, also exist, the latter two compounds being described respectively as a 2D Heisenberg square lattice and a 1D Haldane spin-chain.

The structural and magnetic diversity of metal-halides can be expanded even further by incorporation of organic Lewis bases such as pyrazine (pyz),^{1b-1e,5} pyrazine- N,N' -dioxide (pyzdo)⁶, tetrahydrofuran (THF),⁷ pyridine (py),⁸ 2,2'-bipyridine (2,2'-bipy)⁹ and 4,4'-bipyridine (4,4'-bipy)¹⁰ just to list a few. Interesting physical properties presented by these materials include, but are not limited to, antiferromagnetism (AFM), ferrimagnetism (FIM), ferromagnetism (FM), and metamagnetism (MM), the particular state depending on the metal ion, its oxidation number and presence of spin-exchange anisotropy.¹¹ The chain-type structural motifs that have been reported primarily consist of bi-bridged $M\text{-Cl}_2\text{-}M$ ribbons as opposed to single $M\text{-Cl-M}$ interactions. Of note is that the organic ligand appears to perturb the $M\text{-Cl-M}$ angle in both bridge types which in turn perturbs the magnitude and sign of the (super)exchange interaction.

In our quest to design model systems composed of selected types of interchain or interlayer hydrogen bonds, we have been exploring urea [$\text{CO}(\text{NH}_2)_2$] as an ancillary ligand in conjunction with metal-halide structural units. Urea contains amine groups that could facilitate extensive hydrogen bond formation with suitable ligands such as Cl^- and Br^- . Other coordination polymers that contain metal-bound urea are $[\text{Gd}(\text{urea})_4(\text{H}_2\text{O}_2)_2]_2[\text{Cr}(\text{CN})_6]_2$ ¹² and $[\text{Mn}(\text{urea})_2(\text{H}_2\text{O})]_2[\text{Nb}(\text{CN})_8]$.¹³ In the present work, we describe the structural and magnetic properties of $\text{MnCl}_2(\text{urea})_2$ which contains bi-bridged $\text{Mn-Cl}_2\text{-Mn}$ linear chains linked in three-dimensions by $\text{Cl}\cdots\text{H-N}$ and $\text{O}\cdots\text{H-N}$ hydrogen bond types. Various magnetic probes indicate short- and long-range ($T_N = 3.1$ K) magnetic ordering of the high-spin ($S = 5/2$) ions where the ordered moments are aligned antiferromagnetically along the chain c -axis but *ferromagnetically* coupled along the a - and b -directions. This behavior was not evident from the bulk magnetometry data and was revealed only through neutron experimentation.

Experimental section

Synthesis

All chemicals were purchased from Aldrich Chemical Co. and used as received. In a typical synthesis, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.3503 g, 1.77 mmol) and urea (0.2126 g, 3.54 mmol) were dissolved separately in ~10 mL of ethanol. While stirring, the ethanolic MnCl_2 solution was poured into the urea solution to yield a pale pink precipitate. The solid was collected by suction filtration and dried *in vacuo* for around 2 hours (0.4005 g, 92% yield). Pink crystals suitable for the X-ray structure determination were obtained by slow evaporation of the filtrate over a period of a few days.

X-ray crystallography

A pink parallelepiped crystal measuring $0.25 \times 0.06 \times 0.06 \text{ mm}^3$ was mounted on a Bruker AXS SMART X-ray diffractometer equipped with a CCD area detector. Monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) was used in the data collection. Approximately a hemisphere of data was measured to a resolution of $0.75 \text{ \AA}$ at 295 K. The area detector frames were integrated by use of the program SAINT,¹⁴ and the resulting intensities corrected for absorption by Gaussian integration (SADABS).¹⁵ The SHELXTL¹⁶ program package was employed in the structure solution, using direct methods and full matrix least-squares refinement on F^2 (using all data).¹⁶ Urea H-atoms were placed in idealized positions and allowed to ride on the atom to which they are attached. All non-hydrogen atoms were refined with anisotropic thermal parameters. Additional details of the data collection are given in Table 1 while selected bond lengths and angles are listed in Table 2. Further structure details are available as electronic Supporting Information.

Magnetic susceptibility

Quasistatic measurements were conducted using a Quantum Design PPMS-9 T ac/dc magnetometer equipped with the reciprocating sample option (RSO). Polycrystalline samples of $\text{MnCl}_2(\text{urea})_2$ were loaded into gelatin capsules and mounted on the end of a carbon fiber rod. The samples were cooled in approximately zero-field to the lowest attainable base temperature of 2 K and data were collected upon warming in a 0.1 T magnetic field. Experimental susceptibilities were corrected for the diamagnetism of the constituent atoms.

Pulsed-field magnetization

Measurements up to 60 T were made at the Pulsed-Field Facility of the National High Magnetic Field Facility using a 1.5 mm bore, 1.5 mm long, 1500-turn compensated-coil susceptometer, constructed from 50 gauge high-purity copper wire.¹⁷ When a sample is within the coil, the signal voltage V is proportional to (dM/dt) , where t is the time. Numerical integration of V is used to evaluate M . The sample is mounted within a 1.3 mm diameter ampoule that can be moved in and out of the coil. Accurate values of M are obtained by subtracting empty coil data from that measured under identical conditions with the sample present. The susceptometer was placed inside a ^3He cryostat providing temperatures down to 0.5 K. The field B was measured by integrating the voltage induced in

a ten-turn coil that was calibrated by observing the de Haas-van Alphen oscillations of the belly orbits of the copper coils of the susceptometer.

Neutron scattering

Diffraction studies were made using the 32-detector high-resolution BT-1 powder diffractometer located at the NIST Center for Neutron Research (NCNR, Gaithersburg, MD). A neutron wavelength of 2.078 Å produced by a Ge(311) monochromator was used. Collimators with horizontal divergences of 15', 20', and 15' full-width-at-half-maximum (FWHM) were used for the in-pile, monochromatic and diffracted beams, respectively. Intensities were measured in steps of 0.05° 2θ between 3 and 165° at temperatures of 1.4 and 5 K, i.e., below and above T_N . A hydrogenated powder sample of $\text{MnCl}_2(\text{urea})_2$ weighing approximately 2 g was loaded into a vanadium can, mounted in a Janis top-loading ^3He cryostat and positioned in the center of the neutron beam. Nuclear and magnetic structure refinements were performed using GSAS.¹⁸ Initial atomic positions, including H-atoms, were taken from the single-crystal X-ray structure and then freely refined. The magnetic-order parameter was deduced using a series of scans obtained in temperature increments of approximately 0.1 K between 1.4 and 5 K.

Inelastic neutron scattering measurements were performed at 1.6 and 5 K on the same sample of $\text{MnCl}_2(\text{urea})_2$ using the Fermi chopper time-of-flight spectrometer also located at the NCNR. The sample was contained within a 1-cm diameter Al can backfilled with ^4He exchange gas. The temperature was controlled using a flow-type pumped-liquid ^4He cryostat. The neutron wavelength for the measurement was fixed at 6 Å, which results in a measured elastic energy resolution FWHM of 0.07 meV. Data were collected for approximately 6 hours at each temperature. For the neutron data, uncertainties are statistical in origin and represent one standard deviation.

Results and discussion

Crystal structure

The structure of $\text{MnCl}_2(\text{urea})_2$ was investigated at 295, 15 and 1.4 K using a combination of single-crystal X-ray and neutron powder-diffraction measurements. Because there is little variation between the structures obtained at these temperatures, other than the usual lattice contraction, we describe only the room temperature X-ray result in detail. In the *Iba2* space group, the Mn(II) ion has 2-fold rotation symmetry about the crystallographic *c*-axis, occupying Wyckoff position 4*b*. All other atoms occupy general positions. As shown in Figure 1, each Mn(II) ion is six-coordinate with four Cl^- occupying the equatorial plane [$\text{Mn}-\text{Cl} = 2.5864(6)$ and $2.6004(7)$ Å] while two oxygen atoms [$\text{Mn}-\text{O} = 2.119(1)$ Å] from urea ligands residing on the axial positions. The MnCl_4O_2 octahedron is rather distorted from ideal octahedral symmetry with the largest deviations being 85.94(6) and 175.23(2)° for O-Mn-Cl and Cl-Mn-ClC, respectively. The chloride ions link the Mn centers into linear chains (Figure 2) along the *c*-direction with Mn···Mn separations of 3.670 Å which is one-half of the *c* lattice parameter. Each Cl^- bridge makes nearly orthogonal Mn-Cl-Mn bond angles of 90.07(1)°.

The Mn_2Cl_2 rhombic-core observed in $\text{MnCl}_2(\text{urea})_2$ is common to several other Mn(II) -chloride chain compounds, including $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$,³ $\text{MnCl}_2(\text{mppma})$ [mppma = *N*-(3-methoxypropyl)-*N*-(pyridine-2-ylmethyl)amine],¹⁹ $\text{MnCl}_2(\text{pz})_2$ (pz = pyrazole)²⁰ and $\text{MnCl}_2(2,2'\text{-bipy})$ (bipy = bipyridine).⁹ The corresponding Mn···Mn distance/Mn-Cl-Mn bond angle in the dihydrate, mppma and bipy complexes are 3.691 Å/92.55°, 3.790 Å (average)/94.14° and 3.835 Å/96.4°. These Mn···Mn distances are shorter than that found in polymeric $\text{MnCl}_2(\text{tmen})$ (tmen = *N, N, N', N'*-tetramethylethylenediamine)²¹ which is consistent with a slightly larger Mn-Cl-Mn bond angle. Neighboring rhomboids in these Mn-Cl₂-Mn chains including $\text{MnCl}_2(\text{urea})_2$, feature planes tilted by 6.6° as one moves between rhomboids along the *c*-axis.

In $\text{MnCl}_2(\text{urea})_2$, the chains do not stagger as typically encountered in structures of this type.^{3,19,20} Instead, adjacent chains pack in-registry and are linked into an intricate three-dimensional (3D) network via N-H···Cl and N-H···O hydrogen bonds as illustrated in Figures 3(a) and (b). This packing arrangement provides interchain Mn···Mn separations of 7.780 and 8.601 Å along the face-diagonal of the *ab*-plane and body-diagonals of the unit cell, respectively.

Magnetic susceptibility, $\chi(T)$

The bulk magnetic susceptibility of $\text{MnCl}_2(\text{urea})_2$ has been investigated between 2 and 300 K; data are shown in Figure 4. $\chi(T)$ increases gradually upon cooling until a broad maximum is reached at 9 K. Upon cooling further down to 2 K, $\chi(T)$ gradually decreases and then rises slightly. This small increase in the susceptibility could be due to a trace amount of paramagnetic impurity. The broad maximum however, is attributed to short-range magnetic ordering between $S = 5/2$ Mn(II) ions along the bi-bridged chains. The $\chi(T)$ data were fit between 50 and 300 K to a Curie-Weiss law, $\chi = Ng^2\mu_B^2 S(S+1)/3k_B(T-\theta)$, where θ is the Weiss constant and the remaining symbols have their usual meaning.²² The resulting fit gave a slightly anisotropic *g*-value of 2.027(1) and $\theta = -17.7(3)$ K, where a negative θ -value indicates antiferromagnetic (AFM) coupling between Mn(II) spins. Since spin-orbit coupling is largely quenched in high-spin, six-coordinate Mn(II) complexes, as found in $\text{MnCl}_2(\text{urea})_2$ and many related systems, the obtained θ -value is almost entirely attributable to magnetic interactions between metal centers. We caution, however, that a small zero-field splitting could result due to even the slightest structural distortion about the metal center.

Considering that the crystal structure consists of uniformly spaced Mn(II) ions arranged as chemical chains, we elected to fit the $\chi(T)$ data to a classical-spin Fisher AFM chain model based on the Hamiltonian, $H = J\sum S_i \cdot S_j + J'\sum S_i \cdot S_j$ (*J* and *J'* > 0 is AFM coupling), with *J* and *J'* referring to intra- and interchain interactions, respectively.²³ A least-squares fit of these data between 5 and 300 K, excluding single-ion anisotropy (*D*),²⁴ yielded good agreement (solid line in Figure 4) with the following parameters; *g* = 2.03(2), *J* = 1.35(1) K and *zJ'* = -0.31(1) K. It should be noted that this *J*-value exceeds those generally found in related Mn(II) chain compounds (Table 4). At issue, however, is that *zJ'* is roughly 20% of *J*, which renders the aforementioned mean-field approach questionable (as *zJ'/J* should be limited to no larger than ~10%).²⁴ Below, we describe a more reliable method to determine the exchange energies in this material using inelastic neutron scattering.

An alternative description for the magnetism in $\text{MnCl}_2(\text{urea})_2$ is to assume isotropic spin interactions, not only along the chains, but between them as well. Thus, a Rushbrooke-Wood 3D Heisenberg AFM model based on a body-centered cubic (bcc) lattice²⁵ was used to fit $\chi(T)$ and compared to the results of the above 1D model. Over the fitting range of 25-300 K, good reproducibility was achieved for the parameters, $g = 2.03(2)$ and $J = -0.82(1)$ K. However, the low-dimensionality of the structure and expectedly weaker interchain interactions should yield spatial exchange anisotropy, making the bcc model less plausible despite the good comparison with the measurement.

However, it is significant that the g -values obtained from both magnetic models slightly exceed the expected free electron value of 2.0023. This points to a possible single-ion anisotropy arising from a splitting of the six magnetic sublevels of the $S = \pm 5/2$ ground state in zero-field (D).²⁶ For instance, in a series of mononuclear complexes $\text{MnX}_2(\text{tpa})$ (tpa = *tris*-2-picolylamine), D was found to be 0.17, -0.50 , and -0.84 K for $X = \text{Cl}$, Br and I , respectively.²⁷ Granted, these compounds consist of MnN_4Cl_2 cores, as opposed to MnN_2Cl_4 , but the important feature is that D is finite.

High-field magnetization

Figure 5(a) shows the magnetization $M(H)$ of $\text{MnCl}_2(\text{urea})_2$ measured in pulsed magnetic fields at four different temperatures; the differential susceptibility (dM/dH) is shown in the lower panel for the 0.6 K data set. Many similar studies have been carried out on $S = 1/2$ and $S = 1$ quantum magnets.¹⁷ In those low-spin (compared to Mn) systems, low-temperature $M(H)$ data exhibit a concave (i.e. gradual steepening with increasing field) curve before a relatively sudden saturation at a well-defined magnetic field.¹⁷ In general, the lower the effective magnetic dimensionality, the more concave the data, a behavior that has been modeled successfully using a quantum Monte Carlo approach.¹⁷ By contrast, the lowest temperature $M(H)$ data for $\text{MnCl}_2(\text{urea})_2$ exhibit a constant gradient from 2.8 T up to the saturation field. In the context of the $S = 1/2$ and $S = 1$ systems, such behavior would suggest isotropic (three-dimensional) exchange interactions. However, similar, very linear approaches to saturation have been observed in a wide variety of Mn complexes, including MOFs in which the Mn ions populate small, magnetically-isolated clusters²⁸ and crystalline organic magnets known to be quasi-one or two-dimensional considering spatial exchange anisotropy.²⁹ In all of these Mn(II) compounds, it seems that the large number of possible spin projections of the Mn(II) ions circumvents the geometrical restrictions caused by reduced dimensionality that dictate the approach to saturation in the low-spin complexes; thus, a linear $M(H)$ is “universal” behavior in metal-organic magnets featuring ions such as Mn(II).³⁰

In addition to the low-temperature, linear approach to saturation (Figure 5(a), $T = 0.6$ K data), there is a sharp change in gradient at 2.8 T (Figure 5(b), indicated by an arrow). This suggests some form of metamagnetic or spin-flop transition, i.e., a field-driven reconfiguration of the low-field ground state.

The saturation magnetization of $5.3 \pm 0.2 \mu_B$ per formula unit (Figure 5(a)) suggests that the Mn(II) ions contribute their full moment at high fields, in contrast to the reduced moment extracted above from the low-field data. In addition, the saturation field represents the point

at which the magnetic energy of the spins finally overcomes the exchange interactions; with knowledge of the g -factor one can extract the effective exchange energy acting on the Mn(II) ions.¹⁷ Assuming a chain-like configuration (two nearest neighbors) and using the g -factor given above, the saturation field of 19.6 T yields an effective $J = 5.3$ K. This is a factor of ~ 2.5 higher than the individual exchange energies derived below from the inelastic neutron scattering study.

All of this suggests that there may be an underlying degree of frustration inherent to the low-field ground-state that reduces both the effective exchange energies and magnetic moment available from the Mn(II) ions. Therefore, the metamagnetic-like transition at 2.8 T probably represents a rearrangement of the spins that overcomes the frustration, at least in part, resulting in a higher effective exchange energy and recovery of the full Mn(II) moment.

Zero-field magnetic structure

A comparison of neutron diffraction patterns made at 1.4 and 5 K, the latter not shown, reveal several additional Bragg peaks at the lower temperature (Figure 6) that are magnetic in origin. These additional peaks, indexed as (001), (020) or (111), (021), (201) and (221), are a result of long-range AFM order in the material. Rietveld profile analysis of the 1.4 K data yielded a propagation vector (τ) of [0, 0, 0] indicating that the magnetic and nuclear unit cells are equivalent.

The magnetic structure (Figure 7) of $\text{MnCl}_2(\text{urea})_2$ can be rationalized in the following manner: (1) along the chain, Mn(II) magnetic moments align antiparallel relative to adjoining neighbors, i.e. are antiferromagnetic; (2) the Mn(II) moments that lie on the vertices of the unit cell align ferromagnetically relative to the chain running through the body-center; and (3) the total magnetic moment, M_T , per Mn(II) ion is $4.06(6) \mu_B$ which is the vector sum of the spatial components $M_x = M_z = 0$ and $M_y = 4.06(6) \mu_B$. The determined M_T value is reduced by $\sim 1 \mu_B$ from the expected value of $5 \mu_B$ for isotropic high-spin $S = 5/2$ Mn(II). This observation could arise if a portion of the Mn(II) spin density was diffused onto the polarizable Cl^- ligands. Should this occur, each Cl would bear a magnetic moment of roughly $0.13 \mu_B$ and be aligned antiparallel to the Mn(II) moment, which is $\sim 3\%$ of M_T . This is not unreasonable in that $\sim 5\%$ of the Ir(IV) magnetic moment is delocalized onto the Cl's in K_2IrCl_6 due to covalency effects, for example.³¹ For $\text{MnCl}_2(\text{urea})_2$ in zero-field, the net effect would be cancellation of the Cl magnetic moments since each Cl is shared by two antiparallel Mn, which is consistent with the lack of such evidence from the BT-1 data. Presumably in high magnetic fields the Cl moments would reorient parallel (possibly by 2.8 T because this corresponds to $\sim 14\%$ of B_{sat} , i.e., $\sim 0.8 \mu_B$), thus explaining the larger total moment observed in the high-field magnetization data. Of note is that the presence of quantum fluctuations in $\text{MnCl}_2(\text{urea})_2$, as needed to reduce the size of the ordered moment, is inconceivable for $S = 5/2$.

To determine the Néel temperature, the intensity of the (111) magnetic peak was monitored as a function of temperature as shown in Figure 8. From the plot it can be seen that the peak intensity becomes invariant for temperatures above approximately 3 K. We fit these data in two ways. First, we use a power-law of the form $I(T) = A + B(T_N - T)^{2\beta}$ for $T < T_N$, where the value A accounts for the background and β is the critical exponent. For $T > T_N$ the data were

fit to obtain the A value. From Figure 8, this comparison results in a good representation of the measurement with $\beta = 0.19(7)$ and $T_N = 2.99(4)$ K. While β is consistent with magnetic interactions of reduced dimensionality, we caution that it is only meaningful in the critical region. Second, we use mean-field theory ($\beta = 0.5$) for comparison which gives $T_N = 3.2(1)$ K. Of consequence is that the mean-field fit is flat all the way down to $T = 0$ whereas the power law fit continues to increase slightly. In common however, is that neither fit satisfactorily account for the missing ordered moment outside of the uncertainty.

Inelastic neutron scattering

Figure 9 shows the measured wave-vector (Q) integrated scattering intensity as a function of neutron energy transfer, $\hbar\omega$. The $T = 1.6$ K data exhibit a band of excitations between approximately 0.4 and 1.1 meV. Upon heating to $T = 5$ K, these excitations broaden out substantially, with the paramagnetic scattering becoming diffusive (quasielastic) in nature. The range of scattering angles available with the Fermi chopper spectrometer ranges between 5 and 140 degrees. For the band of excitations observed at $T = 1.6$ K, this range of scattering angle corresponds to a range of approximately 0.17 to 1.83 Å⁻¹ in wave-vector transfer. These low Q values, together with the temperature-dependence, clearly indicate that this scattering is magnetic. There are three individual peaks that make up the broader distribution of magnetic scattering. Two correspond to the top and bottom of the magnetic density of states. We show below that these local maxima can be used to constrain the exchange constants in MnCl₂(urea)₂.

At 1.6 K, MnCl₂(urea)₂ is within the ordered bulk magnetic phase. Accordingly, we analyze the measured magnetic spectrum using linear spin-wave theory based upon the pedagogical Heisenberg Hamiltonian that includes single-ion anisotropy, D (eq. 1);

$$H = \sum_{\alpha} \sum_{\langle i,j \rangle} J_{\alpha} S_i \cdot S_j + \sum_i D (S_z^2)_i \quad (1)$$

where α is summed over the a , b , and c axes; we define the y -axis to be parallel to the ordered moment.³² Based upon the ordered magnetic structure shown in Figure 7, we consider the moments to point along the (110) axis of the crystal. Although single-crystal inelastic neutron scattering is the preferred method for extracting exchange parameters based upon measured dispersion curves,³³ we are able to use the powder measurement to determine the primary exchange interactions in MnCl₂(urea)₂. For $T < T_N$, the gap in the magnon density of states is due to D .³⁴ We consider the dominant exchange interaction based upon the crystal structure to be along the crystallographic c -axis, J_c . The next largest exchange interaction is most likely J_a , since the distance between Mn(II) sites along the a -axis is the next shortest in the crystal structure at 9.16 Å. This results in the spin-wave dispersion (eqs. 2–4),

$$A_Q = 2S \{ J_a [\cos(2\pi H) - 1] + J_c - D \} \quad (2)$$

$$B_Q = 2S [J_c \cos(\pi L)] \quad (3)$$

$$\hbar\omega(\mathbf{Q}) = \sqrt{A_Q^2 - B_Q^2}, \quad (4)$$

where S is the magnitude of the spin, J_c is the antiferromagnetic exchange along the chain axis, and J_a is a ferromagnetic nearest neighbor exchange along the a -axis.³⁵ We powder-average the calculated scattering intensity associated with a linear spin wave cross-section for the dispersion in equations 2–4.³⁶ The B_Q term has a $\cos(\pi L)$ factor due to there being two Mn(II) moments oriented along the c -axis of the unit cell. The spectrum is then integrated for the measured range of wave-vectors, convolved with a Gaussian with the same width as the elastic energy resolution, and compared to the measured scattering intensity. We fix the background and only include a multiplicative pre-factor in this fitting procedure. By performing this calculation over a range of J_a , J_c , and D space we are able to determine the minimum value of reduced χ^2 . The fitted range of data used to determine the exchange constants was between 0.32 and 1.23 meV in energy transfer. The determined lineshape shown in Figure 9 is based upon the best fit parameters of $J_c = 0.191 \pm 0.005$ meV (~ 2.22 K), $D = -0.012 \pm 0.003$ meV (~ -0.14 K), and $J_a = -0.009 \pm 0.002$ meV (~ -0.10 K) with a reduced χ^2 of 0.887 indicating an excellent fit. The signs of J_a and J_c are in keeping with those used in the previous Hamiltonian used to model the magnetic susceptibility data. Error bars for an individual variable are based upon fixing the other variables and determining at what value the reduced χ^2 increases by one. The value of J_c is larger than the other exchange constants in this compound by more than a factor of ten, and it is the quasi-1D nature of $\text{MnCl}_2(\text{urea})_2$ that is responsible for the sharp magnetic density of states at the top and bottom of the spectrum. The additional peak in the spectrum at approximately 0.5 meV is attributed to weaker interchain interactions.

The calculated wave-vector-dependent dispersion has local minima at $(h\ 0\ 0)$, $(0\ 0\ l)$, and $(h\ 0\ l)$ positions for integer h and l values. These values correspond to the locations of the magnetic peaks observed in the diffraction data, as expected for this magnetic structure.

The distance between moments along the c -axis is small such that the next-nearest neighbor (nnn) distance along the c -axis (7.338 Angstroms) is shorter than the nearest-neighbor distance between moments along the a -axis (9.163 Angstroms). The powder inelastic neutron scattering measurement is able to identify the significant exchange interactions, but cannot distinguish the possibility of a non-zero nnn exchange along the c -axis. Likewise the exchange interaction along the $(1\ 0\ \pm 0.5)$ direction may be comparable to J_a but would require INS measurements on single crystals to determine. These additional exchange interactions would likely be frustrated. Adding additional interactions along other potential exchange paths did not improve the comparison with the data with any statistical significance. These would be of a smaller magnitude than the J_a we determined and potentially contribute to some degree of geometric frustration in this compound.

Conclusions

We employed X-ray and neutron scattering techniques along with susceptibility and high-field magnetization data to determine the crystal structure and microscopic magnetic properties of the coordination polymer $\text{MnCl}_2(\text{urea})_2$. A quasi-1D structure was found with

Mn(II) sites in close proximity along the *c*-axis. Thermodynamic measurements observe that the Mn(II) sites are AFM-exchange coupled with an energy scale of the order of 2.2 K. A combination of magnetic neutron diffraction and inelastic neutron scattering measurements confirms the existence of AFM coupled $S = 5/2$ moments along the *c*-axis of the crystal structure. $\text{MnCl}_2(\text{urea})_2$ orders at a temperature of 3 K such that three-dimensional magnetic interactions ultimately contribute to the exchange interactions in the system, even though the intrachain is an order-of-magnitude larger and dominates the magnetic behavior. This compound represents an unusual example of a classical-spin chain exhibiting *intrachain* AFM and *interchain* FM interactions, the latter being contrary to the usual cases. Examining other metal-organic crystal structures based upon the urea ligand are likely to further contribute to our general understanding of structural influences on the magnetic properties on materials of this type.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Synopsis

Using neutron scattering methods, we determined the magnetic structure and exchange constants in the quasi-1D chain polymer $\text{MnCl}_2(\text{urea})_2$. It exhibits rarely observed intra- and interchain AFM and FM couplings, respectively.

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Figure 1. Crystal structure of $\text{MnCl}_2(\text{urea})_2$ determined by single crystal X-ray and powder neutron diffraction data, showing the asymmetric unit and atom labeling scheme. Thermal displacement parameters are drawn for room temperature at the 35% probability level.

Figure 2. Segment of a linear chain for $\text{MnCl}_2(\text{urea})_2$. Note the successive rocking of adjacent MnCl_4O_2 octahedra along the chain axis. The atom labeling scheme is given in Figure 1.

Figure 3. Chain packing diagrams for $\text{MnCl}_2(\text{urea})_2$ viewed along the (a) a -axis and (b) c -axis. The atom labeling scheme is given in Figure 1. Cylindrical and dashed lines indicate N-H...O and N-H...Cl hydrogen bonds, respectively, as described in the text.

Figure 4.

Magnetic susceptibility data for a powder sample of $\text{MnCl}_2(\text{urea})_2$ for $T < 100$ K. The solid and dashed lines denote theoretical fits to the Rushbrook-Wood AFM model based on a body-centered cubic lattice and the Fisher 1D uniform AFM chain model as described in the text. Note that $1 \text{ emu} = 10^{-3} \text{ A m}^2$.

Figure 5. Pulsed-field magnetization data obtained for a powder sample of $\text{MnCl}_2(\text{urea})_2$. The $T = 0.6$ K $M(H)$ curve in (a) was smoothed using a 111-point adjacent-averaging algorithm and the derivative subsequently calculated. The arrow in (b) indicates the change in the magnetization at 2.8 T indicating a metamagnetic or spin-flop transition at this field.

Figure 6. Neutron diffraction pattern obtained at 1.4 K temperature, well below $T_N = 3.1$ K, showing the difference between the (a) nuclear-only well above T_N and (b) nuclear + magnetic models. Residual peaks of magnetic origin are indexed in the difference plot of (a).

Figure 7. Zero-field magnetic structure of $\text{MnCl}_2(\text{urea})_2$ as determined from powder neutron diffraction. The bi-bridged MnCl_2Mn chains run parallel to the crystallographic c -axis with the collinear magnetic moments aligned along the b -axis.

Figure 8. Temperature-dependence of the (111) magnetic Bragg peak obtained from the BT-1 powder diffractometer. The solid and dashed lines correspond to mean-field and power law fits as described in the text.

Figure 9.

(a) Wave-vector integrated scattering intensity as a function of energy transfer for $\text{MnCl}_2(\text{urea})_2$ at $T = 1.6$ and $T = 5.0$ K. Solid line is the result of the powder averaged linear spin-wave theory discussed in the text. An elastic Gaussian peak is included in the fit to account for the incoherent nuclear scattering. Details of the measurement and fitting procedure are discussed in the text. The single high point at $\hbar\omega = 1.35$ meV is much sharper than the instrumental energy resolution and is spurious scattering.

Table 1Crystallographic data for $\text{MnCl}_2(\text{urea})_2$ obtained from X-ray and neutron diffraction.

Formula	$\text{C}_2\text{H}_8\text{N}_4\text{O}_2\text{MnCl}_2$	$\text{C}_2\text{H}_8\text{N}_4\text{O}_2\text{MnCl}_2$
Diff. method	X-rays	Neutrons
Sample type	single crystal	powder
fw, g/mol	245.96	245.96
T , K	295	1.4
Space group	<i>Iba</i> 2	<i>Iba</i> 2
a , Å	9.1630(3)	9.0278(2)
b , Å	12.5772(4)	12.6317(3)
c , Å	7.3398(2)	7.2353(2)
V , Å ³	845.87(4)	825.09(4)
Z	4	4
ρ_{calc} , g/cm ³	1.931	1.980
λ , Å	0.71073	2.0775
μ , mm ⁻¹	2.150	N/A
$R(F)^a$	0.0200	0.0106
$R_w(F)^b$	0.0486	0.0130
GOF	1.082	1.05

$$^a R = \sum ||F_O| - |F_C|| / \sum |F_O|$$

$$^b R_w = [\sum w[|F_O| - |F_C|]^2 / \sum w|F_O|^2]^{1/2}$$

Table 2Selected bond lengths (Å) and angles (°) for MnCl₂(urea)₂ at 295 and 1.4 K.

Bond or angle	X-rays (295 K)	Neutrons (1.4 K)
Mn-Cl	2.5864(6)	2.540(13)
Mn-Cl#	2.6004(7)	2.622(13)
Mn-O	2.119(1)	2.134(6)
O-C	1.256(2)	1.220(7)
C-N(1)	1.330(3)	1.357(7)
C-N(2)	1.326(3)	1.381(6)
N(1)-H(1)	0.882	0.97(3)
N(1)-H(2)	0.877	1.06(2)
N(2)-H(3)	0.877	1.06(2)
N(2)-H(4)	0.880	0.90(3)
O-Mn-O#	176.3(1)	173.5(10)
O-Mn-Cl	85.94(6)	86.4(4)
O-Mn-Cl#	88.06(5)	88.0(4)
Cl-Mn-Cl#	89.62(3)	89.44(11)
Mn-O-C	135.4(1)	134.9(4)
O-C-N(1)	120.2(2)	120.3(5)
N(1)-C-N(2)	118.3(2)	116.9(5)

Symmetry code: # = -x, 1-y, z

Table 3

Interchain hydrogen bond distances and angles.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A $\angle$ (°)
X-rays (295 K)				
N1-H2...Cl	0.88	2.65	3.461(2)	154
N2-H4...O	0.88	2.11	2.917(2)	152
Neutrons (1.4 K)				
N1-H2...Cl	1.06(2)	2.49	3.43	148
N2-H4...O	0.89(3)	2.06	2.84	145

Table 4

Summary of magnetic data for selected $S = 5/2$ bi-bridged Mn(II)-chloride chains. Given J -values are based on a Heisenberg 1D model for which $J > 0$ corresponds to AFM coupling.

Compound	Mn-Cl-Mn bridge angle (°)	J/k_B (K)	reference
MnCl ₂ ·2H ₂ O	~90	0.45	3
MnCl ₂ (mppma)	94.1	0.36	19
MnCl ₂ (tmen)	80.0, 93.7, 94.1, 100.0, 106.5, 169.9	~0	21
MnCl ₂ (2,2'-bipy)	96.4	N/A	9
MnCl ₂ (4,4'-bipy)	92.2	N/A	10
MnCl ₂ (4-CNpy) ₂	93.5	0.8	30
MnCl ₂ (H ₂ dapd)	99.5	-0.29	31
MnCl ₂ (urea) ₂	90.1	1.35, ^{&} 2.22 [*]	This work

Chemical abbreviations: mppma = *N*-(3-methoxy-propyl)-*N*-(pyridine-2-ylmethyl)amine; tmen = *N*, *N*, *N'*, *N'*-tetramethylethylenediamine; bipy = bipyridine; CNpy = cyanopyridine; TMA = tetramethylammonium; Hbipy = bipyridinium; H₂dapd = 2,6-diacetylpyridinedioxime

[&] obtained from the fit of $\chi(T)$ as described in the text

^{*} determined from the INS study